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Atomic Oxygen Concentration in a Flowing Post-Discharge Reactor

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Concentration of neutral oxygen atoms in the flowing post-discharge of a pure oxygen microwave discharge at different experimental conditions was determined with a nickel catalytic probe. The post-discharge reactor was setup for metal surface cleaning. It worked at the pressure between 20 and 100 Pa and at output power of the microwave plasma generator between 80 and 150 W. At those experimental conditions the O-atom density was found to be of the order of 10^{21} m^{-3}. It increased both with increasing pressure and microwave power. The degree of dissociation of oxygen molecules, on the other hand, decreased with increasing pressure.

KEY WORDS: Reactive plasma; microwave discharge; oxygen atoms; catalytic probe.

1. INTRODUCTION

In the past decade, technologies based on application of oxygen plasma have been successfully applied to different branches of science and industry. The technologies include the an-isotropic plasma etching, plasma drilling, plasma oxidation, plasma cleaning, plasma ashing and plasma surface activation.[1–6] Different technologies require application of plasma with different parameters. For an-isotropic etching and drilling, a plasma with a high degree of ionization is needed, while for some other technologies, an oxygen plasma with a low density of charged particles performs better. For very delicate treatments of samples, for instance during plasma ashing and selective plasma etching, a state of a gas with a negligible concentration of charged particles should be used. In such cases, it is much better to treat samples in post-discharges rather than in plasmas themselves. In systems used for delicate plasma treatments, the most important parameter is

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the density of neutral oxygen atoms. It can be measured by different means including laser spectroscopy (LIF),[7,8] NO titration[9] and catalytic probes.[10,11] The latter technique was applied to determine the O concentration in the post-discharge reactor for the experimental study of the role neutral oxygen atoms play in low temperature degreasing.

2. EXPERIMENTAL

The experimental system is shown in Fig. 1a. The system is pumped with a two stage oil rotary pump with a pumping speed of 48 m^3/h. The experimental chamber is a Pyrex cylinder of length 20 cm and of diameter 15 cm. A pyrex tube of diameter 2 cm and length 20 cm leads to the discharge that is inside a quartz tube of outer diameter 7 mm and of inner diameter 5 mm. The plasma is created with a surfatron cavity at 2.45 GHz MW and output power adjustable between 0 and 300 W. The surfatron is placed 20 cm away from the junction of pyrex and quartz

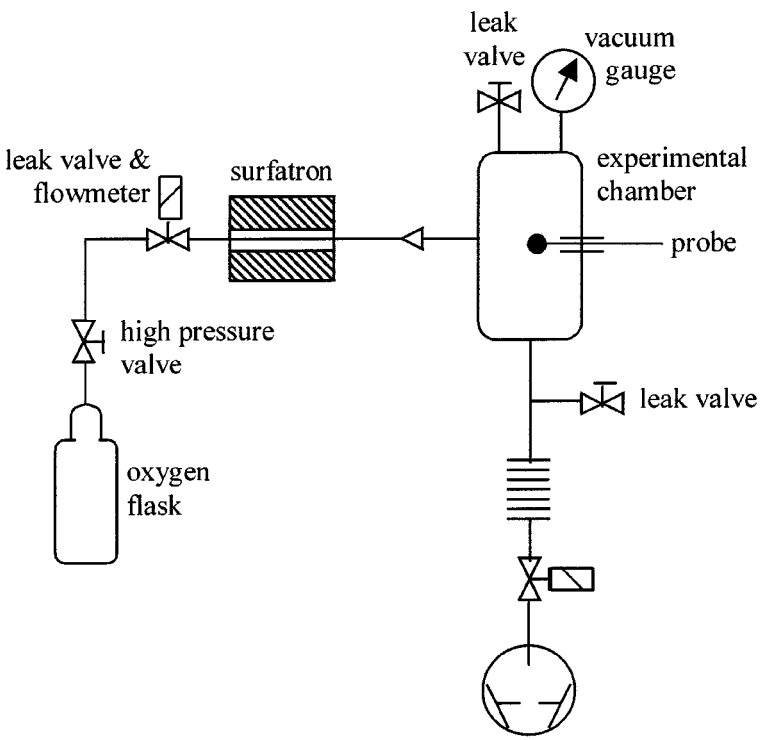

Fig. 1a. Schematic of the experimental setup.

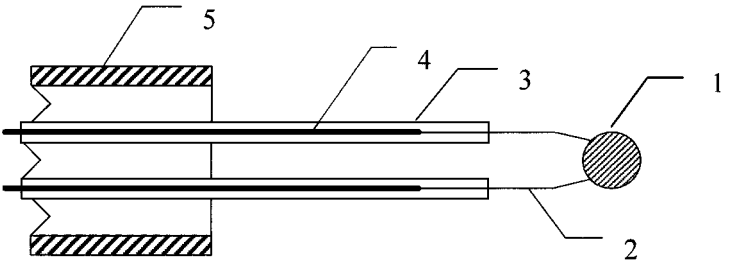

Fig. 1b. Nickel catalytic probe. 1-nickel disc, 2-chromel-alumel thermocouple wires, 3-thin glass tube, 4-kovar wire, 5-glass tube.

tubes in order to prevent propagation of MW plasma into the pyrex tube. The quartz tube is cooled with forced air so that the tube temperature never increased over 150°C. Other parts of the system are kept at room temperature. Pressure is measured in the post–discharge reactor with an Edwards vacuum gauge. Pressure in the reactor is adjusted with an Alphagas volume flow controller. In the range between 20 and 100 Pa the pressure increases roughly linearly with increasing flow.

Concentration of neutral oxygen atoms is measured with a nickel catalytic probe.[11] The probe is shown in Fig. 1b. It is made of polycrystalline nickel disc (purity 99.8 at.%) with the diameter of 1 mm and the thickness of 0.2 mm. The disc is spot welded to thermocouple wires with the diameter of 0.125 mm and the length of 20 mm. On the other side, the thermocouple wires are spot welded to kovar wires with the diameter of 1 mm. The thermocouple wires are covered with narrow glass tubes (Schott 8250) with the outer diameter of about 1.3 mm and the thickness of approximately 0.1 mm. The narrow glass tubes prevented oxygen atoms to recombine on thermocouple and kovar wires. The kovar wires are sealed into a glass tube with the diameter of 7 mm.

The recombination coefficient for the reaction $O + O \rightarrow O_2$ on well oxidized (often called "well activated") polycrystalline nickel is 0.27 ± 0.04.[(11)] Due to extensive recombination of oxygen atoms on the nickel disc its temperature rises substantially over the ambient temperature when the plasma source is turned on. The density of oxygen atoms could be determined from the probe temperature. However, since the calculation is not trivial and since it includes not precisely determined constants, it is much easier and more accurate to determine the O density from the first time derivative of the $T = T(t)$, just after turning off the plasma source.

At the steady conditions the heating of the nickel disc due to recombination of oxygen atoms on its surface is equal to the cooling due to gray body radiation, thermal conductivity of gas and thermal conductivity of thermocouple wires. As soon as the plasma source is turned off, the heating vanishes in a short time of the order of 0.1 s (atoms are pumped away and/or recombined on reactor walls). At that moment, the cooling of the probe is still the same as before turning off the

source. Measuring the cooling rate just after plasma is turned off therefore leads to the information of the heating rate at steady conditions. The flux of O atoms on the disc surface is described in Eq. [1]:

$$j = \frac{1}{4} n v \tag{1}$$

where n is the O density in the vicinity of the probe and v its average random velocity. The heat dissipated on the probe per unit time is equal to the product of the flux with the average energy that an atom brings to the surface and with the surface area as in Eq. [2]:

$$P = j^{1/2} \gamma W_D 2\pi r^2 \tag{2}$$

Here, W_D is the dissociation energy of an oxygen molecule (5.12 eV), γ the recombination coefficient, and $2\pi r^2$ the total surface area. The factor of $^1/_2$ comes from the fact that an oxygen molecule consists of 2 atoms. The cooling rate of the disc just after the plasma source is turned off is Eq. [3]:

$$P = M c_p (dT/dt) \tag{3}$$

where M is the mass of the nickel disc, c_p its heat capacity and dT/dt the derivative of the probe temperature with time just after the plasma source is turned off. Combining the Eqs. [1]–[3] and rearranging, one gets Eq. [4] which gives the density of neutral oxygen atoms (n_O) in the vicinity of the disc:

$$n_O = \frac{4 M c_p \, dT}{v \gamma W_D \pi r^2 dt} \tag{4}$$

The probe was placed in the center of the experimental vessel. The data were collected with our own hardware/software system. The period between two consecutive measured points was 30 ms and the total time for measuring a probe characteristics was about 1 min. Measurements of probe characteristics were performed at different pressure and output power of the MW generator. At any condition, three subsequent measurements were performed. As for example, a set of characteristics measured at the pressure of 40 Pa and the power of 120 W is plotted in Fig. 2. In Fig. 3a, the characteristics measured were plotted at the same pressure but different power. In Fig. 3b the characteristics measured at the power of 100 W and different pressure.

3. RESULTS

The density of neutral oxygen atoms in the vicinity of the probe was determined from the first time derivative of the probe characteristics just after the plasma source is turned off. The density of oxygen atoms in the reactor chamber versus pressure is shown in Fig. 4. It is noticeable that the density increases with

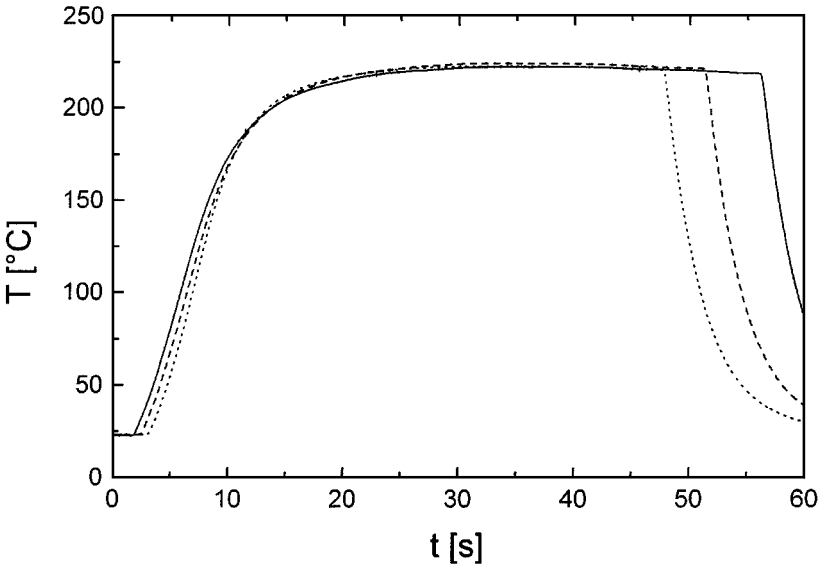

Fig. 2. Catalytic probe characteristics as measured at pressure of 40 Pa and at MW power of 120 W. Characteristics obtained at three subsequent measurements are show. A steep increase in the curve indicates that the MW generator turned on, and a decrease indicates that the generator is turned off.

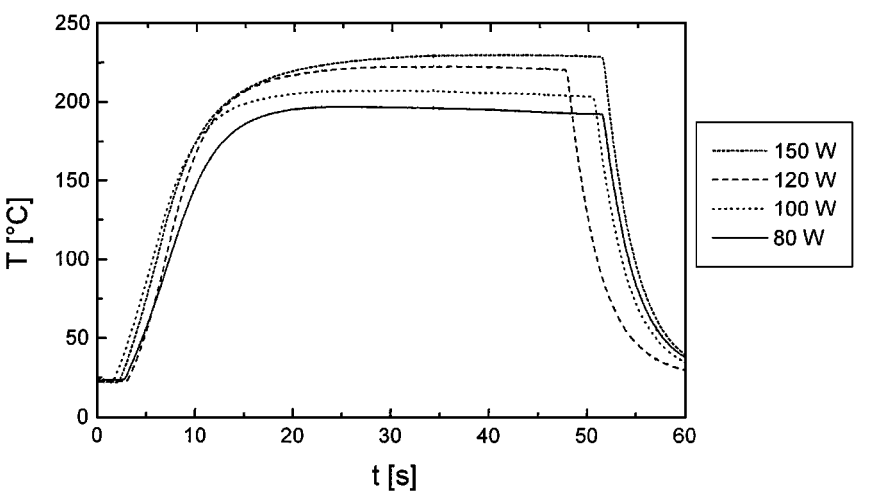

Fig. 3a. Catalytic probe characteristics measured at pressure of 40 Pa and several MW power values.

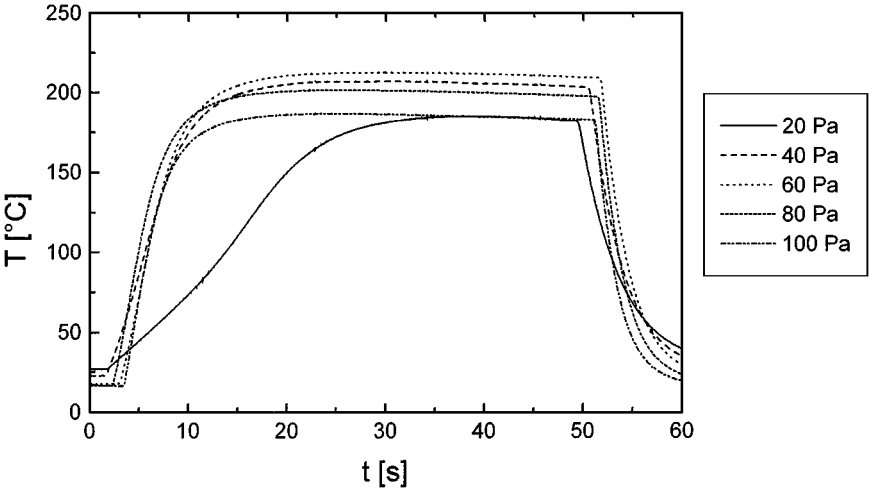

Fig. 3b. Catalytic probe characteristics measured at MW power of 100 W and several pressures in the post-discharge reactor.

increasing pressure. It also increases with increasing power of the plasma generator. At the lowest pressure tested, i.e., 20 Pa, the difference in density between measurements at different power is small. At any power, the O density at the pressure of 20 Pa is close to 6.10^{20} m^{-3}. At higher pressure, the difference in O density

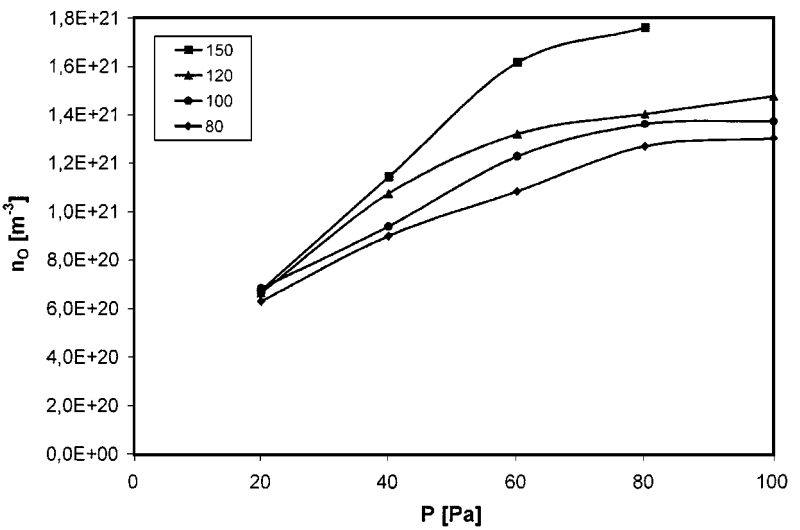

Fig. 4. Density of oxygen atoms in the reactor chamber versus pressure. The parameter is the output power (in watts) of the MW generator.

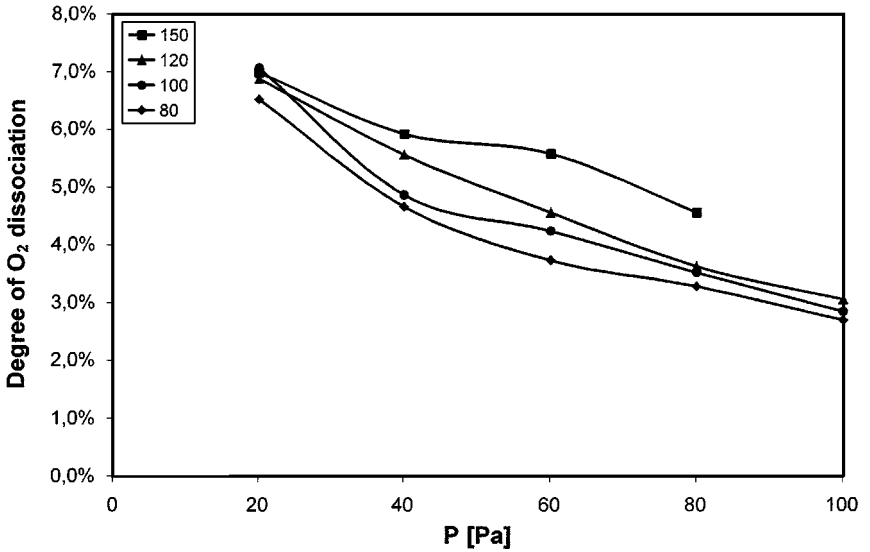

Fig. 5. Degree of dissociation of oxygen molecules in the reactor chamber versus pressure. The parameter is the output power (in watts) of the MW generator.

increases, and at the pressure of 80 Pa the O concentration at the power of 80 W is only two thirds of the concentration at 150 W.

The degree of dissociation of oxygen molecules in the experimental vessel is plotted in Fig. 5. It was calculated using equation ($\eta = n_O kT/2p$, where n_O is the density of oxygen atoms, p the pressure and T the temperature of the reactor walls (room temperature). The degree of dissociation decreases with increasing pressure. At the pressure of 20 Pa it is about 7%, while at pressure of 100 Pa it drops to only 3%. It is interesting to note that the degree is linearly decreasing against pressure and practically independent of the MW power.

4. DISCUSSION

The density of neutral oxygen atoms was determined with a nickel catalytic probe. The method proved to be suitable for the measurements in our particular experimental system. In general, however, there are limitations on the use of the technique that are briefly addressed later.

The probe gives accurate results only in post-discharges. In plasma itself, the concentration of neutral oxygen atoms is always overestimated due to additional heating of the probe mainly caused by recombination of charged particles and absorption of light quanta. In order to estimate the density of oxygen atoms in

plasma itself, one has two options: (i) measuring the O density in a post-discharge and calculating the density in plasma by taking into account the conductivity of the connecting tube between discharge and the post-discharge chamber for oxygen atoms. This conductivity can be measured with a moveable probe as demonstrated by Mozetič[11] for the case of oxygen and by Mozetič and Drobnič[12] for the case of hydrogen. (ii) introducing another probe in plasma. The other probe should be made of a material with a very small recombination coefficient—for instance aluminum with a surface layer of oxide.

The catalytic probe described in this paper is sensitive to stray effects caused by electromagnetic fields. Since the probe signal (thermocouple voltage) is of the order of mV and the stray fields of the order of 10V, it is clear that the measurements are vague as long as the high frequency generator is on. Again, a solution of this problem is placing the probe far enough from the discharge region (as in our case) and/or shielding the probe. Still, it should be stressed that for the determination of the O density one needs only the time derivative of the probe signal when the generator is off.

In order to assure proper determination of the O density, the probe surface should be well activated. This phenomenon limits the range of application of the method to well dissociated states of gas. At low O concentration the surface remains poorly activated—the recombination coefficient in this case is much lower than 0.27. Here, it is worth mentioning that a variety of values of the recombination coefficients for the same material have been reported. In order to avoid possible systematic errors of this type it is best to measure the recombination coefficient of the material a particular probe is made of. A method of measuring the recombination coefficient is described by Mozetič.[11] In our case, we used exactly the same probes as Mozetič.[11] If still in doubt, one can compare the results of catalytic probes with another technique. In our case, direct comparison with NO titration was done and the results did not differ for more than 30%.[13]

5. CONCLUSIONS

The density of neutral oxygen atoms was measured in the present reactor chamber for plasma degreasing. We used standard nickel catalytic probes for determination of O concentration at several pressures and output powers of the microwave generator. We found that at low pressure, the concentration of neutral oxygen atoms does not depend much on the output power of the plasma generator. At higher pressure, the density increased with increasing pressure and also with increasing power. At the pressure of 80 Pa the density of oxygen atoms in the post discharge was nearly 50% higher when the oxygen plasma power was increased from 80 to 150 W.

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