Optical Characterization of Glow and Afterglow Regions of Ar/O₂ Microwave Plasma: Effect of Applied Power and Gas Flow

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Abstract. In this work, the effect of microwave power and gas flow on formation of atomic oxygen (O) was investigated by actinometry method in the two different regions of Ar/O₂ microwave plasma: the glow and afterglow regions. The experiments were performed keeping constant the Ar/O₂ gas flow ratio at proportion of 3/2 and varying the microwave power from 200 to 1100 W and the total gas flow from 50 to 300 sccm. The results showed that the production of O depends on both discharge parameters investigated and that the microwave power has the greater influence in the production of O. At afterglow region the production of O tends to be uniform and not dependent on the gas flow and microwave power. This may be due to homogenization of the processes of recombination and loss in the gas phase and to the walls along the afterglow region.

1. Introduction
The afterglow discharge region of oxygen microwave plasma has been used with great interest in surface modification of materials. In the case of polymeric material, the major interest is to modify the surface energy in order to improve the adhesion properties [1]. In the case of inorganic and metallic materials the major interest is the surface cleaning (oil removing, for example) [2] and sterilization of medical instruments [3].

In this scope, the densities of neutral and metastable atomic oxygen in the reactor are of great concern since the processing speed depends on the flux of these particles onto substrate, which is greatly influenced by process conditions such as gas pressure and applied power. Moreover, it is known that the addition of argon in the oxygen plasma produces a significant enhancement of the dissociation rate of oxygen gas [4]. At the same time, it creates a condition for a simple and low cost measurement of atomic oxygen (O) concentrations by comparing the emission from argon and oxygen atoms [5].

Nowadays, there are several experimental techniques to measure the amount of O formed during an electrical discharge in a gas, and one of the more commonly used is optical emission spectroscopy (OES) [6]. Through the use of this technique, in conjunction with the actinometry method [7, 8], the relative amount of O formed in gas phase can be estimated through the intensities of the spectral lines of oxygen OI (844.6 nm) and argon ArI (750.4 nm), i.e. the I₀ᵢ/Iᵦᵢ ratio.

In this work, the effect of microwave power and total gas flow on formation of O was investigated by actinometry method in the glow and afterglow regions of Ar/O₂ microwave plasma. The
experiments were performed varying the microwave power and the total flow, while keeping constant the Ar/O\textsubscript{2} ratio. In order to characterize the glow and afterglow regions, the OES measurements were realized at three different points along the microwave plasma.

2. Experimental setup
A schematic of microwave plasma system used in this investigation is presented in Fig. 1. The gas is injected in a 10 mm outer diameter quartz tube that is connected to a 200 mm diameter and 1300 mm length Pyrex tube (pos-discharge chamber). The system is pumped by mechanical and root pumps. The total Ar/O\textsubscript{2} gas flow was varied from 50 to 300 sccm. The microwave plasma was generated inside the 10 mm quartz tube coupled to a 2,45 GHz rectangular waveguide and resonant cavity. The microwave power was varied from 200 to 1100 W. The waveguide is of adjustable size and has three manual stubs used as matching network system.

The pressures were varied from 12 to 32 mTorr in the lower and higher flow condition, respectively.

![Figure 1: Experimental setup used for generation of microwave plasma. The optical spectra were obtained in the position A, B and C](image)

For the accomplishment of the optical characterization of glow and afterglow regions of Ar/O\textsubscript{2} microwave plasma an optic fiber was installed at three points (A, B and C, Figure 1) of quartz tube in order to collect the light emitted from the plasma and the afterglow regions. These fibers are connected externally to an optical emission spectrometer (Ocean Optical USB4000) with resolution of 1.5 nm, operating in the range of 200-850 nm.

The actinometry method consists in correlate the optical emission spectrum, more specifically the intensity ratio of the gas of interest (in this case, the oxygen) with the intensity of the gas used as actinometer. For oxygen plasmas, the reactive specie to be studied is the atomic oxygen O(3p) with emission at 844.6 nm and the actinometer gas was used the argon Ar(4p) with emission at 750.4 nm. The actinometry is a qualitative method to estimate the concentration of certain active specie formed in the plasma or to observe its behavior with the variation of plasma parameters. The qualitative concentration of oxygen [O] is obtained using equation 1. The [Ar] is controlled inserted in the plasma, and the I\textsubscript{O} and I\textsubscript{Ar} are measured using an optical spectrometer. The weak point of this method is to obtain the reaction constant k(O), that take into account all kinetic reactions on the plasma. This constant also strongly depends of the plasma parameters (microwave power, pressure, gas flow, etc.) and oxygen argon gas ratio.

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\frac{I_{O}}{I_{Ar}} = k(O)[O]/[N]
\] (1)
In order to certify the results obtained by actinometry, quantitative method as gas titration has been used by several researchers [9-11]. The results obtained by these authors show that the actinometric method produces results that are in good agreement with the titration method an Ar/O$_2$ gas ratio up to about 2. Based on the literature, the behavior of the atomic oxygen concentration for different plasma conditions was studied using an Ar/O$_2$ ratio of 1.5.

3. Results and discussions

Surface plots of optical intensities ratio, I$_{O/I}$/I$_{ArI}$, as function of total gas flow and microwave power, obtained at positions A, B and C are presented at Figure 3a, 3b and 3c, respectively. The surfaces representing the trends of experimental data (black points) were created using the spline method.

As expected, the more important variation on the values of I$_{O/I}$/I$_{ArI}$ with variation of microwave power and with total gas flow occurs in point A. This point is the center of microwave applicator where the highest microwave field intensity is concentrated. For a given microwave power the value of I$_{O/I}$/I$_{ArI}$ decrease with the increase of the total gas flow. On the other hand, the I$_{O/I}$/I$_{ArI}$ for a given total gas flow increase with the increase of microwave power. However, the increase is less pronounced for high gas flow.

Figure 3: I$_{O/I}$/I$_{ArI}$ as a function of microwave power and total gas flow rate along the microwave discharge axis at: a) point A; b) point B; and c) point C.
The lower rate of atomic oxygen production with the increase of total gas flow may be related with the increase of the pressure inside the quartz tube. The pressure varied from 14 mTorr to 34 mTorr for the total gas flow variation from 50 sccm to 300 sccm, respectively. The increase of pressure decreases the mean free path and the residence time of the gas molecules in the microwave field area, which increase the number of molecules that will not acquire enough energy to ionize the gas. The decrease of the mean free path also contributes to the recombination process. All these processes contribute to the decrease of the atomic oxygen with the increase of gas flow.

The higher values of atomic oxygen obtained for low gas flow are mainly related with the lower pressure inside the quartz tube, which increase the molecules mean free path, and the increase of residence time of the molecules inside the microwave field region. These effects contribute to the increase of the dissociation process [12, 13].

Figure 4 shows the dependence of $I_{\text{O I}}/I_{\text{Ar I}}$ with microwave power on the three measuring points for a total gas flow of 100 sccm. Here, we can better observe the variation of $I_{\text{O I}}/I_{\text{Ar I}}$ along plasma region. In the afterglow regions (positions B and C) the $I_{\text{O I}}/I_{\text{Ar I}}$ values to not change for microwave power higher than about 650 W, indicating that the creation and recombination processes in the volume and in the tube walls are in equilibrium in the afterglow region.

![Figure 4: $I_{\text{O I}}/I_{\text{Ar I}}$ as function of microwave power for total gas flow rate of 100 sccm measured at the positions A, B and C.](image)

4. Conclusions

Using the OES technique associated with the actinometry method was possible to qualitatively study the behavior of atomic oxygen production in glow and afterglow regions of microwave plasma. The behavior of $I_{\text{O I}}/I_{\text{Ar I}}$ was investigated as function of discharge microwave power (200 - 1100 W) and total gas flow (50 - 300 sccm) for an Ar/O$_2$ gas flow ratio of 3/2.

The $I_{\text{O I}}/I_{\text{Ar I}}$ and consequently, the relative concentration of atomic oxygen showed different behaviors with microwave power and total gas flow along the discharge axis. Within the range of parameters analyzed the higher production of atomic oxygen can be associated to the elevated microwave power and low gas flow.

Concerning the variation of concentration of O along the plasma axis, it was observed that in the afterglow regions the atomic oxygen concentration decreases due to the recombination processes in the volume and in the tube walls. In the afterglow regions the creation and recombination processes are equivalent and the atomic oxygen concentration are kept constant for microwave power higher than about 650 W.
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