ELSEVIER

Surface and Coatings Technology 142–144 (2001) 333–336

SURFACE & COATINGS TECHNOLOGY

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Excited species in H_2, N_2, O_2 microwave flowing discharges and post-discharges

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Abstract

The density of O and H atoms have been measured by emission spectroscopy and by catalytic probes in a flowing post-discharge reactor. In the post-discharge reactor at 1 torr and a time of $2-3\times10^{-2}$ s after a 2.45-GHz Ar−10%O_2 discharge (quartz tube of diameter 6 mm) at 60 W, approximately the same values of $1(\pm0.3)\times10^{15}$ cm^{-3} oxygen atom densities were obtained by NO titration and by a Ni catalytic probe. In Ar−H_2 post-discharge, the Ni catalytic probe gave a H-atom density of $(1-1.2)\times10^{15}$ cm^{-3} for an Ar−4%H_2 gas mixture at 3 torr and a time less than 10^{-3} s after a microwave discharge of 50 W.

Keywords: Post-discharge reactor; Oxygen and hydrogen atom densities; Optical spectroscopy; Catalytic probes

1. Introduction

Reactive plasmas in H_2, N_2 and O_2 molecular gases are extensively studied for surface treatments, such as surface cleaning and nitriding. The present analysed process is a flowing post-discharge at low gas temperature without the interaction of ions and electrons with the treated surfaces. The production of H, N and O active atoms has been previously determined in such flowing microwave post-discharges [1]. In previous work, the plasma nitriding of iron surfaces has been analysed in Ar−N_2−H_2 post-discharge. More recently [2], the cleaning of oil contaminated metal surfaces (steel and aluminium) has been successfully performed in an Ar−O_2 flowing microwave post-discharge.

In the present study, catalytic probes [3,4] have been set up in the post-discharge reactor to determine the absolute densities of H and O atoms. Variations of atom densities in Ar−H_2 and Ar−O_2 gas mixtures have been measured vs. the microwave power and the H_2 and O_2 percentages into Ar. A comparison is first given between the measurements of O-atom densities by NO titration and by catalytic probes in the post-discharge.

Within the Ar−H_2 microwave discharges, the H-atom relative densities are obtained by emission spectroscopy with interpretation from the relevant kinetics reactions. Such relative densities in the discharge are compared with the quantitative results obtained by the catalytic probe in the early post-discharge.

2. Experimental set-up

The experimental set-up is reproduced in Fig. 1. The flowing post-discharge reactor is made in three parts. Upstream in the first part are two discharge tubes of 5-mm diameter to produce d.c. or microwave plasmas. In the present study, the microwave discharge alone was switched on, since it has been previously found [5], by comparing the two discharges, that a higher O-atom density is obtained after the microwave discharge. The microwave plasma is then produced by a surfatron cavity at 2.45 GHz in a quartz tube of 5 mm in diameter, with a power less than 100 W. The second part of the reactor is a Pyrex cross tube of 2 cm in diameter and 20 cm in length. Finally, the third part is the Pyrex treatment chamber of 15-cm diameter and 20

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0257-8972/01/$ - see front matter
PII: S0257-8972(01)01276-2

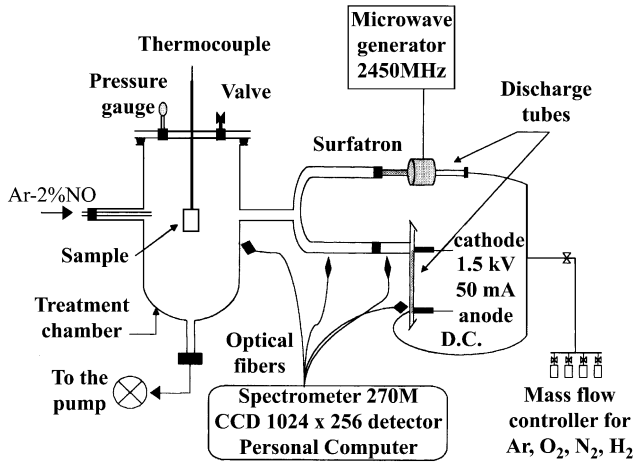

Fig. 1. The experimental set-up of flowing post-discharge reactor with d.c. and microwave discharges.

cm in height. The gas flow can be up to 1500 sccm (standard cm^3 per min) and the gas pressure inside the post-discharge reactor is between 1 and 10 mbar, depending on the gas flow. Samples can be placed in the centre of the treatment chamber in front or opposite the inlet of the reactive gas flow.

The optical emission is collected by optical fibres which are connected to a Jobin–Yvon 270M spectrometer with a CCD 1024*256 UV detector. The titration by NO of N and O-atoms is performed as shown in Fig. 1. The NO inlet is replaced by a catalytic probe for the measurement of O and H-atom densities in the chamber without substrate.

3. The O-atom density by NO titration and by catalytic probe

The NO titration method is detailed elsewhere [2,5]. Briefly, the O-atom density is measured after that of the N-atom density by NO titration in an $Ar–N_2$ post-discharge. The flow of NO (here, an Ar–2%NO gas mixture) is progressively introduced into the $Ar–N_2$ post-discharge. It produces an extinction point where both the N and NO flow rates are equal in quantity. The N-atom density is then determined from that of NO. After that, only O-atoms remain with a density equal to that of the initial N-atoms. Then an excess of NO produces the emission of a NO_2 continuum with an intensity which varies linearly vs. the introduced NO by a slope r_1. By replacing N_2 with O_2 in the Ar plasma, the NO_2 emission is directly produced by the O-atoms coming from the plasma with an intensity varying with NO by a slope r_2. Then the O-atom density is related to the N-atom density by the following equation:

$$[O] = [N]r_2/r_1 \quad (1)$$

Variations of the O-atom density vs. the O_2 percentages in Ar are reproduced in Fig. 2 for two $Ar–O_2$ gas flows and pressures with 60 W in the microwave discharge. The O-atom density is sharply increasing with the O_2 percentage to reach a saturated value of $(1–1.2) \times 10^{15}$ cm^{-3} for more than 20% of O_2 in Ar. The uncertainty of this NO titration method is estimated to be $\pm 30\%$.

The density of O-atoms was also measured with a catalytic probe [3,4] at the centre of the post discharge reactor. A small Ni cylinder of 2 mm in diameter and 0.2 mm in thickness was spot welded to a chromel–aluminel thermocouple. The signal from the thermocouple was sent to an amplifier and to a computer interface, where it was filtered and recorded in an x–y diagram. The time between two subsequent points was 30 ms and the total acquisition time is for a discharge time of approximately 1 min.

The probe was activated in few min after exposure to a pure oxygen post-discharge of 1 torr and 150 W. An example of probe signal characteristics is reproduced in Fig. 3 for an O_2 post-discharge at 0.3 torr and 120 W. It is shown in Fig. 3 that characteristics were obtained for three subsequent measurements. The increases occurred when the discharge was turned on, and decreased when it was turned off.

The density of O-atoms in the vicinity of the probe was determined from the first derivative of the probe signal just after turning off the plasma source, by using the following equation:

$$[O] = 4mc_p/\gamma\nu E_d \pi r^2 \mathrm{d}T/\mathrm{d}t \quad (2)$$

where m is the probe mass; c_p is the thermal capacity of the probe (here in nickel); γ is the recombination coefficient of the atoms on the probe; ν is the thermal

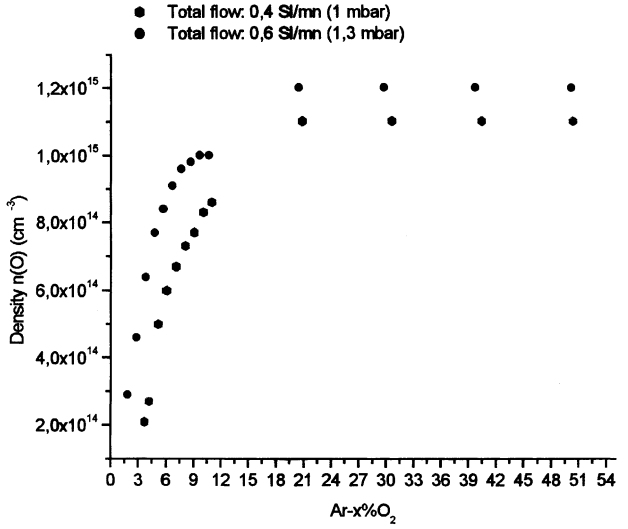

Fig. 2. Density of O-atoms by NO titration vs. the O_2 percentage into Ar. Microwave power: 50 W.

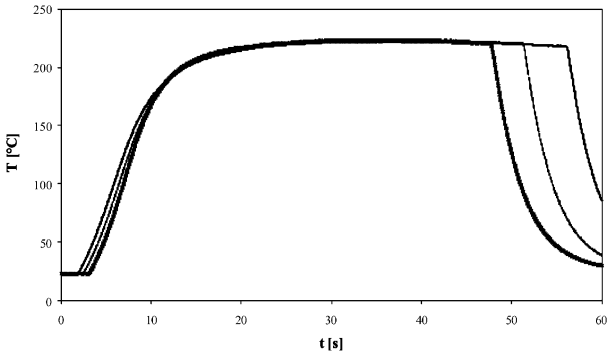

Fig. 3. Catalytic probe characteristics (3) in O_2 post-discharge at 0.3 torr, 120 W in the microwave discharge.

velocity of atoms ($j = n\nu/4$ where j is the atom flux); E_d is the dissociation energy of the molecules; r is the probe radius; and T is the probe temperature. When the nickel probe is covered by a thin film of nickel oxide, γ has been determined [4] as $\gamma = 0.27$.

The other values in Eq. (2) are the following: $m(\mathrm{Ni}) = 5.6 \times 10^{-6}$ kg, $c_p = 444$ J/kg, $\nu = 700$ m/s, $E_d = 5.12$ eV, $r = 1$ mm.

The density of O-atoms vs. the O_2 flow rate in Ar is reproduced in Fig. 4 for an Ar flow rate of 0.6 slm^{-1} (pressure of 1 torr) at several microwave powers.

Comparing Fig. 2 and Fig. 4, it is first deduced that the density of O-atoms reached saturation value with increasing values of O_2%, but at lower O_2 values with the probe than with the titration: 30 sccm of O_2 (5% O_2 into Ar) with the probe and 20% O_2 with the NO titration, for 60 W in the microwave discharge. The saturated values are of the same order of magnitude: $1\text{–}1.2 \times 10^{-15}$ cm^{-3} with the NO titration and $0.7\text{–}0.8 \times 10^{-15} \mathrm{cm}^{-3}$ with the probe, i.e. inside the 30% uncertainty range.

4. The H-atom density by emission spectroscopy and by probe

The spectroscopic analysis and the kinetic reactions in an $\mathrm{Ar}\text{–}\mathrm{H}_2$ microwave discharge are reported in ref.6. The intensities of Ar, H and H_2 radiative states have been recorded versus the H_2 percent into Argon for given gas flow rate and power in the discharge. It has been shown by Monna and Ricard [6] that the H radiative states are mainly produced by electron collisions on the atomic ground state. If x is the H_2 percentage in Ar, it is calculated:

$$I_H/I_{Ar} \cong [H]/[Ar] = [H]/(1-x)[M] \quad (3)$$

where I_H, I_{Ar} are the intensities of chosen H and Ar spectral lines and $M = Ar + H_2$. By taking H_α as 656.3 nm and Ar as 750.4 nm, we can observe the variations $(1-x)I_H/I_{Ar}$ vs. the percentage H_2, as reproduced in Fig. 5, for $x = 1\text{–}5\%$. A broad maximum value of H-atom relative densities is observed. For higher x values [6], the H-atom density decreased sharply by a factor of 2 between 5 and 20% of H_2 and more slowly between 20 and 95% of H_2.

Now we consider the measurements, which were performed with a fresh catalytic probe in the H_2 post-discharge. The activation of the Ni probe with H_2 was not so easy to obtain as for the O_2 post-discharge. First, with the experimental arrangement, as shown in Fig. 1, the activation failed with a H_2 post-discharge for 0.5 h at 0.3 slm−1, 0.5 torr and a 100-W discharge. A sensitive heating of the cross Pyrex tube was observed (diameter 2 cm) in the shoulder after the discharge (see Fig. 1). Such heating was the result of efficient H-atom recombination on the Pyrex shoulder.

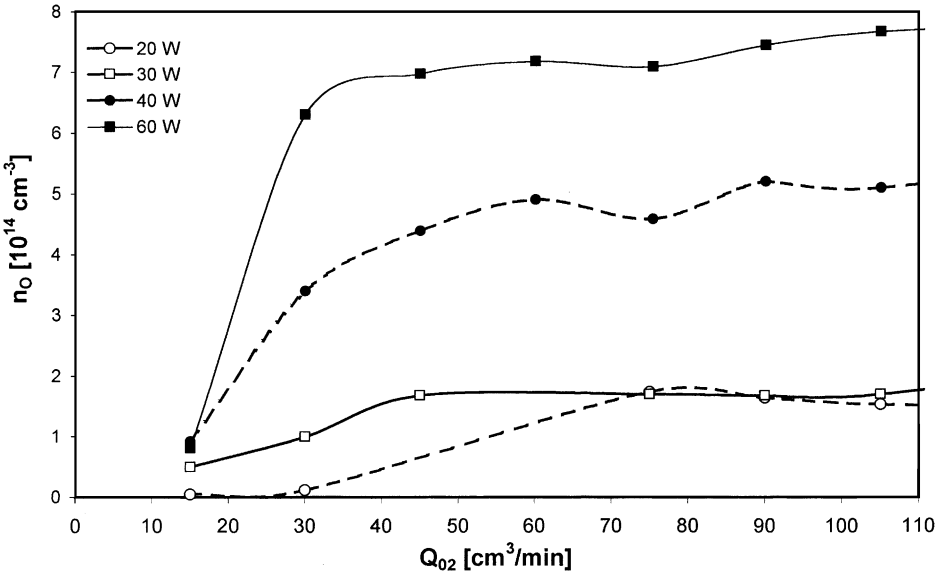

Fig. 4. Density of O-atoms by the catalytic probe vs. the O_2 flow rate into Ar at 0.6 slm. Post-discharge time was 3×10^{-2} s.

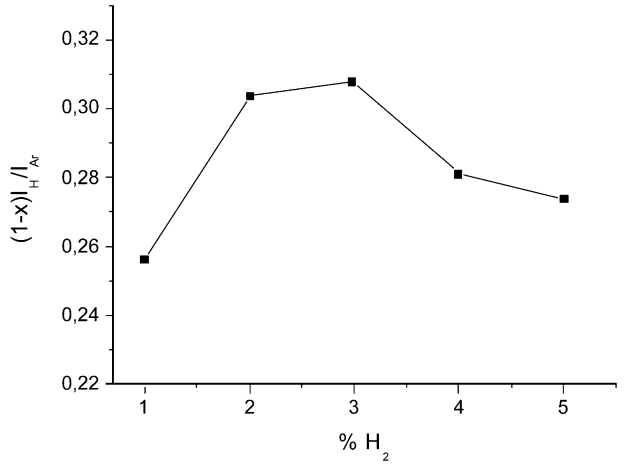

Fig. 5. Variations of $(1-x)I_H/I_{Ar}$ (proportional to relative values of H-atom density) vs. $x = H_2\%$ near the surfatron gap.

The cross tube was removed and the discharge tube was directly connected to the post-discharge reactor. Then the probe was easily activated and the distance between the end of the discharge quartz tube and the probe was fixed at 7 cm to avoid excessive heating of the probe (red hot =). Variations of H-atom densities vs. $x(H_2)$ are reproduced in Fig. 6 for x between 1 and 5% in Ar, in practically the same conditions as in Fig. 5: $Q = 3$ slm^{-1} and 50 W in the discharge. Under these conditions. $\nu = 2.500$ ms^{-1}, $\gamma = 0.16$ and $W = 4.45$ eV.

A slow increase of H densities was observed up to 4% and decreased after that. The mean value of H densities was between 1 and 1.2×10^{15} cm^{-3}. It can be considered that such a value is near the H-atom density at the end of the discharge.

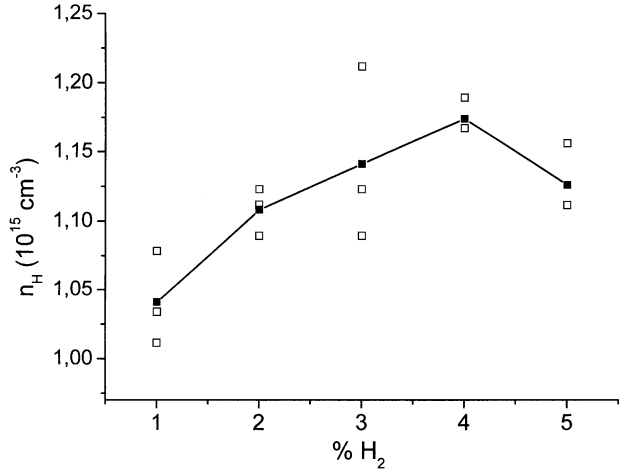

Fig. 6. Density of H-atoms by the catalytic probe vs. $H_2\%$ in Ar. Post-discharge time was approximately 10^{-3} s. Plasma conditions as in Fig. 5.

5. Concluding remarks

The diagnosis of O and H atoms by emission spectroscopy in Ar–O_2 and Ar–H_2 flowing microwave discharges and by NO titration in the post-discharge are compared to measurements with a Ni catalytic probe in the post-discharge. In Ar–O_2, the measurements were performed in the late post-discharge by NO titration and with the probe. Similar quantitative results were obtained with these two diagnostics, i.e. a mean O-atom density of $1 \pm 0.3 \times 10^{15}$ cm^{-3} in the post-discharge reactor, at 1 torr and at times of $2–3 \times 10^{-2}$ s after an Ar–O_2 discharge, i.e. a dissociation degree $O/2O_2$ of 15% for an Ar–10%O_2 gas mixture. In the Ar–H_2 gas mixture, reliable probe measurements (mainly for the probe activation) needed to be in the early afterglow, at times less than 10^{-3} s after the discharge. The plasma radiative states, as analysed at the beginning of the microwave discharge, indicated a maximum H atom density for an Ar–(2–3)%H_2 gas mixture at $Q = 3$ slm^{-1}, 3 torr and 50 W.

Such a result is also practically found with the probe with a maximum of 4%H_2. The main interest of the catalytic probe is to give quantitative values. In the above conditions, the H-atom density was $1–1.2 \times 10^{15}$ cm^{-3}, i.e. a $H/2H_2$ dissociation degree of 15% for Ar–4%H_2. Note that this value is approximately the same as that in the above Ar–10%O_2 gas mixture, but for a post-discharge time more than one order shorter.

Works are in progress to determine the O and H atom densities by optical spectroscopy and catalytic probes for more extended discharge and post-discharge conditions.

Acknowledgements

The implement of catalytic probes on the Toulouse post-discharge reactor has been performed in the frame of the M. Mozetic NATO: PST.EV.976469 expert visit grant.

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