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Discharges in N₂ flowing gas for steel surface nitriding

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Résumé. — La modélisation de réacteurs à plasma pour la nitruration de surfaces métalliques a été réalisée dans des conditions de décharges et de post-décharges d'azote en écoulement. Les diagnostics et les calculs ont été focalisés sur les molécules vibrationnellement excitées N₂(X, V) et sur les atomes N qui sont les espèces à longues durées de vie les plus peuplées. Il a été démontré que ces espèces neutres actives produisent une nitruration en surface de l'acier avec les mêmes caractéristiques que les procédés ioniques classiques : composition et épaisseur des couches de γ' -Fe₄N et de diffusion de N en accord avec les lois de diffusion de Fe-N.

Abstract. — Modelling of plasma reactors for steel surface nitriding has been achieved in discharge and post-discharge conditions of N₂ flowing gas. Diagnostics and calculations have been focused on the N₂(X, V) vibrational molecules and N atoms which are the most populated long living species. It has been demonstrated that these neutral active species produce steel surface nitriding with the same characteristics than classical ion processes : composition and depth of γ' -Fe₄N and N diffusion coating following the Fe-N diffusion laws.

1. Introduction.

Metallic surface nitriding is applied to improve surface properties such as resistance to corrosion, hardness, wear or fatigue by the development of thin surface layer (depth of 1-10 μ m) having high resistance properties. Low pressure gas discharges (1-5 torr) are commonly used for steel surface nitriding in industrial reactors. In such plasma treatments, the sample to be nitrided is usually connected as a cathode of a glow discharge in flowing N₂-H₂ gas mixtures [1]. The active species in the negative glow near the steel cathode surface have been detected by emission spectroscopy as being the radiative states of N₂, N₂⁺, N, N⁺, H and NH [2].

In the purpose to separate the contribution of ionic species such as N₂⁺ and that of neutral active species such as N₂(V) vibrational excited molecules and N atoms, a plasma reactor working in post-discharge regime has been set up [3]. The N₂(V) and N appear the most important neutral species as being inactive in colliding cold surface walls as glass discharge tube.

Diagnostics of N₂(V) and N have been performed by CARS and chemiluminescent titration, respectively. The experimental results obtained in dis-

charges and post-discharges of flowing N₂ gases are compared to calculated values obtained by coupling vibrational and electronic energy distributions [4].

2. Glow discharge in N₂ flowing gas.

The plasma reactor is schematized in figure 1. A discharge tube of diameter 2 cm is connected to a vessel of diameter 15 cm. A glow discharge in flowing N₂ gas can be switched on between the anode (A) which is a side-armed cylindrical electrode in Nickel (dia. 0.8 cm) and the cathode (K) which is the steel sample (dia. 3 cm, thickness 0.8 cm) to be nitrided. The glow discharge is made up of a positive column along the discharge tube ($R = 1$ cm) and a negative glow and a cathode fall at the end of the discharge tube in front of the cathode surface.

2.1 NITROGEN EXCITATION IN THE POSITIVE COLUMN. — A large number of plasma diagnostics has been applied to the N₂ positive column. The plasma electric field and electron density have been determined by Langmuir probes and the gas temperature has been deduced from the rotational distribution of N₂ and N₂⁺ [5]. Metastable species as N₂(A ³ Σ^+), N(²D, ²P) have been measured by opti-

Fig. 1. — Plasma reactor for steel surface nitriding : (K) steel surface cathode (dia. 3 cm), A anode. 27.

cal absorption [6] and $N_2(X, V)$ vibrational distribution by CARS [7].

The N-atom densities have been evaluated by using the NO chemiluminescent titration method [6].

A synthetic result of these works [5-7] is reported in table I.

From the results reported in table I, the vibrational distribution of $N_2(X, V)$ can be calculated by coupling the vibrational master equations and the Boltzman equation for electrons [4]. Such calculated values are reported in figure 2 for a N_2 positive column ($R = 1$ cm) with residence times of species in the discharge of $t = 0.35, 1$ and 2×10^{-2} s. The

experimental results obtained by CARS [7] are for a residence time of $t = 10^{-2}$ s and are in good agreement with the calculated model.

From the calculated model and the experimental results reported in table I and figure 2, it can be deduced that the $N_2(X, V < 12)$ molecules and N atoms are the more populated active species in the positive column.

2.2 NITROGEN EXCITATION IN THE NEGATIVE GLOW AND THE CATHODE FALL. — The CARS has been applied to the negative glow and the cathode fall study by using the set-up as shown in figure 1. The steel cathode (K) can be translated along the

Table I. — Plasma parameters and densities of species in N_2 positive column ($R = 1$ cm) [5-7].

Plasma parameters

Pressure	0.1-10 torr
Current density	0.3-50 mA cm ⁻²
Gas temperature	400-700 K
Electric field	10-40 V cm ⁻¹

Densities (experimental values)

$N_2(X)$	n_0	$= 3 \times 10^{15} - 3 \times 10^{17}$ cm ⁻³
e, N_2^+	$n_e = n_i$	$= 10^9 - 10^{11}$ cm ⁻³
N	n_N	$= 10^{13} - 10^{15}$ cm ⁻³
$N_2(A)$	n_A	$= 10^{11} - 10^{12}$ cm ⁻³
$N(^2D, ^2P)$	n_N^*	$= 10^{10} - 10^{11}$ cm ⁻³
$N_2(X, V = 10)$	$n_{V=10}$	$= 10^{14}$ cm ⁻³
	$(P_{N_2}$	$= 2$ torr, $n_e = 1.7 \times 10^{10}$ cm ⁻³ ,
		residence time 10^{-2} s.)

Fig. 2. — Vibrational distribution of N₂(X, V) in N₂ positive column. Rectangles are the CARS results for a residence time $t = 10^{-2}$ s. Full lines are calculated results

for (1) $t = 3.5 \times 10^{-3}$ s, (2) $t = 10^{-2}$ s, (3) $t = 2 \times 10^{-2}$ s. $P = 2$ torr, $E/n = 5 \times 10^{-16}$ V cm², $n_e = 1.7 \times 10^{10}$ cm⁻³ and $T_g = 550$ K.

discharge axis in order to change the distance (Z) between the CARS laser beams and its surface. The probe volume was 10 mm long and 50 μ m thick and it was located parallel to the steel surface.

The θ_1 -characteristic vibrational temperatures are reported in figure 3 with

$$\theta_1 = \frac{\Delta E_{1,0}}{k \log \left| N_2 \frac{V=0}{V=1} \right|}.$$

From these experimental results, it can be observed that the negative glow is characterized by $\theta_1 \approx 4000$ K and the cathode fall by $\theta_1 \approx 2500$ K.

The T_R -rotational temperatures of N₂(X, V), also measured by CARS, are reported in figure 4 for the same experimental conditions as in figure 3. Here, the rotational temperature which is close to the gas temperature in the negative glow ($T_R \sim 400$ K) is increasing in the cathode fall to reach $T_R \sim 750$ K for $Z < 1$ mm. This rotational temperature near the

cathode is nearly identical to the steel surface temperature as measured with a thermocouple ($T_K = 710 \pm 20$ K).

The rotational temperature of N₂(X) is increasing in the cathode fall as a result of the following efficient charge transfer [8]:

where the subscripts (f) and (s) are for fast and slow species, respectively. As a consequence of these symmetric charge transfer whose the mean free path $\lambda_i \sim 10^{-2}$ cm is about ten times smaller than the dark space length, there is a gas heating in the cathode fall. Then the cathode surface is heated by ion bombardment and neutral gas collisions.

The weaker vibrational excitation in the cathode fall as shown in figure 3 is the result of less efficient electron excitation and more important loss terms when interacting with the cathode.

Fig. 3. — θ_1 -characteristic vibrational temperature ($\theta_1 = \frac{\Delta E_{1,0}}{k \log \frac{[N_2, V=0]}{[N_2, V=1]}}$) measured by CARS in function of Z -distance from the cathode K. N_2 plasma $p = 2$ torr, $I = 50$ mA, $Q = 0.9$ lmn⁻¹ STP.

Fig. 4. — T_R -rotational temperature measured by CARS in function of Z -distance from the cathode K. Plasma parameters as in figure 3.

3. Post-discharge in N_2 flowing gas.

The plasma reactor as schematized in figure 1 can be easily transformed to process the steel surface in post-discharge conditions. As shown in figure 5, the glow discharge in flowing N_2 or N_2-H_2 is now switched on in the first part of the discharge tube of diameter 2 cm. The A-anode and K-cathode are two identical side-armed electrodes as shown in figure 5. In these conditions, the flowing glow discharge is a N_2 positive column. The following experimental results have been obtained with identical residence times of $t = 10^{-2}$ s in the discharge and $\Delta t = 10^{-2}$ s in the post-discharge. The glow discharge is

Fig. 5. — Post-discharge for steel surface nitriding. S-Steel substrate (dia. 3 cm), K-cathode, A-anode.

followed by a post-discharge which is characterized by the Lewis-Rayleigh afterglow due to the following recombination mechanisms :

For the nitriding process in post-discharge conditions, the steel substrate (S) is externally heated up to reach a surface temperature in the range 800-850 K.

3.1 NITROGEN EXCITATION IN THE POST-DISCHARGE. — Relaxation of the $N_2(X, V)$ distribution has been calculated by eliminating the electron collisions at the end of the positive column [9]. Results are shown in figure 6 for relaxation times

Fig. 6. — Calculations of $N_2(X, V)$ vibrational distribution in post-discharge conditions after a discharge (positive column) in N_2 with $P = 5$ torr, $T_g = 500$ K, $E/n = 6 \times 10^{-16}$ V cm², $n_e = 10^{12}$ cm⁻³.

smaller than 10^{-2} s. The parameters (E/n , n_e and p) of the initial discharge have been chosen in order to reproduce the θ_1 characteristic temperatures experimentally found [10] in a N₂ d.c. discharge (dia. 0.5 cm, pressure 5 torr, flow rate 0.18 l min^{-1} STP, current discharge 80 mA).

It can be observed in figure 6 that initial θ_1 -value of 8 500 K in the discharge is lowered to 5 000 K in the post-discharge at $\Delta t = 3 \times 10^{-3}$ s.

CARS has been previously [7] performed in a discharge and post-discharge tube of dia. 2 cm, pressure 2 torr and residence times in the range 10^{-2} s. Experimental results are reproduced in figure 7 for a positive column discharge with $\theta_1 = 4\,500\text{ K}$ ($E/n = 5 \times 10^{-16}\text{ V cm}^2$, $n_e = 5 \times 10^{10}\text{ cm}^{-3}$, $t = 10^{-2}\text{ s}$) and post-discharge with $\theta_1 = 3\,000\text{ K}$ for a relaxation time $\Delta t = 10^{-2}$ s after the discharge in the preceding conditions.

Similar trends are observed for the calculated values in figure 6 and the experimental results in figure 7. In late post-discharges, the vibrational N₂(X, V) distribution keeps high values. Calculated densities for $V > 20$ in post-discharges overlap the corresponding ones in discharges as a result of V-V vibrational excitation which propagates the vibrational quanta initially introduced by the electron collisions [8].

As a consequence of this V-V pumping up mechanism, N atoms production are also produced in the post-discharge.

Fig. 7. — CARS of N₂ discharge ($P = 2$ torr, $E/n = 5 \times 10^{-16}\text{ V cm}^2$, $n_e = 5 \times 10^{10}\text{ cm}^{-3}$, $t = 10^{-2}\text{ s}$) and the following post-discharge ($\Delta t = 10^{-2}\text{ s}$).

3.2 STEEL SURFACE NITRIDING IN POST DISCHARGE. — Treatment in post-discharge conditions of figure 5 has been performed in the same conditions as the classical ion nitriding process [1] by heating the steel surface up to 820 K and by applying a treatment of 2 h. It has been obtained a steel nitriding with a coating of $5\text{--}8\text{ }\mu\text{ Fe}_4\text{N}$ and diffusion depth of N in Fe of about $300\text{ }\mu$ having high resistance properties (for corrosion wear of fatigue) as a classical ion nitriding.

In late post-discharges ($\Delta t = 10^{-2}\text{ s}$), the electrons and ions disappear by recombination and diffusion on the tube wall. So a current as low as $0.1\text{ }\mu\text{A}$ has been measured on the substrate (S) (cf. Fig. 5) by polarizing (S) from -100 V to $+300\text{ V}$ (floating potential $+100\text{ V}$) for a 2 torr, $\Delta t = 10^{-2}\text{ s}$ post-discharge.

In these conditions, steel nitriding in late post-discharges is the result of the long lived active species N₂(X, V) and N.

By introducing small concentrations (1-5 %) of H₂ in N₂, it has been observed by CARS at $Z = 8\text{ mm}$ (experimental set-up of Fig. 1 for CARS measurements near the substrat) a small increasing of T_R and θ_1 values as indicated in table II.

Similar variations have been previously found in discharge conditions [11] by analysing the negative glow, at $Z = 10\text{ mm}$, in front of the steel cathode surface. By varying H₂ from 1 to 90 % in N₂, it has been observed a weak maximum of θ_1 and T_s for less than 10 % in H₂.

Table II. — CARS in a $\Delta t = 10^{-2}\text{ s}$ post-discharge after a discharge at $P = 2$ torr, $I = 50\text{ mA}$ ($R = 1\text{ cm}$), $t = 10^{-2}\text{ s}$. Substrate heating $T_s = 820\text{ K}$, CARS analysis at $Z = 8\text{ mm}$.

GAS	T_R (K)	θ_1 (K)
N ₂	400	3 030
N ₂ -1% H ₂	440	3 400
N ₂ -5% H ₂	420	3 070

4. Concluding remarks.

A plasma reactor for steel surface nitriding has been studied in glow discharge and post-discharge regimes of N₂ flowing gases.

Diagnostics and plasma modelling have been focused on the neutral N₂(X, V) vibrational molecules and N atoms which are the most highly populated long living species. Concentrations of N₂(X, $V = 10$) $\sim 10^{14}\text{ cm}^{-3}$ and of N $\sim 10^{14}\text{--}10^{15}\text{ cm}^{-3}$ have been measured in positive columns

of N_2 flowing gas ($p = 2$ torr, $I = 50$ mA, $R = 1$ cm).

The vibrational distributions measured by CARS are in good agreement with a plasma modelling obtained by coupling the vibrational master equations and the Boltzman equation for electrons. The spatial distributions of characteristic θ_1 -vibrational temperature and T_R -rotational temperature near the cathode, obtained by CARS with a resolution of 50μ , vary in opposite direction in the cathode fall: T_R increasing due to resonant charge

transfers and θ_1 decreasing as a result of lower production yield.

In post-discharges, the $N_2(X, V)$ molecule and N atom production rates remain populated as a result of a pumping up mechanism by vibrational (V-V) interchange collisions.

Steel surface nitriding has been effectively achieved in late post-discharges ($\Delta t = 10^{-2}$ s), with additional heating of the steel substrate ($T_s = 800$ -850 K), demonstrating the efficiency in the process of the neutral $N_2(X, V)$ and N active species.

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