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Spectroscopic diagnostics of the plasma in the cathode region of a nitrogen glow discharge

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Résumé. — On utilise des diagnostics spectroscopiques tels que l'émission, la fluorescence induite par laser et l'effet optogalvanique, procurant une très bonne résolution spatiale, pour caractériser la chute cathodique et la lueur négative d'une décharge continue fonctionnant en mode luminescent anormal dans l'azote. Ces diagnostics donnent des informations locales sur les fonctions d'excitation et d'ionisation, sur les concentrations d'ions et sur les températures rotationnelles des différentes espèces du plasma dans la région cathodique de la décharge.

Abstract. — Spatially resolved spectroscopic diagnostics such as plasma-induced emission, laser-induced fluorescence and laser optogalvanic spectroscopy are used to characterize the cathode sheath and the negative glow of an abnormal glow dc discharge in nitrogen. These diagnostics provide local information on the excitation and ionization functions, on the concentrations of ions and on the rotational temperature of the various species in the plasma of the cathode region.

1. Introduction.

The widespread use of plasma techniques in industrial processes, such as surface treatments, deposits and microcircuits etching, is spawning many studies on glow discharges, and more particularly on the ionized gas interfacing with a surface. It is only by knowing the characteristics of the plasma in the vicinity of the material that the governing mechanisms can be better understood; numerical models can then be developed in order to optimize and control the processes in any other than the trial-and-error approach, that most often prevails, when there are no experimental data or numerical models to go by.

In the region of the plasma-material interface, where the presence of electrical sheaths produces very high gradients for most of the characteristic quantities of the plasma, the diagnostics must be made *in situ* by non-intrusive methods that offer good space and time resolution. For example, a resolution of 0.1 to 0.5 mm is desirable for the measurements in the cathode fall of a discharge, depending on the pressure and the reaction rates.

Spectroscopic methods such as plasma-induced emission, laser-induced fluorescence and the laser optogalvanic effect can be used to generate diagnostics satisfying the above criteria [1, 12].

In this article, we present the results of diagnostics made in the cathode fall and the negative glow of a glow discharge in nitrogen, used to study the plasma nitriding of steels. The measurements concern the spatial distributions of the excited states $N_2(C)$ and $N_2^+(B)$, the determination of the concentration of $N_2^+(X)$ ions on the axis and radially, and the axial variation of the rotational temperatures of the different species.

2. Experimental setup.

The experimental setup (Fig. 1) shows the discharge and all of the diagnostic systems used in this study.

The plasma is created in a discharge of diode structure, between an iron cathode 29 mm diameter and an anode of the same size. The interelectrode distance can be adjusted to about 1 cm by moving the cathode. The cathode is encased in a ceramic insulator, so as to define the emissive surface of the

Fig. 1. — Schematic of the experimental setup.

electrode. The discharge operates in a flow of nitrogen (≈ 0.2 l/min) and the pressure, measured with a capacitive gauge, is varied between 0.5 and 2 torr. The discharge current is supplied by a stabilized dc power generator (0.5 to 5 kV, 20 mA) through a 76 k Ω load resistor.

The spectroscopic systems include a high-resolution monochromator ($\lambda/\Delta\lambda \leq 150\,000$) providing a good spectral definition in the emission and induced fluorescence modes, a dye laser emitting in the wavelength range 2 200-7 500 Å, and a low-resolution monochromator ($\lambda/\Delta\lambda \leq 1\,000$) to observe the plasma globally in order to monitor and normalize the laser excitation. The light signals are detected by photomultipliers coupled with a digitizer or sampler-boxcar averager offering a good time resolution (2 ns).

3. Spectroscopic diagnostics.

3.1 EMISSION SPECTROSCOPY. — It is clear that emission spectroscopy is very important in plasma diagnostics. In this study we observed the space-resolved emission of two excited levels of nitrogen: the $N_2(C)$ state on the (0-0, $\lambda = 3\,371$ Å) transition of the second positive system and the ionic state $N_2^+(B)$ on the (0-0, $\lambda = 3\,914$ Å) or (0-1, $\lambda = 4\,278$ Å) transition of the first negative system.

Figure 2 diagrams the optical setup used to study the spatial distribution of the plasma. The light emitted by the plasma is collimated and then focused onto the monochromator inlet slit by a set of moving lenses and mirrors. The spatial resolution is defined by the height and width of the monochromator slit and by the geometrical aperture of the beam as determined by the diaphragm. The plasma is studied locally, radially or along the axis of the

Fig. 2. — Optical setup for determining plasma emission and laser-induced fluorescence, resolved spatially.

discharge, by moving the mirrors. The lens and mirrors are motor-driven to record the spatial profiles continuously.

3.2 LASER-INDUCED FLUORESCENCE. — The possibility of using laser-induced fluorescence to obtain information directly on the population of the ground and metastable states of the active species has an undeniable advantage.

The intensity of the induced fluorescence, emitted by a level n' populated by the laser from a level n , is expressed as a function of the population $[n]$ of the lower level by

$$I_n^l = K_n^l \cdot [n], \quad (1)$$

where the coefficient K_n^l can be expressed (when no saturation or optical pumping effects occur) in terms of the oscillator strengths of the transitions used for the laser and the fluorescence detection, and of the number of photons available at the energy corresponding to the laser transition [2]. Then, for a given transition and species, the fluorescence signal is proportional to the concentration of the species in the starting level, independently of the experimental conditions of the plasma, provided that the deactivation of the upper level is principally control by radiations.

In this study, we have used laser-induced fluorescence to determine the concentration of the N_2^+ ions. The molecules in the $N_2^+(X, v'' = 0, N'')$ level are photo-excited to the $N_2^+(B, v' = 0, N')$ state by the tunable dye laser (N' and N'' are respectively the upper and lower rotational levels). The laser allows us to populate a given rotational level. The fluorescence is observed perpendicularly to the axis of the discharge and the laser beam, through a monochromator, on the $N_2^+(B, v' = 0) \rightarrow N_2^+(X, v'' = 1)$ transition.

The fluorescence is detected using the setup in figure 2. The local measurements are made by moving the laser beam between the electrodes or,

for certain measurements, by moving the discharge in the crossed fields of the laser and optical detection system.

3.3 LASER OPTOGALVANIC EFFECT. — The resonant optogalvanic effect is defined as the modification of the plasma impedance by absorption of photons at a wavelength corresponding to an atomic or molecular transition of the gas. For nitrogen ions, the optogalvanic effect resulting from the absorption of photons corresponding to the $N_2^+(X, v'' = 0) \rightarrow N_2^+(B, v' = 0)$ transition is due to the difference of mobility between the two species of ions [3]. In the cathode sheath of the discharge, the mobility of the ions in the ground level is mainly limited by symmetrical charge exchange collisions in which the ions give up their energy to the neutral molecules in the reaction

The corresponding cross section is of the order of $50 \text{ \AA}^2$ at an energy of $\approx 10 \text{ eV}$ [4]. For nitrogen, and under the experimental conditions of this study, the mean free path is 0.1 mm , thus very much less than the thickness of the cathode sheath (3 mm). Some thirty charge exchange collisions will occur as an $N_2^+(X)$ ion passes through the cathode sheath.

In the case of the $N_2^+(B)$ ion, no bibliographical data exist concerning this cross section. But it is clear that the symmetrical charge transfer corresponds to a much more « complicated » collision as it would involve the transfer not only of a valence electron but also of electronic excitation. An asymmetrical charge transfer would be possible, but there again, an energy conversion would be necessary. The result is that the charge transfer of the $N_2^+(B)$ ions is much less probable, and therefore its mean free path will be much greater than that of the ground level ions. We will adopt the hypothesis that the $N_2^+(B)$ ions undergo no charge transfer collisions during their transit through the cathode sheath; however, the mean free path is limited by their radiative lifetime (60 ns). The $N_2^+(B)$ ions created by the laser are freely accelerated in the cathode fall. They reach the cathode with a much higher velocity than the ground state ions, slowed down by the charge transfer collisions. The excitation of the ions by the laser will thus result in a temporary increase in the discharge current constituting the optogalvanic effect.

The current increase induced by the laser pulse is expressed as a function of time by :

$$\delta_i(t) = en_i^*(t)(v_i^* - v_i^0) S \frac{V_\ell}{V_g} \quad (3)$$

where n_i^* is the density of excited ions created by the laser radiation and reaching the cathode, $v_i^* -$

v_i^0 is the difference between the velocities of the excited ions and the ground state ions at the cathode surface, S is the area of the cathode and V_ℓ/V_g is the volume fraction of the sheath disturbed by the laser. The difference in velocity at the cathode between the two types of ion is calculated assuming a linear electric field in the cathode fall [5], and also considering that the excited ion created by the laser has the same initial velocity as the ion in the ground state and is then accelerated in the electric field. In figure 3 we show the experimentally observed optogalvanic current pulse, resolved in time, as well as the curve computed from formula (3) when the entire cathode fall is illuminated by the laser. The theoretical curve is adjusted to the maximum of the experimental values because the number of excited ions created by the laser is not determined. The good agreement between computed and experimental data verifies the hypothesis of greater mobility for the excited ion.

The optogalvanic effect on the nitrogen ions, which depends on the difference between the drift velocity of the ions, exists only in that part of the discharge in which the electric field is large, i.e. in the cathode fall. In this region, the optogalvanic effect substitutes for the induced fluorescence as a means of ion diagnostics, as the induced fluorescence loses much of its sensitivity because of the low concentration and the drift velocity of the ions.

Fig. 3. — Time dependence of the optogalvanic signal on the N_2^+ ions. The entire cathode sheath is illuminated by the laser. The experimental data are compared with the theoretical curve adjusted to the signal maximum.

4. Experimental results and interpretation.

All of the experiments reported in this study were carried out for a nitrogen pressure of 1 torr and a discharge current of 10 mA (1.5 mA/cm^2 on the cathode). The voltage across the discharge under these conditions is 550 V and the thickness of the cathode fall is of the order of 3 mm , which corresponds to a field of $3\,200 \text{ V/cm}$ on the cathode, for

an electric field varying linearly through the cathode sheath. We first present the spatial profiles of the excited states of nitrogen and then that of the ground state ions.

4.1 SPATIAL PROFILE OF THE EXCITED STATES OF NITROGEN. — The profiles of the excited states $N_2(C)$ and $N_2^+(B)$ observed in emission on the (centerline) axis of the discharge are shown in figure 4A. The spatial resolution is about 0.2 mm. For the neutrals, we observe a dark space starting at the cathode and corresponding to the cathode sheath, then a sharp increase of the light intensity followed by a slower decrease in the negative glow. For the ions, the increase of the light emitted at the border of the cathode fall is less abrupt, but the decrease in the negative glow is very similar to that of the neutrals. The shape of these profiles can be explained very well by considering the energy dependence of the cross sections of electron collision excitation on these levels [6] and their radiative lifetimes [7].

For the level $N_2(C)$, the electronic excitation cross section is very tight. It has a threshold at 11 eV, a maximum at 15 eV and decreases rapidly by a factor of thirty at 50 eV [6]. The electrons emitted by the cathode reach and very quickly exceed the energy corresponding to the maximum of the cross section.

Fig. 4. — Axial profiles in the cathode sheath and negative glow. The cathode is at abscissa 0 and the anode is 10 mm apart. A) Emission profile of the levels $N_2(C)$ (lower curve) and $N_2^+(B)$ (upper curve). The dotted line represents the profile of $N_2^+(B)$ ion creation in the cathode sheath; B) profile of the concentration of ions: (+) Intensity of the laser-induced fluorescence signal, (•) Corrected fluorescence signal.

This explains the small maximum of light observed in the immediate vicinity of the cathode. The secondary electrons created also quickly exceed the energy of the maximum of the cross section and it is only at the edge of the cathode sheath, where the electrons are large in number and the electric field weaker, that the excitation efficiency becomes large. In the negative glow, the electrons no longer gain energy as the electric field is nearly zero, and so they gradually lose not only their energy but also the possibility of exciting the molecule. This explains the decrease of emitted light. Considering the low velocity of the particles and the short lifetime of the $N_2(C)$ level, the molecules relax at the point where they were created. The profile of emitted light thus represents the axial excitation function.

There are two distinct reasons for the different shape of the emission profile of the $N_2^+(B)$ ion in the cathode fall. Firstly, the form of the cross section for direct electron excitation is very different than that of the neutral molecule. It has a maximum at 100 eV and decreases slowly by a factor of 1/3 at 500 eV [6]. The cross section is large for the high-energy electrons. So it is expected to find relatively more excited ions than excited molecules in the cathode sheath. Secondly, the ions are accelerated toward the cathode in the cathode fall. Their emission profile is therefore not directly representative of the place where they were created. The $N_2^+(B)$ ions relax at a distance that is, on the average, equal to the space travelled through during their radiative lifetime. This is true according to the hypothesis adopted in paragraph 3.2 above, in which we assume that the excited ions make no charge exchange collisions in the cathode sheath. We can then use the emission profile to compute the $N_2^+(B)$ ion creation profile in the cathode sheath (dotted curve in Fig. 4A). This curve more closely resembles that of the excited molecules, though with a relatively larger number of $N_2^+(B)$ ions than $N_2(C)$ molecules.

4.2 SPATIAL DISTRIBUTION OF THE NITROGEN IONS.

— Using laser-induced fluorescence, we determined the axial ion concentration profile as well as the radial distributions at different distances from the cathode.

The axial profile is obtained by moving the laser beam, with its 0.5×2 mm cross section, from one electrode to the other and detecting the corresponding induced fluorescence. It is the laser that defines the spatial resolution of this measurement, while the fluorescence is observed nonlocally on the centerline of the discharge. In the negative glow, the fluorescence signal is directly proportional to the local concentration of the ions. On the other hand, in the cathode fall, where the ions are accelerated toward the cathode, the fluorescence photon is detected only if the excited ion has enough time to emit

before reaching the cathode. This is all the more important as the excited ions created by the laser have a greater mobility than those at the ground level. We have computed the correction to be applied to the fluorescence signal as a function of the point where the ion is excited in the cathode sheath. If $t_c(x)$ is the time the ion created at distance x takes to reach the cathode, then the factor $1 - \exp(-t_c(x)/\tau)$ is the correction to be applied to the observed profile, in which τ is the lifetime of the excited ion.

The profile of the fluorescence signal and the corrected curve in the cathode sheath are given in figure 4B. The absolute values of the ion density are determined from the ion current, computed at the cathode by assuming that the discharge current i_d in this region is entirely ionic. We get

$$\frac{i_d}{S} = j_i(x=0) = en_i(x=0) v_i E(x=0) \quad (4)$$

where $E(x=0)$ is the electric field on the cathode and v_i the mean velocity of the ions in their last mean free path before reaching the cathode.

The lack of precision, as concerns the intensity of the fluorescence signal in the cathode sheath, brings in a major uncertainty (about 50 %) in the absolute value of the ion concentration.

The ion density curve is very much different from that of the emitted light. In the negative glow, the maximum density of the ions is located at a greater distance from the cathode than that of the light emitted by the $N_2^+(B)$ state, while the cross sections of creation of these two states by electron collision have the same energy dependence. This is due to the large difference in lifetime between the excited ions and the ions in the ground state (60 ns for the $N_2^+(B)$ ions and $\approx 40 \mu s$ for $N_2^+(X)$ [8]). So the ground state ions have the time to diffuse in the negative glow where the electric field is zero. The neutrality of the plasma is established in this region, so that the ion concentration profile is identical to that of the electron concentration.

The radial distributions of the ion density are determined by moving the discharge perpendicular to the laser beam along a line parallel with the cathode, and making measurements at several distances from it. The ion concentration is then directly proportional to the intensity of the fluorescence signal. The densities on the axis are normalized with respect to the concentrations of figure 4B.

The results are presented in figure 5. The radial profiles are symmetrical and remain relatively the same as we move away from the cathode, which indicates that the transverse diffusion of the ions is not important compared with the axial diffusion.

4.3 AXIAL PROFILE OF THE ROTATIONAL TEMPERATURES. — The temperature of the gas in the various

Fig. 5. — Radial distribution of the concentration of ions at different distances from the cathode.

regions of the discharge plays an important role, since it determines the concentration of the gas and then the population of molecular levels. We measured the rotational temperatures, resolved spatially, for the excited states $N_2(C)$ and $N_2^+(B)$ and for the ground state of the ion $N_2^+(X)$.

The rotational spectra of the excited states are observed in emission as described in paragraph 3.1. The rotational spectrum of the ground level of the ion is determined by laser-induced fluorescence in the negative glow, and by optogalvanic effect in the cathode fall. The experimental techniques are identical to those described in sections 3.2 and 3.3, with the dye laser wavelength scanning the rotational structure of the transition. Figure 6 presents, as examples, the rotational spectra of the nitrogen ion recorded along the discharge axis, in emission mode for the level $N_2^+(B)$ and using induced fluorescence and optogalvanic spectroscopy for the ground level $N_2^+(X)$. The rotational temperatures are computed from the relative intensities of the rotational R-branch lines mentioned on the figure 6 [9].

The temperatures are presented in figure 7. In the negative glow, all the measured temperatures are identical, within the experimental uncertainties; they show a weak dependence on the distance from the cathode. The rotational temperatures of the various states are in equilibrium with the translational temperature of the gas. In the cathode sheath, the rotational temperature of the $N_2(C)$ level increases slowly. The neutrals acquire energy by charge exchange collisions. This energy of translation is redistributed by collisions within the gas. Moreover, at the surface of the cathode, the gas is in thermal equilibrium with the electrode [10, 11]. This heating of the gas decreases the concentration of the

Fig. 6. — Rotational spectra of the nitrogen ions. A) Emission spectrum of $N_2^+(B)$ recorded 5 mm from the cathode ; B) induced fluorescence spectrum and C) optogalvanic spectrum of the $N_2^+(X)$ fundamental level, as recorded 2.5 mm and 1.5 mm from the cathode, respectively. The rotational temperatures computed from these spectra are, in order : 445 K, 550 K and 850 K. The iron lines in the spectrum C result from optogalvanic effect on sputtered atoms.

molecules in the cathode sheath. For the ions, the increase of temperature is much more sudden because they rapidly gain energy in the electric field. A part of this increase of energy is transferred to the rotations by the collisions with the gas. The rotational temperature is no longer representative of the translational temperature of the gas but of the rotational energy that the ions acquire in the electric field.

5. Conclusion.

The spectroscopic diagnostics discussed here can be used to characterize the plasma constituting the ionized gas-material interface, with a good spatial resolution. Optical emission is used mainly to characterize the energy distribution of the electrons along the centerline of the discharge from the excitation and ionization functions. It also makes possible to

Fig. 7. — Variation of the rotational temperature of the $N_2(C)$, $N_2^+(B)$ and $N_2^+(X)$ states along the centerline of the discharge.

determine the rotational temperature of the excited states of the molecule which, in the case where thermal equilibrium exists, provides information concerning the temperature of the gas. Laser-induced fluorescence is used to measure locally the concentrations of non emitting species, such as the ions in the ground state, and to obtain rotational temperatures for the same species. The laser optogalvanic effect complements the measurements made by laser-induced fluorescence, in the discharge regions such as the sheaths, where the induced fluorescence is not very sensitive.

The experimental data, e.g. the emission profiles of the excited states of nitrogen and more particularly the population profile of the ions determined using laser-induced fluorescence, are very useful for the development of numerical models, as measurements can be compared with the predictions from existing theoretical models. Then, by analyzing any discrepancies there may be between the computed and experimental data, it may help a better understanding of the basic mechanisms occurring in the cathode region of glow discharges.

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References

- [1] GOTTSCHO R. A. and MILLER T. A., *Pure Appl. Chem.* **56** (1984) 189.
- [2] KINSEY J. L., *Ann. Rev. Phys. Chem.* **28** (1977) 349.
MILLER T. A. and BONDYBEY V. E., *J. Chem. Phys.* **77** (1980) 695.
- [3] WALKUP R., DREYFUS R. W. and AVOURIS Ph., *Phys. Rev. Lett.* **50** (1983) 1846.
- [4] KOBAYASHI N., *J. Phys. Soc. Jpn.* **38** (1975) 519.
- [5] DOUGHTY D. K. and LAWLER J. E., *Appl. Phys. Lett.* **45** (1984) 611 ;
DOUGHTY D. K., SALIH S. and LAWLER J. E., *Phys. Lett.* **103A** (1984) 41.
- [6] LABORIE P., ROCARD J.-M. et REES J. A., *Tables de sections efficaces électroniques et coefficients macroscopiques. T. 2 : Vapeurs métalliques et gaz moléculaires* (Dunod, Paris) 1971.
- [7] LOFTHUS A. and KRUPENIE P. H., *J. Phys. Chem. Ref. Data* **6** (1977) 113.
- [8] BÖHRINGER H. and ARNOLD F., *J. Chem. Phys.* **77** (1982) 5534 ;
GOTTSCHO R. A., BURTON R. H., FLAMM D. L., DONNELLY V. M. and DAVIS G. P., *J. Appl. Phys.* **55** (1984) 2707.
- [9] HERZBERG G., *Molecular Spectra and Molecular Structure. Vol. I: Spectra of Diatomic Molecules* (Van Nostrand Reinhold Company, New-York) 1950.
- [10] LEFEBVRE M., PÉALAT M., MASSABIEAUX B., PILORGET A. et RICARD A., *I.S.P.C. Tokyo* (1987) 483.
- [11] DAVIS G. P. and GOTTSCHO R. A., *J. Appl. Phys.* **54** (1983) 3080.
- [12] JOLLY J., *Interactions Plasmas Froids Matériaux*, Ed. GRECO 57 (Les éditions de physique) 1988, 53.