

PROBABILITY OF RECOMBINATION AND OXIDATION OF O ATOMS ON a-C:H SURFACE

VERJETNOST ZA REKOMBINACIJO IN OKSIDACIJO ZA ATOME KISIKA NA POVRŠINI a-C:H

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In the search for a sustainable energy source for future generations, thermonuclear fusion should not be left unconsidered. One of the important problems of current and near-future fusion devices is the formation of amorphous hydrogenated carbon deposits (a-C:H), which have to be removed regularly. Removal of a-C:H by atomic oxygen seems like a suitable candidate for a cleaning method. Efficiency of the cleaning method will depend on the efficiency of atomic oxygen delivery. This in turn will depend on the atom loss on reactor walls, which is predominantly governed by recombination. An experiment was performed to measure the recombination coefficient of a-C:H for neutral oxygen atoms. The source of atomic oxygen was an inductively coupled RF discharge, created in pure oxygen. The oxygen densities were measured by a nickel tipped FOCP. The a-C:H sample was prepared by thermionic arc sputtering of a graphite target in a mixed argon / acetylene atmosphere. The recombination coefficient was found to be of the order of 10^{-5} . Moreover, it was discovered that the a-C:H deposition was eroded by O atoms during the experiment. In a rough estimate, the probability of oxidation was found to be two orders of magnitude lower than the probability of recombination.

Key words: weakly ionised plasma, atomic oxygen, recombination, a-C:H, Fiber Optic Catalytic Probe

Pri iskanju trajnostnega energijskega vira za prihodnje generacije ne smemo prezreti termionuklearne fuzije. Ena od najpomembnejših težav sodobnih in prihodnjih fuzijskih naprav je nalaganje amorfnih hidrogeniziranih ogljikovih nanosov (a-C:H), ki jih je treba redno odstranjevati. Primeren kandidat za metodo čiščenja se ponuja odstranjevanje a-C:H z atomskim kisikom. Učinkovitost te metode bo odvisna od učinkovitosti dotoka atomskega kisika k površini. Ta pa bo odvisna od izgub atomov na stenah reaktorja, v katerih je največji delež rekombinacija. Izvedli smo eksperiment z namenom izmeriti rekombinacijski koeficient a-C:H za nevtralne kisikove atome. Vir atomskega kisika je bila induktivno sklopljena RF-razelektritev v čistem kisiku. Gostote atomskega kisika smo merili z nikljevo optično katalitično sondo. Vzorec a-C:H je bil pripravljen z razprševanjem grafitne tarče v atmosferi mešanice argona in acetilena s termionskim oblokom. Ugotovili smo, da je rekombinacijski koeficient reda velikosti 10^{-5} . Nadalje smo ugotovili, da je med eksperimentom nastala erozija a-C:H-vzorca zaradi delovanja O-atomov. Z grobo oceno smo ugotovili, da je verjetnost za oksidacijo dva velikostna reda nižja od verjetnosti za rekombinacijo.

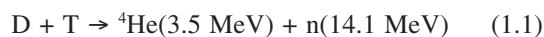
Ključne besede: šibko ionizirana plazma, atomarni kisik, rekombinacija, a-C:H, Optična katalitična sonda

1 INTRODUCTION

In the effort to satisfy the ever growing energy needs of the human civilization, mankind will have to look beyond the horizon of currently used energy sources, among which are fossil fuels are prevalent.¹ Resources of fossil fuels are known to be limited and moreover, the use of fossil fuels is linked to the emission of greenhouse gases, such as CO₂, which is also a very significant problem.^{2,3} While renewable sources offer production of energy without the high environmental costs, they are unfortunately not efficient enough to completely replace the fossil fuels.⁴ Nuclear fission seems like a powerful source of energy, which is also not linked to CO₂ emissions. However, the fission fuel reserves are limited and their use is associated to the problem of nuclear waste. In contrast, when obtaining energy from nuclear fusion, the reaction is fueled by isotopes of hydrogen and lithium that are plentiful in nature. Moreover, the end products of the fusion reaction are stable elements, so there is no problem of radioactive waste. Unfortunately,

the controlling the fusion reaction is much more difficult than the fission reaction. Despite the efforts invested in this field, so far there are no operating fusion power plants. However, individual experiments have shown that fusion can indeed be both achieved in a laboratory and controlled.⁵

The reaction that is most suitable for controlled fusion is:



where a deuterium and tritium nucleus join to form a helium nucleus and a neutron. In order to overcome the electrostatic potential of the positively charged nuclei, a substantial amount of energy must be invested into the reaction (0.4 MeV). This is most easily achieved by heating the fuel to a sufficiently high temperature, so that the thermal kinetic energy of the hydrogen isotopes is high enough – this is referred to as thermonuclear fusion. The required temperature is several thousands of Kelvin, at which the gas is ionized and becomes plasma. Currently, the most promising reactor type for achieving

thermonuclear fusion is the tokamak. It is a toroidal plasma reactor, where the plasma is confined by magnetic field. The confining magnetic field is produced both by external magnets, as well as the electric current of the plasma itself.

While the plasma is magnetically confined, certain contact between the plasma and reactor walls is required for the normal operation of the reactor. In most modern fusion devices, this takes place in the divertor. The heat loads on the surfaces of plasma facing components can be extremely high, in the forthcoming ITER, they are expected to rise up to 10 MW/m².⁶ For that reason, the plasma facing components are constructed using materials which can sustain such high thermal loads. One of such materials is carbon fiber composite (CFC), which features excellent thermal conductivity and can also withstand very high temperatures. The main drawback of the CFC is that it is highly susceptible to chemical erosion by hydrogen.

Hydrogen atoms from the plasma interact with carbon atoms in the PFCs and form carbohydrate molecules which are desorbed from the wall. This way, they can migrate throughout the reactor before they are finally re-deposited on the wall of the reactor. This gives rise to the formation of amorphous hydrogenated carbon deposits (a-C:H) in the walls of the reactor.⁷ Depending on the position of deposit formation, the hydrogen content in the deposit can be as high as 40 %. Because fusion reactors operate on a deuterium-tritium fuel mixture, the a-C:H layers also contain tritium, the radioactive isotope of hydrogen. The buildup of a-C:H layers inside the reactor cause the reactor vessel itself to become radioactive, which is a very much undesired effect, and a serious security risk. In order to ensure an uninterrupted operation of a fusion device, these deposits should be regularly removed.⁸

While there is – and most probably there will not be – one definite method, but rather a combination of various cleaning methods, oxidation of a-C:H deposits is certainly a very suitable candidate. So far, thermal oxidation (baking in O₂ atmosphere) has shown promising results, however the a-C:H removal rates are too low for application in modern day and future fusion devices. A much more efficient technique would be removal of a-C:H by atomic oxygen. Neutral oxygen atoms, which are the predominant species in weakly ionized oxygen plasma, are known to be very reactive, especially in interaction with organic (e.g. carbohydrate) materials.

The interaction of weakly ionized oxygen plasma with organic materials is spread over a very broad spectrum. The effect of oxygen atoms on materials can either be very non-invasive, modifying only the topmost atomic layers of the surface, such as is the case in surface activation,^{9–17} or it can be destructive, as it is with the application of weakly ionized plasma for destruction of bacteria (sterilization).^{18,19} However, it should be noted that even when atomic oxygen interacts destructively with the processed material, the destruction is very

selective. Indeed, the selective etching by neutral oxygen atoms is a well known and documented feature.^{20–24} The selectivity is believed to stem from the different erosion yields, based on different hydrogen content of the processed material. The general rule is that the more hydrogen the material contains (the "softer" it is), the higher is the erosion yield for neutral oxygen atoms.²⁵ The etching efficiency along with the selectivity of etching could allow for successful removal of a-C:H without causing significant damage to carbon based reactor components. Weakly ionized oxygen plasma has already been used as a source of atomic oxygen in experiments of a-C:H removal, yielding removal rates as high as 10 nm/s,²⁶ and in experiments dealing with interaction of oxygen atoms with tungsten containing a-C:H deposits at extreme conditions.²⁷

A successful technique for removal of a-C:H requires efficient delivery of atomic oxygen to the contaminated surface, which means that the density of oxygen atoms at the contaminated surface should be relatively high, even if that surface is not in the direct vicinity of the atom source. The transmission of atoms from the source to the target, so to speak, depends in a great way on losses of atoms on the surrounding reactor walls. Among the many possible reactions that can undergo during the interaction of atomic oxygen with solid materials,^{28–40} heterogeneous recombination, reaction in which two oxygen atoms join to form an oxygen molecule, is in most cases the most probable reaction. Due to the laws of conservation of momentum and energy, in gas phase it requires a three body collision, which is an extremely rare event at low pressures, so it is safe to assume it only takes place on surfaces of solid materials. Since recombination is the most important contribution to atom losses, it has a very significant effect on the atomic oxygen density inside the reactor. Thus, the probability of heterogeneous recombination, or recombination coefficient γ is of key importance when planning a-C:H removal systems.

In this paper, we present an experiment in which we observed both recombination of oxygen atoms on an a-C:H surface, as well as oxidation of a-C:H. Based on these observations, we compare the probability of recombination and the probability of oxidation.

2 EXPERIMENTAL

We performed an experiment in the afterglow of weakly ionized oxygen plasma with the intent to determine the recombination coefficient of a-C:H for oxygen atoms. The a-C:H sample was prepared in a thermionic arc sputtering system, by sputtering a graphite target in an atmosphere of argon and acetylene. The material used for the substrate, was aluminum foil, due to its favorable mechanic properties. The thickness of the deposited a-C:H film was 0.5 μm . The a-C:H covered foil was inserted into a side-arm of our plasma

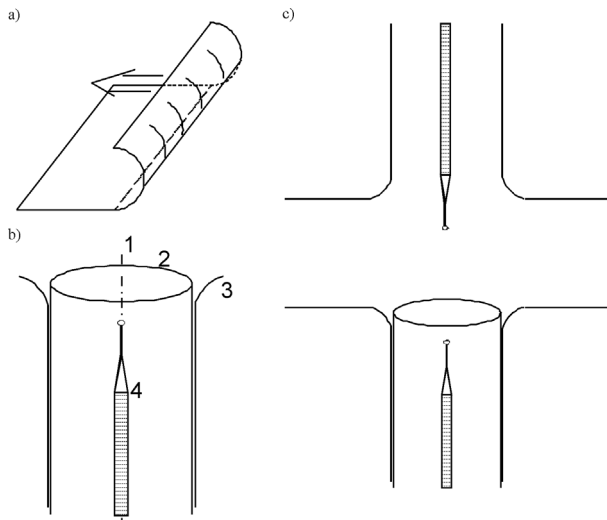


Figure 1: Experimental set-up: a) manipulation of the a-C:H covered foil, arrow indicates direction of folding; b) insertion of foil (2) and the FOCP (4) into the side-arm (2). The FOCP is used to measure the density of atomic oxygen along the axis (1) of the side-arm; c) position of the additional FOCP (top side) that measures the atomic oxygen density at a constant position.

Slika 1: Eksperimentalna postavitev: a) zvijanje folije, pokrite z a-C:H, puščica nakazuje smer zvijanja; b) vstavljanje folije (2) in optične katalitične sonde (4) v stransko cev (2). Z optično katalitično sondo merimo gostoto atomarnega kisika v osi (1) stranske cevi; c) položaj dodatne optične katalitične sonde (zgoraj), s katero merimo gostoto atomskega kisika na nespremenljivem položaju.

reactor, so that the a-C:H covered side was facing the inside of the tube, as seen in **Figure 1**. The reactor was powered by an inductively coupled radiofrequency generator, operating at 27.12 MHz with an approximately 100 W output power. Plasma was ignited in pure oxygen, leaked into the plasma reactor at pressures between 60 Pa and 180 Pa. The resulting atomic oxygen densities in the direct vicinity of the a-C:H sample were from $5 \cdot 10^{21} \text{ m}^{-3}$ to $2 \cdot 10^{22} \text{ m}^{-3}$. A spatially resolved measurement of atomic oxygen densities was performed using a nickel tipped fiber optic catalytic probe (FOCP).⁴¹⁻⁴⁷ The FOCP was used to measure the atomic

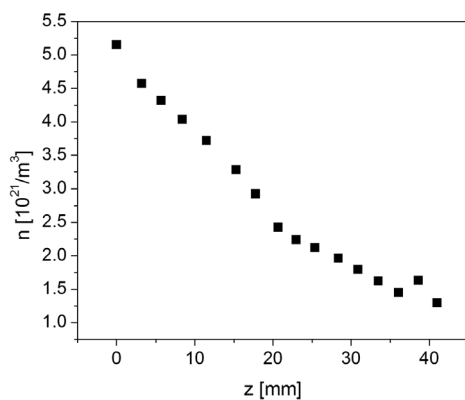


Figure 2: Atomic oxygen density profile recorded at 120 Pa. The term z denotes the distance from the probe tip to the opening of the side-arm.

Slika 2: Profil gostote atomskega kisika, posnet pri 120 Pa. Izraz z označuje razdaljo med ustjem stranske cevi in konico sonde.

oxygen density at several discretely spaced points along the axis of the side-arm, at different pressures. Simultaneously, another nickel tipped FOCP was kept at constant position in the reactor to monitor the fluctuations of the atomic oxygen density that might affect the results.

3 RESULTS AND DISCUSSION

An example of the recorded atomic oxygen density profile, recorded at a fixed pressure, is shown in **Figure 2**. A physical model, based on the diffusion equation,⁴⁸ was employed to determine the values of the recombination coefficient from the recorded atomic oxygen profiles. Fitting the model over the density profiles obtained at all the different pressures, we get the value of the recombination coefficient $\gamma = (1.0 \pm 0,3) \cdot 10^{-3}$.

When we removed the foil from the experimental system, we noticed that the a-C:H film had been partially eroded during the experiment. As seen in **Figure 3**, the deposit was removed from the substrate up to 2 cm away from the edge of the foil. This, of course, means that the obtained values of the recombination coefficient are not accurate, as during the measurement, the surface of the sample changed from a-C:H to aluminum. Using only the data obtained in the non-eroded region, the re-calculated value of recombination coefficient is $(9.9 \pm 0,2) \cdot 10^{-4}$. As the value does not greatly differ from the first calculation, we assume that the value of the recombination coefficient of the substrate (Al) is similar to that of a-C:H. However, that is not the only problem that has arisen due to the erosion of the sample. The model we used to determine the value of the recombination coefficient assumes that the only mechanism of atom loss on the walls is recombination when clearly, the oxygen atoms engage in oxidation as well. However,

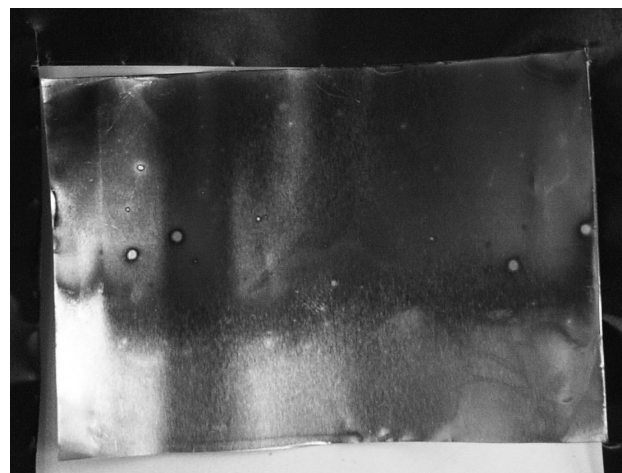


Figure 3: Aluminum foil with the deposited a-C:H thin film after the experiment. The foil used in the experiment was cut out from the piece that is framing it in the picture. The difference between the eroded and non-exposed a-C:H deposits are easily observable.

Slika 3: Aluminijeva folija z nanosom a-C:H po eksperimentu. Folija, ki smo jo uporabili pri eksperimentu, je bila izrezana iz večjega kosa folije, ki jo na sliki uokvirja. Razlika med pojedkanim in nespremenjenim vzorcem je očitna.

while determination of the erosion rate was not the primary aim of this experiment, we can nonetheless make a rough estimate of the erosion rate and subsequently the loss of atoms due to oxidation.

The topmost, eroded layer of the sample received, in approximately two hours of total operation time, a dose of neutral oxygen atoms:

$$\Gamma = 15 \cdot 10^{28} / \text{m}^3 \quad (1.2)$$

The thickness of the deposit was $h = 0.5 \mu\text{m}$, which results in an erosion rate of $\nu \approx 0.06 \text{ nm/s}$. Assuming the density of carbon atoms in the deposit to be the same as the density of carbon atoms in graphite, $n = 1.24 \cdot 10^{29} / \text{m}^3$, we get the number of removed atoms per square meter in those two hours, $N = 6 \cdot 10^{22} / \text{m}^2$. Further assuming that each eroded carbon atom reacts with one oxygen atom from the gas phase, the probability for oxidation is the ratio between the oxygen atoms that engage in oxidation and the total number of impinging oxygen atoms:

$$P = \frac{\Gamma}{N} = \frac{6 \cdot 10^{22}}{15 \cdot 10^{28}} = 4 \cdot 10^{-6} \quad (1.3)$$

which is for a factor of 250 lower than the probability of recombination. Thus, we can safely conclude that probability of the oxygen atom engaging in recombination is at least two orders of magnitude higher than the probability it would engage in an oxidation reaction. Moreover, since oxidation is only a minor contribution to the atom loss on the a-C:H surface, we see that the erosion hasn't further affected the results of this experiment.

4 CONCLUSION

An experiment was performed to determine the recombination coefficient of a-C:H for neutral oxygen atoms. The sample was prepared by thermionic arc sputtering deposition on aluminum foil. An inductively coupled radiofrequency discharge in pure oxygen was used as the source of atomic oxygen. Neutral oxygen atom densities were measured with a fiber optic catalytic probe. After the experiment, it was found that the a-C:H film had been eroded during the experiment. Using a rough estimate, we conclude that an impinging oxygen atom will take part in an oxidation reaction is $4 \cdot 10^{-6}$. The value of the recombination coefficient, obtained using a diffusion model, was found to be $(9.9 \pm 0.2) \cdot 10^{-4}$. Thus, we found the probability of recombination two orders of magnitude greater than the probability of oxidation.

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