RELAXATION OF HIGH ENTHALPY NITROGEN PLASMA FLOWS

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ABSTRACT

The paper reports on the relaxation of the electron gas parameters and some electronically excited species in high enthalpy plasmatron-produced nitrogen plasma jets downstream from the cathode. It is shown that the jet plasma remains atomic even at large distances from the region of the energy deposition and the measured electron number densities exceed here their equilibrium values by almost two orders of magnitude. The longitudinal distributions of $\text{N}_2^+$ molecules in the ground $\text{X}^2\Sigma_g^+$ and irradiating $\text{B}^2\Sigma_u^+$ electronic states presented. The key features of the jet plasma kinetics are discussed.

1. INTRODUCTION

Molecular plasma jets hold much promise for the extended studies on the plasma kinetics at elevated temperatures and for being used in diverse plasma-aided technologies [1,2]. In this connection a considerable attention attract electronically excited radicals, both atomic and molecular, which are abundantly generated in high enthalpy plasma jets and often give rise to fundamentally new physical processes. Specifically, there are strong grounds for believing that formation of polyphase structures in monophase materials and nanocrystalline and/or amorphous structures within the near surface layers can be effectively performed through the interaction of active radicals produced in energetic plasma flows with a metal surface.

The present paper focuses on the relaxation of the electron gas parameters and the number densities of some plasma components in high enthalpy plasmatron-produced nitrogen plasma jets at atmospheric pressure. The electron, $T_e$, and rotational, $T_r$, and electron number densities, $n_e$, are derived from the jet emission spectra taken in the 200-1000nm region downstream form the cathode. Much attention is given to an accurate determination of the axial values of $T_e$ at elevated electron temperatures, which becomes most important for atomic lines. The longitudinal evolution of molecular nitrogen ions in their ground and irradiating electronic states is investigated. Some conclusions concerning the plasma kinetic mechanisms of the considered nitrogen jets are drawn. The totality of the determining plasma chemistry processes is diagrammatically illustrated.

2. EXPERIMENTAL ARRANGEMENT

The investigated high enthalpy nitrogen plasma jets are produced by a high current (I=150+400A) arc plasmatron with a divergent channel-anode vortex-stabilized by the working gas [3]. The inlet nozzle diameter can be varied from 2mm to 6mm, whilst the outlet
diameter is 26mm. In the anode, there exist windows of 10mm in height and 1mm in width placed at different distances Z from the cathode for observation of the plasma jet transversely. The working gas is fed tangentially at flow rates \( G = 1.6 \text{g/s} \). The plasma streams show high hydrodynamic stability and their geometric and thermophysical parameters are firmly reproducible.

For spectral measurements two recording systems are used, one of which involves diffraction grating DFS-452 with two photodiode arrays Toshiba 1250A and the other is based on monochromator MDR-41 with photomultiplier FEU-100. The emission spectra are taken in the 200-1000nm region with high spectral resolution (~0.01nm) at different distances Z from the cathode. To process spectrometric data an automated system SPEC_MCD.100 based on package Mathcad 7.03 Professional is developed [4]. It allows creation of extensive data files (up to 10 Mb per experimental cycle) as well securing of a great body information on physical characteristics of spectral lines emitted by atoms, singly and doubly charged ions, primarily on radiation transition probabilities \( A_n \) and Stark constants \( w_n \). The system also permits the Abel inversion and simulation of rovibronic molecular spectra. Further details concerning the experimental arrangement can be found elsewhere [5].

3. THE ELECTRON GAS TEMPERATURES

The experimental techniques employed in determining the electron temperatures at different distances from the cathode are described in [5,6]. On diminishing the inlet nozzle diameter \( D_n \), the process of measuring the axial values of \( T_e \) needs, however, to be considered in greater detail. This immediately follows from the fact a fairly high electron temperature up to \( \sim 3 \text{eV} \) can be attained at \( D_n \leq 3 \text{mm} \) in the near-cathode region. Therefore the radial distributions of the intensities of atomic and even some ionic lines show their maximum values not at the jet axis (the so-called Mih"{n}e's effect), so that the Abel correction for the laterally measured line intensities becomes vitally important. On the assumption of LTE to be valid, the relative line intensities, thus corrected, for singly charged ions and atoms, \( I_e/I_n \), and for doubly charged ions and atoms, \( I_{ee}/I_n \), are given by the relations as follows

\[
\frac{I_{ee}}{I_e} = \frac{\varepsilon_{ee}^A}{\varepsilon_{e}^A} \frac{A_{ee} g_{ee} a_{ee}}{A_{e} g_{e} a_{e}} \left( \frac{2\pi n_e k T_e}{h^2} \right)^{3/2} \frac{1}{n_e} \exp \left( - \frac{E_e - E_1 + I_e}{k T_e} \right)
\]

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\frac{I_{ee}}{I_e} = \frac{\varepsilon_{ee}^A}{\varepsilon_{e}^A} \frac{A_{ee} g_{ee} a_{ee}}{A_{e} g_{e} a_{e}} \left( \frac{2\pi n_e k T_e}{h^2} \right)^{3/2} \frac{1}{n_e} \exp \left( - \frac{E_e - E_1 + I_e + I_2}{k T_e} \right)
\]

Here \( \varepsilon_{ee}^A \) are the axial correction factors reconstructed through the Abel inversion. The energies \( E_i \) are measured from the continuum threshold, \( g_i \) and \( \lambda_i \) are, correspondingly, the statistical weight of the \( k \)-th level and the wavelength for transition from the \( k \)-th level. All other symbols are commonly accepted. It should be noted that the second ratio, \( I_{ee}/I_e \), provides the most accuracy of determining \( T_e \) values.

Fig.1 illustrates different methods of determining \( T_e \) values in the nitrogen plasma jet near the cathode. The generalized quantities \( (n_i^a g_i^a) \) \((i=1, II, III)\) are reduced to the values of \( n_i^a g_i^a \) in such a way that \( (n_i^a g_i^a) = n_i^a g_i^a \), where \( n_i^a \) is the absolute population of the \( k \)-th level of atom or/and ion. Thus the quantities \( \ln(n_i^a g_i^a) \) as a function of the level
energy $E_e$ should lie along the same straight line if they correspond to the same electron temperature. It is clearly seen that N-atoms are not suitable for deducing electron temperatures at elevated electron temperatures $T_e$, whatever the measuring technique. Conversely, both techniques, as applied to singly and doubly ionized nitrogen, give close values of $T_e$. A slight scatter is apparently caused by that the Miln's effect becomes partly noticeable even for NII ions at $T_e\sim3$eV.

Fig. 1. Determination of the electron temperature in the near-cathode region. Curves 1-3 are constructed using the Boltzmann-plot technique for NIII, NII, and NI, respectively. Curves 4-6 are drawn by the method of relative line intensities. I=400A, G=1.5g/s, D$_m$=3mm, Z=6mm.

4. CONCENTRATIONS OF MOLECULAR IONS $N_2^+(X^2\Sigma_G^+)$ AND $N_2^+(B^2\Sigma_U^+)$

To assess the concentrations of $N_2^+(B^2\Sigma_U^+)$ the following relation was used

$$\int_{\Delta \lambda} \epsilon(\lambda) \, d\lambda = \sum I_{j',j}.$$

The integral is taken over the vicinity $\Delta \lambda$ of the (0-0) band head and the sum is taken over the rotational lines ($j' \rightarrow j''$) falling into the wavelength interval $\Delta \lambda$. $\epsilon(\lambda)$ is the emission coefficient; $J$ and $J'$ are the upper and lower rotational numbers, respectively. On the assumption that the transition frequencies $\nu_{j,j'} \equiv <\nu>$ ($<\nu>$ is the averaged frequency
corresponding to the wavelength interval $\Delta \lambda$, the integrated rotational line intensities $I_{J'}^{J''}$ can be expressed through Einstein coefficient $A_{J',J''}^{n',n''}$ and the absolute molecule population $N_{J'}^{n',n''}$ in the upper electronic, $n'$, and vibrational, $\nu'$, state. In the approximation of the rigid rotator this gives

$$ I_{J'}^{J''} = (h <c>/4\pi v) g_{J'}^{n'} A_{J',J''}^{n',n''} S_{J'}^{n',n''} \exp[-B_{J'}^{n',n''} J(J+1)/kT_e] Q_J(n', \nu') $$  \hspace{1cm} (4)

Here factor $g_{J'}^{n'}$ equals to 1/3 or 2/3 depending on whether the upper rotational term is antisymmetric or symmetric. $Q_J(n', \nu')$ is the rotational partition function for the upper vibronic state. $S_{J'}^{n',n''}$ is the Hön-London factor [7], $B_{J'}^{n',n''}$ the rotational constant. $T_e$ is the rotational temperature. To calculate $N_{J'}^{n',n''}$ concentrations the Boltzmann relations were applied. The $N_{J'}^{n',n''}(B'\Sigma_g')$ concentrations were determined using rotational temperature $T_e$. The latter was derived through numerical simulation of the (0-0) and (0-1) bands of the first negative system of $N_{J'}^{n',n''}$ [6]. The lower and upper limits for the $N_{J'}^{n',n''}$ concentrations can be established using the magnitudes of the rotational temperature $T_e$ and the axial electron temperature $T_\alpha$, respectively. The results of the calculations are presented in Fig. 2. As expected, the populations of term $X'\Sigma_g^+$ thus obtained, appreciably differ in the far relaxation zone of the jet. Also shown are the distributions of the axial magnitudes of the electron temperature, $T_e$, and number density, $n_e$. The latter quantity is determined from the Stark constituents of atomic and ionic line profiles [6].

5. THE KEY FEATURES OF THE PLASMA KINETICS

Basic neutral and charged species, both in their ground and excited states, and the predominant population and depopulation elementary processes in the studied nitrogen plasma flows are diagrammatically shown in Fig. 3. Arrows represent the collision-induced transitions and wavy lines - the radiation processes. The open arrows correspond to the inelastic processes involving electrons, whereas the solid lines are related to the elementary
processes with participation of exclusively heavy species. The line widths correlate with the intensities of the processes. The widths of the horizontal lines correspond to the absolute populations of the associated energy levels. The dashed lines depict vibrational levels. Starting from the general scheme, we now highlight some key features of the plasma kinetics.

The diagram shows that electrons play an important role in the population and depopulation processes and the charge kinetics. Of special importance in this connection is the fact that the electron gas in the far relaxation zone is strongly overcooled. Indeed, it is seen from Fig.2 that at distances of 30-40mm downstream from the near-anode arc zone \( n_e(0)=2\times10^6 \text{ cm}^{-3} \). However at an electron temperature \( T_e=7000 \text{ K} \), typical of this zone the equilibrium value \( n_e(0)=4\times10^7 \text{ cm}^{-3} \). The calculations involving the process of electron-ion recombination and some related ion-molecular reactions allow one to approach the measured \( n_e(0) \)-values. However the difference of 3 to 4 times remains. It should be stressed that the equilibrium magnitudes of the rate coefficients yet locally depending on the kinetic temperatures of electrons and heavy species were used in these calculations. This may be thought of as the main reason for such a disagreement.

The predominant neutral component in the studied jet plasmas is atomic nitrogen. The calculations allowing for the recombination processes \( N+N+\rightarrow 2N \) and \( N+N+N\rightarrow N+N+N \) show that even in the far relaxation zone \( (Z=70 \text{ mm}) \) \( [N]>>[N] \times10^6 \text{ cm}^{-3} \). It also follows from Fig.3 that the concentrations of the low-lying metastables \( N^0(\Delta D) \) and \( N^0(\Delta P) \) attain sufficiently high magnitudes. For the jet core the estimates give \( [N(\Delta D)]\sim2\times10^5 \text{ cm}^{-3} \), \( [N(\Delta P)]\sim2\times10^5 \text{ cm}^{-3} \). It is not however improbable that molecular metastables, such as \( N(\Delta_2^0\Sigma^0 \text{a}) \) and \( N(\Delta_2^0\Sigma^0 \text{a}) \) can form in noticeable quantities outside the plasma filament owing to recombination of N-atoms.

It is seen from Fig.2 that \( n_e>>[N_2] \) throughout the length of the jet. The preliminary calculations show that the formation of ions \( N_2^+ \) from \( N^0 \) in the jet core may be ignored whatever distance \( Z \). The binding energy of ions \( N_2^+ \) is less than \( 1 \text{ eV} \), so that their concentrations are negligible at fairly high temperatures characteristic of all jet segments, including the far relaxation zone. Thus ion \( N^0 \) is the predominant positive ion in the studied plasmas. This ion appears to play the main role in the formation of irradiating molecular ions \( N_2^+(\Delta_2^0\Sigma^0 \text{a}) \) through the charge transfer reaction \( N^0+N_2\rightarrow N_2^++N \).

The foregoing consideration allows some conclusions to be drawn concerning the possible ionization mechanisms in the relaxing nitrogen jets downstream from the region of
energy deposition, where electric fields are negligible. It seems probable that in jet core associative ionization involving metastable atoms N(1D) and N(1P) is the predominate electron production mechanism:

\[ \text{N(1D)} + \text{N(1P)} \rightarrow \text{N}_1^+ + \text{e}. \]  \(5\)

Meanwhile, outside of the jet core associative ionization processes involving molecular metastables \(N_2(A^3\Sigma_u^-)\) and \(N_2(a^3\Sigma_u^-)\) can generally contribute to the electron generation and merit to be taken into account too.

6. CONCLUSION

To briefly summarize, the main results are as follows: (i) The electron gas in the far relaxation zone is strongly overcooled. The simplified kinetic considerations using equilibrium and local rate constants do not allow the measured values of electron density to be approached. (ii) The jet plasma remains atomic up to the largest distances from the plasmatorn. (iii) Associative ionization involving atomic metastable atoms \(N(1D)\) and \(N(1P)\) plays the major role in the electron production process in the core of the relaxing nitrogen plasma jets. However the role of pair ionizing collisions of molecular metastables \(N_2(A^3\Sigma_u^-)\) and \(N_2(a^3\Sigma_u^-)\) may be important outside the jet core. (iv) At sufficiently high values of the electron temperature (~3eV) N-atoms are not suitable for being used in the Boltzmann-plot and relative line intensities techniques.

REFERENCES