Pure & Appl. Chem., Vol. 60, No. 5, pp. 747–751, 1988.
Printed in Great Britain.

Excited states of plasmas for steel surface nitriding and T_iN deposition

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Abstract - The excited states of plasmas for surface treatments have been detected by emission and absorption spectroscopy. For steel nitriding, the absorption spectroscopy using a dye laser (CARS) has given the vibrational N_2 (X,V) densities which are the most relevant species with N atoms and N_2^+ ions. For T_iN deposition, the emission spectroscopy has given the best working conditions of the hollow cathode discharge presently used.

INTRODUCTION

Low pressure discharges are commonly used for surface coatings as steel nitriding (ref. 1) and T_iN deposition on metals (ref. 2). Although plasma nitriding is nowadays widely used commercially and many of the metallurgical problems solved, there are still unanswered questions about the glow discharge, for instance the active species are not well known. It is the purpose of the present work to analyse the glow discharge by emission and absorption spectroscopy in operating conditions of plasma nitriding and plasma deposition of T_iN on steel surfaces.

EXCITED STATES OF PLASMAS FOR STEEL SURFACE NITRIDING

A typical reactor is shown in Fig. 1. It has been described in detail elsewhere (ref. 3). A flowing N_2-H_2 plasma was performed between the metal surface to nitride which is the cathode (K) and the reactor walls which are the anode (A) at the ground potential. The plasma fulfills the two functions of to heat the metal surface by ions bombardment and to create the active species for the metal surface nitriding. The light emitted by the plasma is detected through a hole (O) in the plasma reactor by using a Jobin-Yvon monochromator (resolution limit $\delta\lambda$ = 0.2 Å).

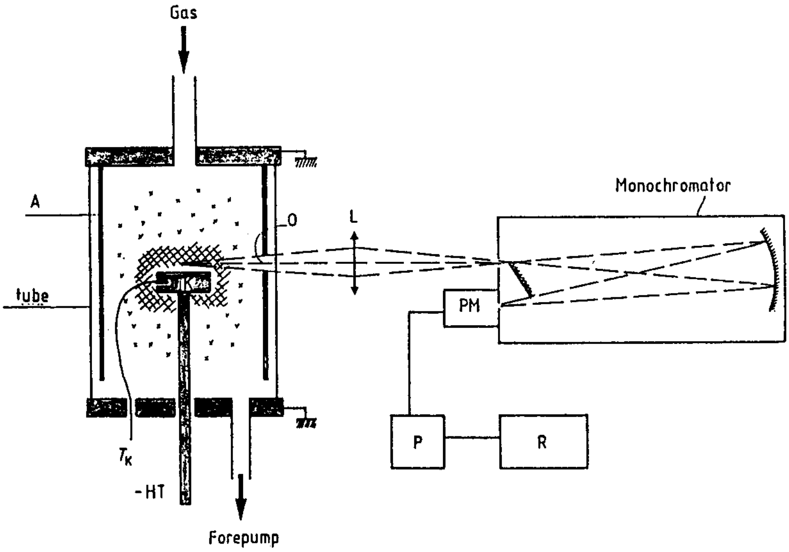


Fig. 1. Experimental set-up for steel surface nitriding : A anode, K Steel cathode (dia.3cm, surface 20cm^2), O hole (dia.1cm) and pinholes (dia. 2mm), L optical lens, PM photomultiplier, P picoammeter, R. recorder. Gas flow 1-5ℓ h^{-1} STP, P = 1-5 Torr.

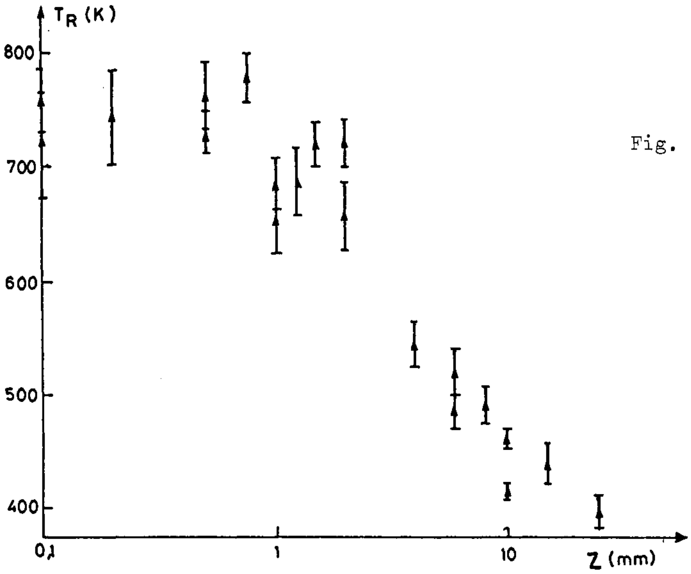


Fig. 2. Spatial profile of T_R near an iron cathode (P_{N_2} = 2 Torr, I = 50mA, dia. 3cm, Q = 0.9 lmn^{-1} STP).

The excited states of N_2^+, N_2, NH, H, N, N^+ and F_e have been detected (ref. 3). The N_2^+ emission (1st negative) was found to be the most intense in N_2 and N_2-H_2 mixtures at pressure of 2-3 Torr and current density of about 5 mA cm^{-2}. The rotational structure of the N_2^+ , 1st negative R-branch, has been recorded and N_2^+ rotational temperature ($T_{N_2^+}$) has been calculated from the boltzman graph. In the negative glow near the cathode fall of the N_2-H_2 discharges, $T_{N_2^+}$ has been found to be close (ref. 3) to the cathode temperature (T_K) which has been measured with a thermocouple. Precise results on ground state N_2 rotational temperature T_R have recently been obtained (ref. 4) by CARS analysis from the cathode fall to the negative glow of d.c. discharges. As shown in Fig. 2, it has been determined in a 2 Torr, 2 mA cm^{-2} N_2 discharge, T_R values which are growing from about 400 K in the negative glow (Z > 5mm) to 750 K in the cathode fall (Z = 0.1-1mm). The N_2 molecule heating in the cathode fall can be explained by charge transfers from N_2^+ ions.

Special attention has been devoted to the vibrational distribution of $N_2(X,V)$ ground state in the glow discharge. First the master equations for vibrational excitation coupled to be Boltzman equation for electron have been calculated by M.Capitelli et al (ref. 5). Second, the vibrational distribution has been measured in N_2 positive column by CARS(ref. 4). The N_2 (X,V) densities are given in Fig. 3 for P_{N_2} = 2 Torr, $E/n_o = 5 \times 10^{-16}$ V cm^{-2}, $n_e = 1.7 \times 10^{10}$ cm^{-3}, T_g = 550 K and residence time in the discharge t = 10^{-2} sec.

The calculated values are increasing with the residence time (10^{-3}-10^{-2} sec.) in the discharge and are well related to the experimental results. Densities as high than 10^{14} cm^{-3} for N_2 (X,V=10) are reproduced in the N_2 glow discharge. Such vibrational states are the most populated excited molecules as shown in Table 1, 10^3 to 10^5 higher in density that for N_2^+ ions and electrons.

The N atoms which are coupled to the final step of the vibrational distribution (N_2 (V=46) + $N_2 \rightleftharpoons N+N+N_2$) are also strongly populated in the glow discharge, in the order of 1% as detected by NO titration (ref. 6).

Table 1. Plasma parameters and densities of species in N_2 positive column (R=1cm). (From experimental results obtained in the Orsay LPGP).

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_o	$= 3 \times 10^{15} - 3 \times 10^{17}$ 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(^{2}D, ^{2}P)	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} sec.)

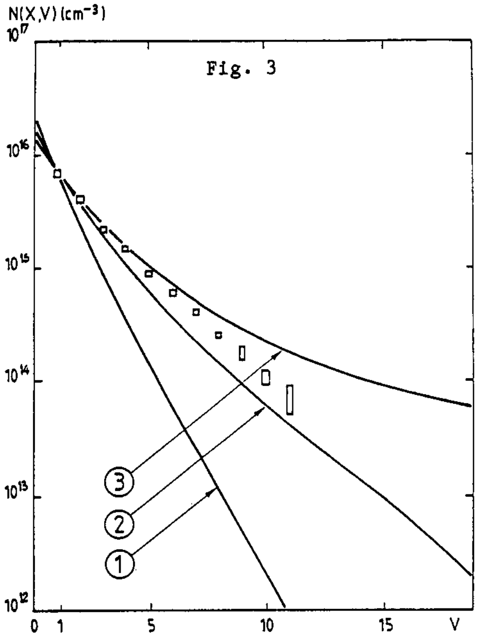


Fig. 3

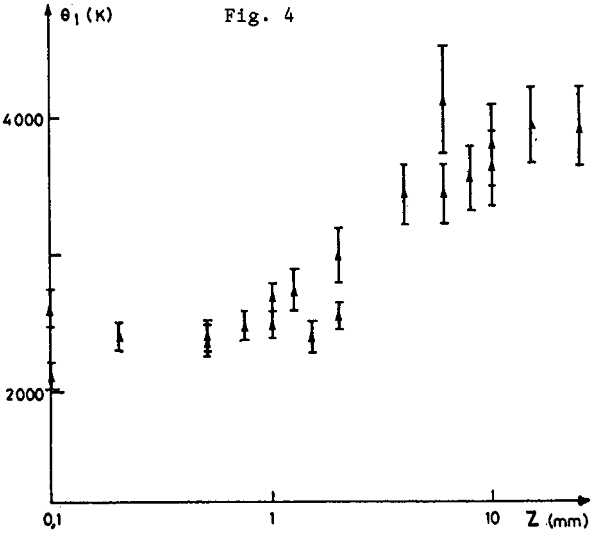


Fig. 4

Fig.3. Vibrational distribution of $N_2(X,V)$ in N_2 positive column. Rectangles are the CARS experimental results for a residence time t = 10^{-2} sec. Full lines are calculated results (1) t = 3.5×10^{-3} sec, (2) t= 10^{-2} sec, (3) t = 2×10^{-2} sec. P_{N_2} = 2 Torr, $E/n_o = 5\times10^{-16}$ V cm^2, n_e = 1.7×10^{10} cm^{-3}, Tg = 550 K.

Fig. 4. Spatial profile of θ_1 near an iron cathode (P_{N_2} = 2 Torr, I = 50mA dia. 3cm, Q = 0,9 lmn^{-1} STP).

The characteristic vibrational temperature θ_1 ($N_2(v=1)/N_2(v=o) = \exp{-\Delta E_{1,0}/k\,\theta_1}$) has been determined in the same conditionsas in Fig. 2 (ref. 4). As indicated in Fig. 4, the θ_1-values are decreasing in the cathode fall from 4000 K in the negative glow to 2500 K near the cathode. The T_R and θ_1 temperatures of N_2 are varying in the opposite direction suggesting that the gas heating in the cathode fall increases the vibrational quenching of $N_2(X,V)$ molecules.

EXCITED STATES OF PLASMAS FOR T_iN DEPOSITION

The excited states of A_r-N_2-H_2 reactive sputtering plasmas used for T_iN deposition on steel substrates have been analysed by emission spectroscopy as shown in Fig. 5. More details on the experimental set-up are given in ref. 7. The plasma reactot is a stainless steel chamber, 45cm in diameter and 90cm high. As shown in Fig. 5, a T_i emitter is located at the centre of the reactor. It is a circular array (5.2cm in diameter and 15cm hihh) of eight T_i rods (dia. 1cm). A plain steel substrate was positioned at a distance Z = 16cm from the T_i cathode. A d.c. negative voltage (-1500 V) was applied to the cathode. The substrate was biased up to -400V (usually - 150V). The reactor wall was grounded. The discharge current was about 3A on the cathode and 0.5A on the substrate. Typically the gas mixture was 65% Ar-32.5% H_2-2.5% N_2 at a pressure of 10^{-1} Torr and a flow rate of 5ℓh^{-1} STP. The light emitted by the plasma was detected by the same optical arrangement as shown in Fig. 1. The optical system rested on a rotating table that allowed a spatial distribution study between the T_i cathode (K_c) and the substrate (S).

The excited states of T_i, T_i^+, H, N_2^+, N_2, A_r and A_r^+ have been detected. The spatial distribution of oexcited states are characterized by a nearly exponentially decreasing of T_i atoms from the T_i cathode to the substrate and by a slow increasing of N_2 with a maximum value near the substrate. This result has been correlated to the resulting coatings which vary from $T_{i2}N$ close to the T_i emitter (7cm) to T_iN further away (ref. 7).

A special effect of H_2 had been observed in this reactive sputtering discharge. The spatial distributions of A_r^+, A_r, T_i^+, T_i and H excited states are given in Fig. 6 from the hollow cathode center (z=0) to the substrate (z=120mm) in a A_r - 10% H_2 gas mixture at p=0.1 Torr. By cutting off the hydrogen gas feed and by outgasing the

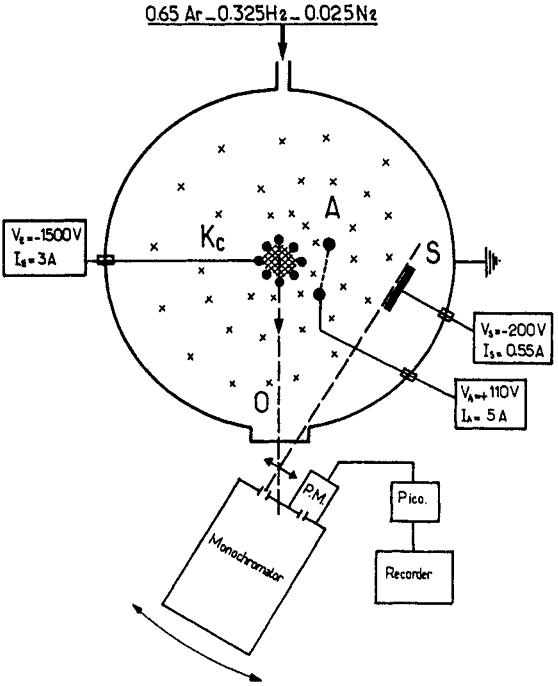
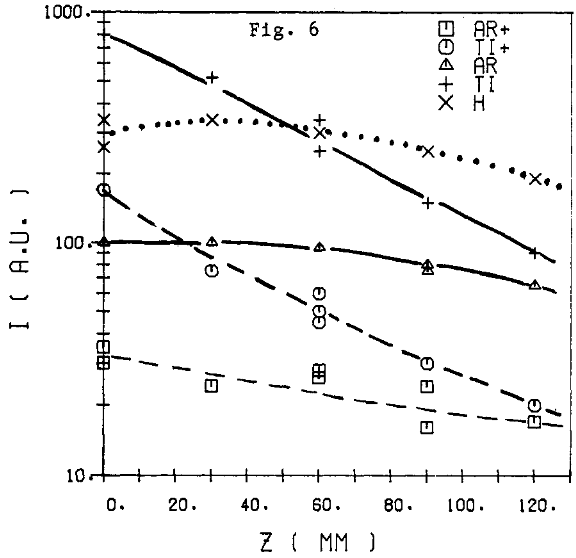


Fig. 5. Experimental set-up of T_i hollow cathode discharge for titanium nitride deposition (p = 7.6×10^{-2} Torr, flow rate 5-6 ℓ h^{-1} STP, K_c titanium emitter comprising an array of 8 T_i rods (dia. 1cm), S steel substrate, A loop electrode, O Pyrex window.

substrate with a negative voltage up to 600 volts (ion bombarding), only a weak emission of hydrogen lines was observed from the A_r plasma. Then by introduction gain 10% of H_2 in A_r it was observed the emission of excited species as shown in Fig. 7. A weak H emission an inversily strong T_i and $T_i{}^+$ emission were recorded during all the time when the discharge was running. Inside the T_i cathode array, the $A_r{}^+$, $T_i{}^+$ and T_i excited state which are related to the pulverizing process were strong in intensity and the H and A_r emission disappeared (cf. Fig. 7). Such results were unchanged when 2% of N_2 was introduced into the A_r-10% H_2 gas mixture and when the substrate was polarized or not.



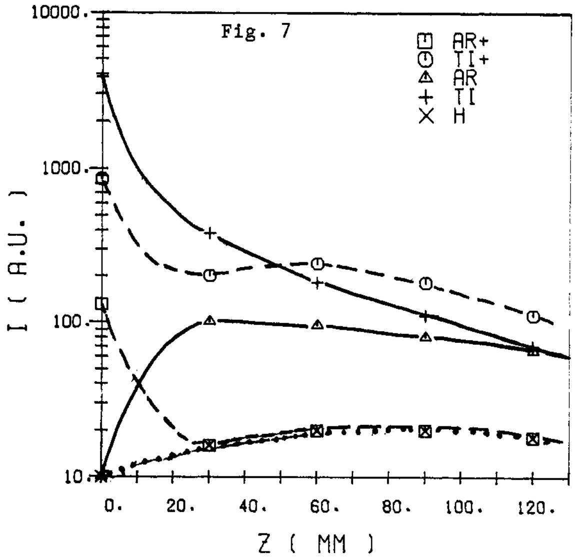


Fig. 6. Intensities (relative units) of H, T_i, $T_i{}^+$, A_r, $A_r{}^+$ excited states from the hollow cathode center (Z=0) to the substrate (Z=120mm). A_r-10% H_2 gas mixture, substrate not degasing by A_r ion pulverizing.

Fig. 7. Same radiative states as in Fig. 6. Substrate degasing by A_r ion pulverizing and then introduction of 10% H_2 in A_r (p = 0.1 Torr).

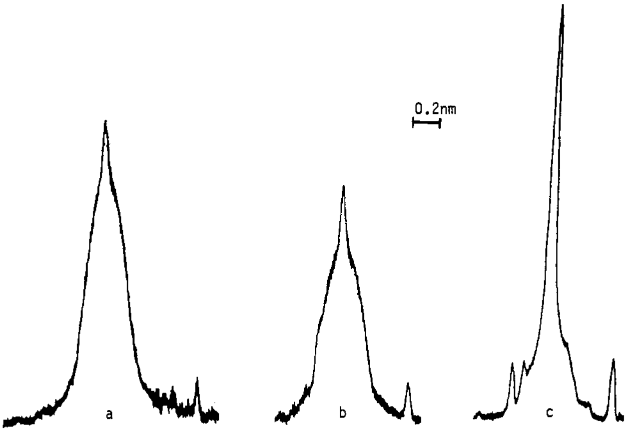


Fig. 8. Hα line profiles respectively near the substrate (a), at 60cm from the T_i emitter (b) and near the T_i emitter (c).

Profiles of Hα emission have been recorded from the T_i emitter to the substrate (ref. 8). As shown in Fig. 8, surprising profiles have been recorded near the substrate (a), at 60cm from the T_i cathode (b) and near the cathode (c) in a A_r-10% N_2 mixture.

The profiles of Hα consist of a narrow central peak of width equal to 0.05nm, which tops a very large and broad non gaussian component of width ≃ 0.35 nm. The narrow peak is the result of Doppler broadening of slow H atoms with energies less than 1 ev. The broad component comes from fast H atoms whose energies are between 10 and 100 ev.
Such fast H atoms are produced by dissociative ionization of H_2 following the reactions :

$$e + H_2(X,V) \longrightarrow e + e + H_2^{+*} \tag{1}$$

$$H_2^{+*} \longrightarrow H^+ + H^* \tag{2}$$

$$H^* \longrightarrow H + h\nu \; (H\alpha)$$

The broad component is dominant near the substrate (Fig. 8 a) when the H_2 gas feed was cut off. Then the H desorption from the substrate can produce H_2^- which lead to vibrationally excited neutral molecules H_2 (X,V) (ref. 9) and to fast excited H atoms following reactions 1 and 2.

It appears from this study that the best working conditions of T_i sputtering are obtained in pure A_r discharge. The reactive H_2 and N_2 gases are necessary to obtain unpowdery T_iN coatings but they must be introduced in such a manner that the A_r-T_i plasma prevents the poisoning of the cathode and substrate metal bodies by these reactive gases.

CONCLUDING REMARKS

The spectroscopy of plasmas for surface treatments is an in situ diagnostics allowing to study the behaviour of the active species during a given process. For steel nitriding, the N_2^+ ions and the N_2(X.V) and N neutral species appear to be relevant species. The H_2 gas is introduced into the nitriding plasmas presumably to destroy the metal surface oxides and also to obtain unpowdery T_iN coatings. But caution must be taken with H_2 in sputtering discharges since the cathode and the substrate could be poisened by this reactive gas perturbing the plasma working conditions.

Acknowledgements This work was supported in part by the DGA-DRET.

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