Active species in Ar-N_2-H_2-CH_4 flowing microwave discharges for hard coatings

A. Ricard, H. Malvos and H. Michel*

LPGP - CNRS - Bat 212, Université Paris-Sud 91405 ORSAY - FRANCE

* LSGS - CNRS - Ecoles des Mines - Parc de Saurupt 54 042 NANCY - FRANCE

Abstract:

High quality iron nitrided layers have been obtained by using flowing microwave post-discharges in Ar-N_2-H_2-CH_4 mixtures.
The afterglow is characterized by emission of spectral bands from N_2 (B,V' = 11-8) and CN (B,V' = 7) radiative states, resulting from N + N and C + N recombination reactions, respectively. The N and C atom densities have been determined by NO titration for N atoms and from band intensities of the spectra emitted by the N + N and C + N reactions. In conditions of 40 Torr - 120 watts, 2.45 GHz discharges with Ar - 11% N_2 - $5x10^{-5}CH_4$, it has been determined [N] ~ $5x10^{-15}$ cm^{-3} and [C] ~ 10^{13} cm^{-3} at a time of 10^{-1} sec. in the post discharge.
With such N and C atom densities in the post-discharge, thick ϵ - Fe_{2-3} N coatings (20-22 μm) have been produced, without oxide layers, for treatment times of 3 hours and a substrate temperature of 550° C.

1. Introduction

A growing interest in the use of flowing nitrogen post-discharges has recently appeared in the field of surface coating processes. For instance, coatings of Fe_4N-γ' of 4-6μm thickness (with a steel substrate temperature of 840K and a processing time of one hour) have been obtained in a microwave (2450 MHz, 70 W) induced flowing post-discharge generated from an Ar-3% N_2 gas mixture. It has been established that the thickness of γ' coating is increasing wiyh N- atom densities which have been measured by NO titration [1].
The afterglow of the Ar-N_2 flowing discharge is characterized by the emission of the N_2(B,V' = 11 - 8) radiative states, resulting from the recombination of N-atoms. Also in the afterglow, a strong emission of CN coming from impurities has been observed. Particularly, a strong intensity of the CN(B,7 - X,7) band results from the C + N recombination process [2].
In the present paper, production of N atoms in the Ar-N_2-H_2 and Ar-N_2-CH_4 post-discharges is first analysed from the afterglow coming from the N_2(B,V' = 11-8) states. The C-atom densities have been determined in the Ar-N_2-CH_4 post-discharge from N-atom densities which is measured by NO titration and from measurements of band intensities which are emitted by the N + N and C + N recombination reactions. Finally, the chemical composition and thickness of nitrided layers on iron substrates are correlated to the N and C atom densities in the post-discharge.

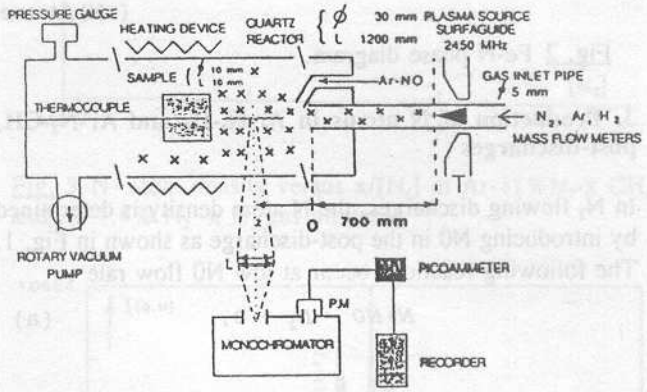

Fig. 1 Microwave post-discharge reactor.

2. The microwave plasma reactor in flowing Ar-N_2-H_2-CH_4 gases

The microwave post-discharge reactor used for steel surface nitriding is reproduced in Fig. 1. The plasma is initiated in a 0.5 cm diam. quartz tube with a surfaguide structure [3]. The post-discharge runs into a reactor of a diam. 3 cm and length of 120 cm at a distance of 70 cm from the sufraguide structure. The Fe-0.1% C samples are cylinders of a diam. of 1 cm and length of 1 cm. They are heated at the nitriding temperature with a conventional heating device. As indicated by the phase diagram of Fig.2, ϵ, γ', and α layers can be obtained at 840 K and the austenite γ layer is obtained in addition at T = 880K. The sample temperature is monitored by a chromel alumel thermocouple whose hot junction is placed 2 mm under the treated surface.
The afterglow has been analyzed by emission spectroscopy using a Jobin-Yvon HR 640 spectrometer with a 1 200 groove diffraction grating and a Hamamatsu R 636 photomultiplier connected to a picoammeter and a chart recorder.

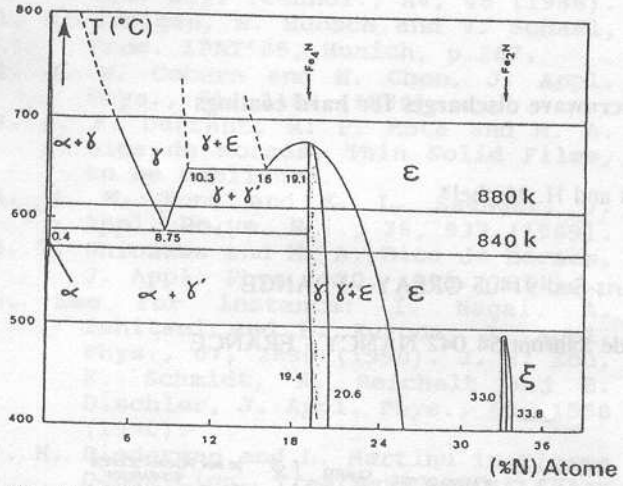

Fig. 2 Fe-N phase diagram.

3. Production of N atoms in Ar-N_2-H_2 and Ar-N_2-CH_4 post-discharges

In N_2 flowing discharges, the N atom density is determined by introducing N0 in the post-discharge as shown in Fig. 1. The following reactions occur at low N0 flow rate :

$$N + NO \rightarrow N_2 + O, \qquad (a)$$

$$N + O + M_2 \rightarrow NO(B) + M_2 \qquad (b)$$
$$NO(B) \rightarrow NO(X) + h\nu \quad (NO_\beta)$$

At high N0 flow rate, all the N atoms being recombined, it follows :

$$O + NO + M_2 \rightarrow NO_2^* + M_2 \qquad (c)$$

$$NO_2^* \rightarrow NO_2 + h\nu \quad \text{(continuum)}$$

The change from $N0_\beta$ to the $N0_2$- continuum is produced when the N0 and N flow rates are equal.
The variation of the $N0_\beta$ band head intensity at 320 nm as a function of Ar-1.3% N0 flow rate is reported in Fig. 3a at 23 Torr in N_2 and in Fig. 3b, at 200 Torr in Ar-3% N_2. The decrease of $N0_\beta$ intensity is followed by a tenuous green emission of NO_2^* which has been detected at 506 and 562.4 nm (Fig. 3).
The extinction point corresponds to the intersection of $N0_\beta$ and NO_2^* curves from which the N atom density is obtained: $N/N_2 = 0.1\%$ in N_2 discharge at 23 Torr and $N/N_2 = 2\%$ in Ar- 3% N_2 discharge at 200 Torr [4].
In N_2 afterglow, the emission spectra is characterized by first positive N_2(B, V'-A, V") emission whose high vibrational levels are out of equilibrium with a maximum on N_2(B, V' = 11) for Ar-(>10%) N_2 gas mixtures (Cf. Fig. 4). This maximum value is the result of the N atom

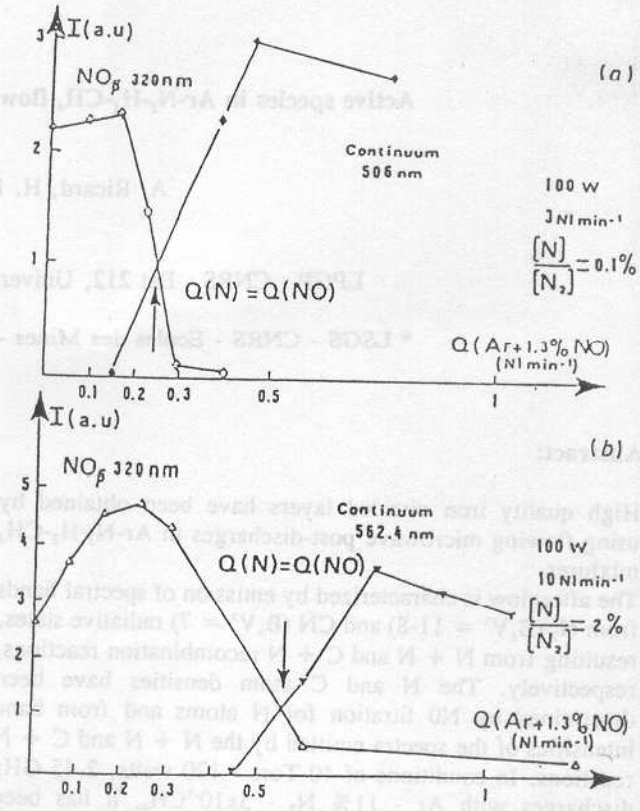

Fig. 3 Intensities of NO_β and NO_2^* bands versus N0 flow rate for N titration by N0.

recombination following the reaction :

$$N + N + N_2 \rightarrow N_2(^5\Sigma) + N_2 \qquad (d)$$

$$N_2(^5\Sigma) \rightleftharpoons N_2(B, V' = 11)$$

$$N_2(B, V' = 11) \rightarrow N_2(A, V') + h\nu \qquad \text{(first positive)}$$

where the N_2 (B, V' = 11) state is produced from the $N_2(^5\Sigma)$ potential curve-crossing [5].

The band intensity (I_{N_2}) from N_2 (B, 11) can be written as it follows :

$$I_{N_2} = C(\lambda_1)\,\frac{hc}{\lambda_1}\,A_1\,[N_2(B, 11)] \qquad (1)$$

where $C(\lambda_1)$ is the spectral response at λ_1 of the optical system (Cf. Fig. 1), $\lambda_1 = 580.4$ nm and $A_1 = 6.2 \times 10^4$ sec^{-1} [6].
The N_2 (B,11) state density is given by the following equation :

$$[N_2(B, 11)] = \frac{[N]^2\,[M_2]\,k_1}{\nu_1^r + [M_2]\,k_q^1} \qquad (2)$$

where $C(\lambda_1)$ is the spectral response at λ_1 of the optical system (Cf. Fig. 1), λ_1 = 580.4 nm and $A_1 = 6.2 \times 10^4$ sec^{-1} [6].

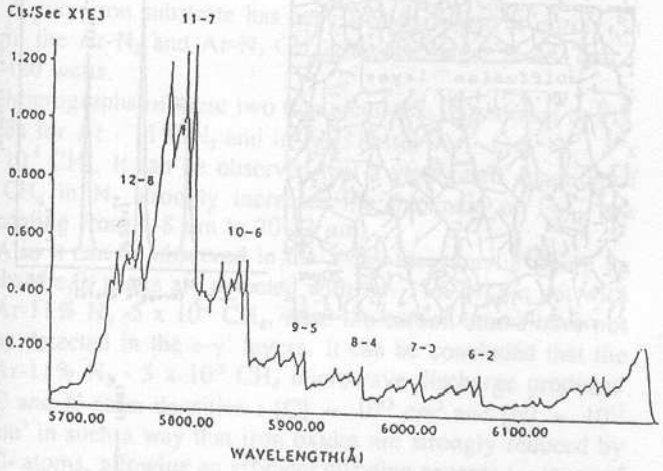

Fig. 4 I[st] positive N_2(B,V'-A,V") intensity in Ar-(> 10%) N_2 post-discharge.

where $\nu_1^r = \Sigma A_{1j} = 2.3 \times 10^5$ sec^{-1} and $k_q^1(Ar) = 0.2 \times 10^{-11}$ cm^3 sec^{-1} and $k_q^1(N_2) = 2.8 \times 10^{-11}$ cm^3 sec^{-1} [7].

It follows from eq. 1 and 2 that :

$$I_{N_2} = K_1 [N]^2 \qquad (3)$$

where K_1 is related to the rate coefficients in eq. 1 and 2. Then the N- atom density can be determined from I_{N_2} intensity measurements after calibration by NO.

Results are reported in Fig. 5 for Ar-N_2-H_2 gas mixtures at a time $\Delta t = 10^{-1}$ sec in the post-discharge. Such a decrease of N atom density with H_2 has been analysed in ref. 8 as resulting from N_2 (V) + H_2 quenching reactions. In condition of a N_2 - 1% H_2 d.c discharge with E/N = 5 x 10^{-16} V cm^2, T_v = 4 000 K and T_g = 400 K, the N_2 dissociation rate is less than 10^{14} cm^3 sec^{-1}, much lower than in pure N_2 discharge where it is 3 x 10^{10} cm^3 sec^{-1}.

4. Production of C atoms in Ar-N_2-CH_4 post-discharges

In the blue part of the Ar - (> 10%) N_2 afterglow, a strong emission of CN coming from olefin impureties has been observed as reproduced in Fig. 6 [2]. Particularly, a strong intensity of CN(B, 7 - X,7) is the result of the following recombination process :

$$C + N + M_2 \rightarrow CN(B,7) + M_2 \qquad (e)$$

By comparing the intensities of CN(B,7-X,7) and N_2 (B, 11-A, 7) bands in the afterglow, the C- atom density can be estimated from the N- atom density obtained by NO titration. The band intensity (I_{CN}) from CN(B,7) is given by the following equation :

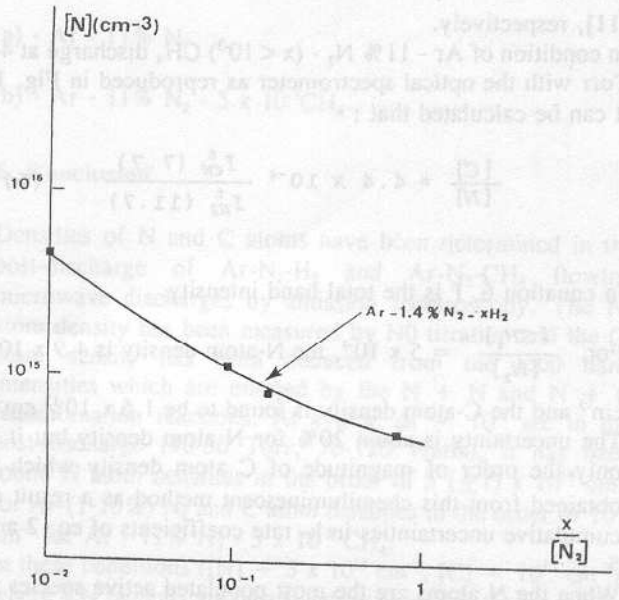

Fig. 5 N- atom density versus x/[N_2] in Ar-11%N_2-x CH_4 and Ar-1.4% N_2 -x H_2 gas mixtures.

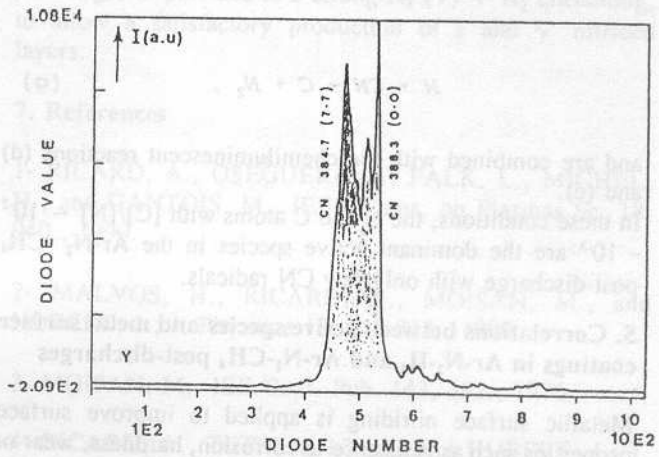

Fig. 6 CN(B,V' - X,V") emission intensity from olefin impurity in Ar-(>10%) N_2 post-discharge.

$$I_{CN} = C(\lambda_2) \frac{hc}{\lambda_2} A_2 [CN(B,7)] \qquad (4)$$

where λ_2 = 384.7 nm and $A_2 = 2.5 \times 10^7$ sec^{-1} [9]. The CN(B,7) state density is given by :

$$[CN(B,7)] = \frac{[C]\ [N]\ k_2}{\nu_2^r + [M_2]\ k_q^2} \qquad (5)$$

where $\nu_2^r = 2.5 \times 10^7$ sec^{-1} and k_q^2 (Ar) = 10^{-11} cm^3 sec^{-1} [10]. The recombination rate coefficient in eq. 2 and 5 are $k_1 = 10^{-33}$ cm^6 sec^{-1} [4] and $k_2 = 10^{-32}$ cm^6 sec^{-1}

[11], respectively.
In condition of Ar - 11% N_2 - ($x < 10^{-3}$) CH_4 discharge at 44 Torr with the optical spectrometer as reproduced in Fig. 1, it can be calculated that :

$$\frac{[C]}{[N]} = 4.4 \times 10^{-4} \frac{I^t_{CN}\ (7.7)}{I^t_{N2}\ (11.7)} \qquad (6)$$

In equation 6, I^t is the total band intensity.

For $\frac{[CH_4]}{[N_2]} = 5 \times 10^{-4}$, the N-atom density is 4.9×10^{15} cm^{-3} and the C-atom density is found to be 1.6×10^{-13} cm^{-3}. The uncertainty is about 20% for N atom density but it is only the order of magnitude of C atom density which is obtained from this chemiluminescent method as a result of cumulative uncertainties in k- rate coefficients of eq. 2 and 5.
When the N atoms are the most populated active species in the post-discharge, the following chain reactions could occur [9].

$$N + CH_x \rightarrow CN + xH\ , \qquad (f)$$

$$N + CN \rightarrow C + N_2\ , \qquad (g)$$

and are combined with the chemiluminescent reactions (d) and (e).
In these conditions, the N and C atoms with [C]/[N] ~ 10^{-2} - 10^{-3} are the dominant active species in the Ar-N_2 -CH_4 post-discharge with only few CN radicals.

5. Correlations between active species and metal surface coatings in Ar-N_2-H_2 and Ar-N_2-CH_4 post-discharges

Metallic surface nitriding is applied to improve surface properties such as resistance to corrosion, hardness, wear or fatigue by the development of thin surface layers (depth of 1-10μm) having high resistance properties. Low pressure gas discharges (1-5 Torr) are commonly used for steel surface nitriding and carburizing in industrial reactors. In such plasma treatments, the sample is usually connected as a cathode of a glow discharge in flowing N_2-H_2 and N_2-H_2-CH_4 gas mixtures.
It is to separate the contribution of ionic species such as N_2^+ and that the neutral active species such as N_2 (V) vibrational excited molecules, N and C atoms, that the post-discharge reactor as reproduced in Fig. 1 has been setup.

5.1 Metal surface coatings in Ar-N_2-H_2 post-discharges

After post-discharge treatments of 1h at 840K in Ar- 1.4% N_2 at 50 Torr, a γ' layer of 4μm with an ϵ layer of about 1μm was obtained as shown in Fig. 7a. The steel substrate is very sensitive to oxidation in the temperature range of

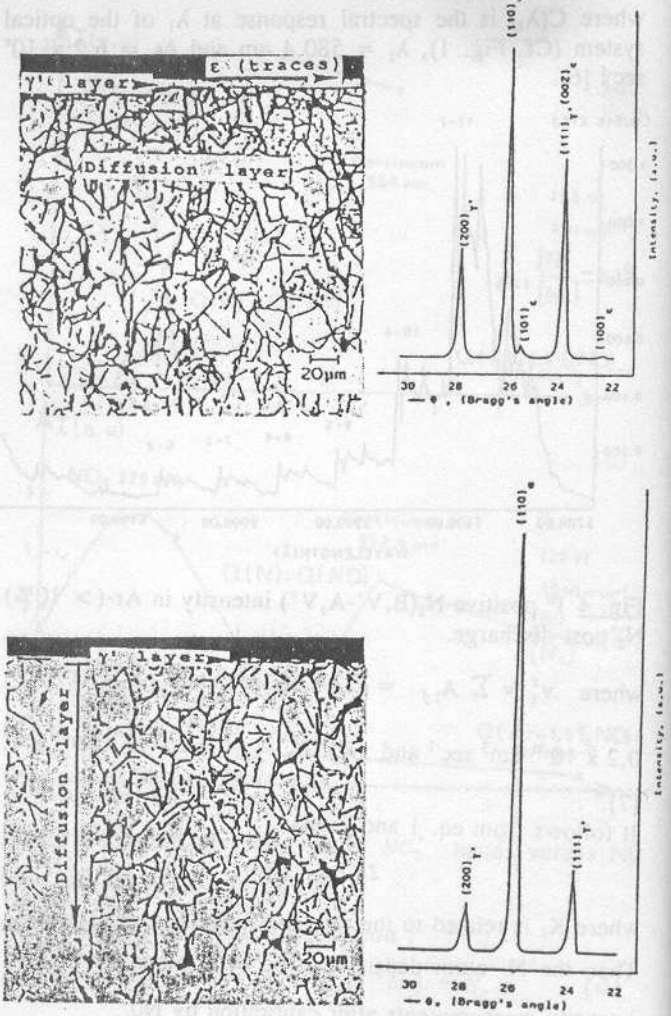

Fig. 7 Micrographs of iron - 0,1% C layers after an 1 hour post-discharge treatment at 840K in 50 Torr-70W discharges. Diffracted X-ray intensity versus Bragg's angle θ at the surface of nitrided layers :

a) Ar - 1.4% N_2 - 0.2% H_2 during the 1st 5 min. of treatment and Ar - 1.4% N_2 alone in the following.

b) Ar - 1.4% N_2 - 0.2% H_2 during all the treatment time.

nitriding, resulting in part from water and air impurities inside the reactor. Thin iron oxides as Fe_3O_4 inhibit the nitriding reaction. To avoid it, small concentrations of H_2 gas (0.2% H_2 in Ar-1.4% N_2 gas mixture) were introduced in the initial part of the treatment (2-3 min). But when H_2 flow was maintened during all the treatment time, a weaker γ' layer of 2 μm and none ϵ- layer was obtained as shown in Fig 7b. Note that ϵ and γ'layer thickness in Fig. 7a and 7b was directly determined by measurements on micrographs or from (110)α and (200)γ' intensity ratio of X diffraction pattern [1].
As shown in Fig. 5, a sharp decrease of N atoms is observed when small H_2 percentage is introduced into the Ar-N_2 discharge which can be related to a reduced γ' layer

as shown in Fig. 7b.

5.2 Metal surface coatings in Ar-N_2-CH_4 post-discharges

A pure iron substrate has been treated at 840 K during 3h in the Ar-N_2 and Ar-N_2-CH_4 post-discharges at 44 Torr - 120 watts.
Micrographs of these two treatments are reproduced in Fig. 8a for Ar - 11% N_2 and in Fig. 8b for Ar - 11% N_2 - 5 x 10^{-5} CH_4. It can be observed that a very small quantitie of CH_4 in N_2 strongly increases the thickness of Fe_{2-3} N-ϵ coating from 4-8 μm to 20-22 μm.
Also it can be observed in the X-ray diagrams in figure 8a that Fe_3O_4 peaks are detected with Ar- 11% N_2 but not with Ar-11% N_2 -5 x 10^{-5} CH_4. Also the carbon atoms have not be detected in the ϵ-γ' layers. It can be concluded that the Ar-11% N_2 - 5 x 10^{-5} CH_4 microwave discharge produced C and N atom densities : [C] ~ 10^{13} cm^3 and [N] ~ 10^{15} cm^3 in such a way that iron oxides are strongly reduced by C- atoms, allowing an efficient nitriding process (ϵ- layer of 20μm).

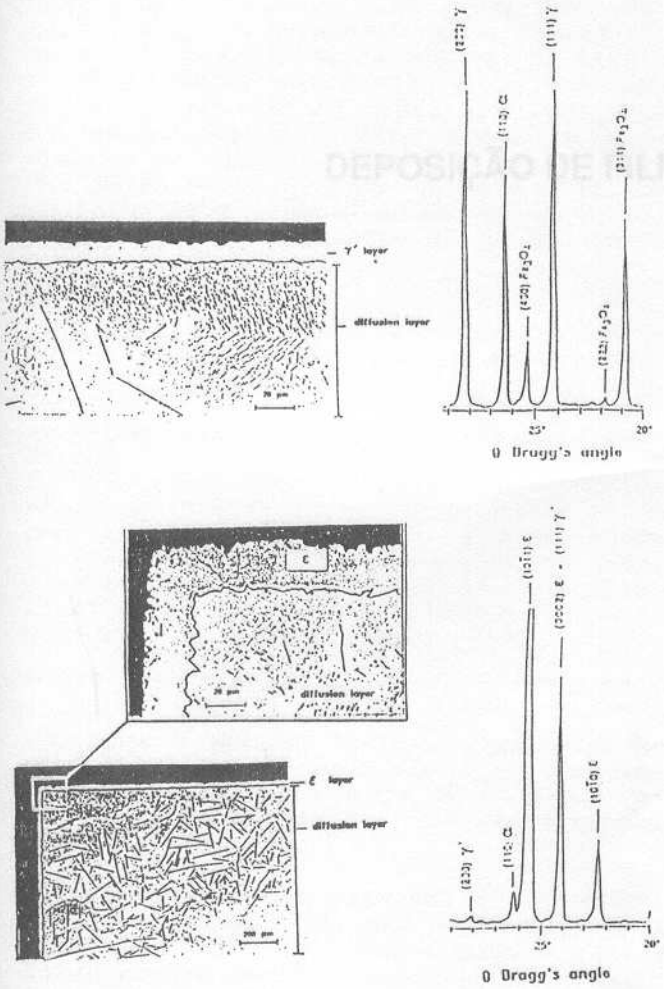

Fig. 8 Micrographs of pure Fe samples after a 3 hours post-discharge treatment at 840 K in 44 Torr - 120W discharges. Diffracted X -ray intensity versus Bragg's angle θ at the surface of nitrided layers.

a) - Ar - 11% N_2

b) - Ar - 11% N_2 - 5 x $10^{-5}$$CH_4$

6. Conclusion

Densities of N and C atoms have been determined in the post-discharge of Ar-N_2-H_2 and Ar-N_2-CH_4 flowing microwave discharges by emission spectroscopy. The N-atom density has been measured by N0 titration and the C-atom density has been deduced from the total band intensities which are emitted by the N + N and N + C recombination reactions. At a time Δt ~ 10^{-1} sec in the post-discharge (40-50 Torr, 70-120 Watts), it has been found N atom densities in the order of 5 ($\pm$1) x 10^{15} cm^{-3} for Ar-(1-10%) N_2 and C atom densities in the order of 10^{13} cm^{-3} for Ar - 11% N_2 - 5 x 10^{-5} CH_4.
In these conditions ([N] ~ 5 x 10^{15} cm^{-3}, [C] ~ 10^{13} cm^{-3}), where CN radicals are destroyed by N atoms, a high quality of iron nitrited layers has been obtained : 20 μm of ϵ- layer without oxides for a 3 hour treatment. With Ar-N_2 - H_2 gas mixtures the N atoms are weakly produced in the flowing discharge, in part due to a strong N_2 (V) + H_2 quenching, to allow a satisfactory production of ϵ and γ' nitrided layers.

7. References

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Fig. 1 Microwave post-discharge reactor.

Fig. 2 Fe-N phase diagram.

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Fig. 4 Ist positive N_2(B,V'-A,V") intensity in Ar-(> 10%) N_2 post-discharge.

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