Microwave N₂–Ar Plasma Torch

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Abstract. This work investigates the spatial structure of a microwave plasma torch driven by an azimuthally symmetric surface wave operating in N₂–Ar mixtures at atmospheric pressure. The main plasma and wave characteristics are obtained in the framework of a self-consistent 2D model that describes the entire spatial structure of this source, including the discharge zone, sustained by the field of the surface TM₀₀ mode, and the post-discharge plasma. The set of equations considered to describe the plasma source include: Maxwell’s equations; the dispersion equation of the surface mode; the rate balance equations for vibrationally excited states of electronic ground state molecules N₂(X'Σ₉⁺,v); the rate balance equations for the triplet N₂(A'Σ⁺₉,v, B'Π₉,v, C'Π₉,v) and singlet N₂(a'Σ₋,v, a'Π₉,v, w'Δ,v, a'Σ₊,v) electronic excited states and the Ar(3p⁵4s) and Ar(3p⁵4p) excited states of Argon; the rate balance equations for N⁺, N⁺, N⁺, N⁺, Ar⁺, Ar⁺ ions and electrons; the rate balance equations for the ground state N(⁴S) and the metastable states N(⁵P, ⁵D) of nitrogen atoms; the gas thermal balance equation; and the equation of mass conservation for the fluid. Model calculations of the 2D spatial distributions of species of interest such as charged particles (electrons and positive ions), N₂(X'Σ₉⁺,v) vibrationally excited molecules, N₂(A'Σ⁺₉,v) metastables and N(⁴S) ground state atoms are presented and discussed.

1. Introduction
The development of microwave-based plasma sources applications [1–8] is an issue of growing interest, in particular in what concerns atmospheric plasma torches. One of the main advantages of such discharges is that they make it possible to inject large power densities into the plasma and thus achieve high population densities of active species of interest. Efficient applications of such sources depend on the ability to control the spatial structure of the source and the relevant plasma properties. Fundamental plasma parameters such as gas temperature and active species density profiles need to be determined in order to have a complete plasma characterization.

The development of high-density plasma torches based on microwave propagation is interesting for improving the next-generation plasma-based technologies [7]. In particular, N₂–Ar plasma sources driven by microwaves have advantageous properties for plasma processing technologies, such as the nitriding of surfaces [3]. These sources provide high number densities of active species. Among these, long-lived species like ground-state N(⁴S) atoms and molecules excited in metastable and vibrational states are of major importance. Moreover, nitrogen atoms play a key role in surface treatment...
processes [6]. One possible way to control the dissociation rate of nitrogen may be the use of mixtures such as N$_2$−Ar [4,5].

The spatial structure of the source, i.e., the spatial distribution of active species of interest is crucial for the purposes of treatment processes. However, investigations of different plasma sources have usually focused either on the discharges or their post-discharges only [8]. Since the processes in the post-discharge plasma depend on the source discharge itself, the discharge and the post-discharge must be investigated together [7].

In the present work, a plasma torch excited by a surface wave operating in N$_2$−Ar mixtures at atmospheric pressure is investigated. The purpose of the work is to describe the physical workings and the spatial structure of this plasma source including its active zone, i.e., the source discharge, which is sustained by the field of the azimuthally symmetric TM$_{00}$ surface mode, as well as the post-discharge plasma resulting from gas flow and species diffusion. A self-consistent, 2D theoretical model is developed to investigate the entire spatial structure of the source and to determine the main plasma and wave characteristics. The 2D spatial profiles of the relevant plasma quantities, such as the densities of charged particles (electrons and positive ions), N$_2$(X$^1\Sigma^+_u$, v) vibrationally excited molecules,

N$_2$(A$^3\Sigma^+_u$) metastable molecules and N($^4S$) ground state atoms are obtained and discussed. A large number of elementary processes occurring both in the plasma bulk and at the wall have been taken into account.

The organization of the article is as follows. In Sec. II the theoretical formulation and the system of equations to be solved are presented and discussed. The numerical algorithm used to solve the system of equations is described in Sec. III. The results are discussed in Sec. IV. The conclusions are presented in Sec. V.

2. Theoretical model

The system under analysis is a cylindrical plasma column in a quartz tube (2$a = 1.5$ cm inner diameter and 2$b = 1.8$ cm outer diameter) in N$_2$−Ar at atmospheric pressure, sustained by an azimuthally symmetric TM$_{00}$ surface wave mode at 2.45 GHz frequency (see figure 1). For this mode, the finite field components are $E_r$, $E_z$ and $H_\phi$, in the usual cylindrical coordinates [10]. The wave power flux is mainly concentrated around the plasma–discharge tube interface. The axial power flux $P_z$ results from the radial electric ($E_r$) and the azimuthal magnetic ($H_\phi$) field components. According to the main mechanisms governing the plasma production and maintenance, the source consists of two different but connected parts, viz., the discharge and the post-discharge regions. Axial gas flow and species diffusion give rise to the latter one.

The system of equations considered to describe the plasma source includes [4, 5, 7, 10, 11]:

i) Maxwell’s equations;

ii) The dispersion equation for a pure TM azimuthally symmetric surface mode;

iii) The electron Boltzmann equation in the local approximation (with a correction for non-local terms in the post-discharge region);

iv) The rate balance equations for vibrationally excited states of electronic ground state molecules, N$_2$(X$^1\Sigma^+_u$, v);

v) The rate balance equations for N$_2$(A$^3\Sigma^+_u$, B$^3\Pi_g$, C$^3\Pi_u$, a$^1\Sigma^-_u$, a$^1\Pi_g$, w $\Delta$ u) excited molecules and for Ar(3p$^4$4s), Ar(3p$^4$4p) and N(2P, 2D) excited atoms;

vi) The rate balance equations for N$^+$, N$_2^+$, N$_3^+$, N$_4^+$, Ar$^+$, Ar$_2^+$ ions and for electrons;

vii) The rate balance equation for ground state N($^4S$) atoms;

viii) The gas thermal balance equation;

ix) The equation of mass conservation for the fluid as a whole.

The above system of equation is solved numerically in a self-consistent manner by iterative procedures (see below). As a result, a self-consistent spatial description of the following quantities is achieved:
electron energy distribution function (EEDF) and its integral quantities; mean power needed for the creation of an electron-ion pair $\theta(r,z)$ in the discharge; electron density $n_e(r,z)$; vibrational distribution function ($\delta_v$) of $N_2(X^1\Sigma_g^+,\nu)$ molecules (up to $\nu = 45$); population densities of the molecular and atomic states $N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u, a^1\Sigma_u^-, a^1\Pi_g, w'\Delta u)$, Ar($3p^54s$), Ar($3p^54p$), N($^2P$, $^2D$), and N($^4S$), and of positive $N^+$, $N_1^+$, $N_2^+$, Ar$^+$, Ar$^{2+}$ ions; spatial 2D structure of the microwave electric field $E$ maintaining the discharge and surface wave dispersion characteristics; and gas temperature $T_g(r,z)$.

Figure 1. Plasma torch.

3. Method of solution
A flow chart of the model illustrating the solution algorithm used is depicted in figure 2. The input parameters are the $N_2$-Ar mixture composition and the gas pressure ($p = N k T_g$, where $N$ is the neutral gas density, $T_g$ is the gas temperature), stimulating frequency $\omega/2\pi$, inner radius of the tube $a$, dielectric tube thickness ($b - a$) and its permittivity ($\varepsilon_0$). The calculation starts with the solution of the dispersion equation (DE) assuming an initial Bessel-like profile of the electron density, with a given radially averaged density value, at the position of the launcher ($z = 0$), a TM$_{00}$ surface mode excitation at 2.45 GHz and a given constant value of the electron-neutral collision frequency $\nu_{ea}$. After this, the propagation constant and the 2D electric field distributions are easily calculated. An arbitrary value for the electric field intensity at the plasma-dielectric interface $E_0$, is introduced to continue the calculations. The iteration procedure starts with an initial Maxwellian electron energy distribution to solve the integro-differential Boltzmann equation by iterations (loop not shown in figure 2) and with arbitrary 2D Bessel-type profiles of charged particles and vibrationally and electronically excited states. Then, the rate balance equations are solved in 2D-geometry consistently with the calculated EEDF, for the chosen value of $E_0$ and taking into account the 2D spatial structure of the electric field components. Thus, a 2D matrix with rate coefficients and diffusion coefficients is generated. Then, the non-linear system of rate balance equations for electrons, positive ions and vibrationally and electronically excited species is linearized and solved by iteration. The unknown constants $E_0$ and $\nu_{ea}$ are varied and the iterations proceed until convergence is obtained in this initial plasma slice. Then, the same procedure continues along $z$ taking into account the electron power balance equation at each axial position. The discharge ends at the axial position $z_{cr}$ where the electron density reaches its critical value, i.e., the cut-off density. Beyond this point, i.e., in the post-discharge region, the procedure is similar but much simpler. Since the electric field vanishes here, only the species rate balance equations
are solved taking the electron rate coefficients from solutions to the Boltzmann equation with zero applied field and the initial values obtained at $z_{cr}$ for the species populations.

As a result, a self-consistent 2D solution for the EEDF and its integral quantities, the population densities of vibrationally and electronically excited species and positive ions, and the electric field distribution is obtained for the whole volume of the plasma source.

4. Results and Discussion

Calculations have been carried out for a 20 % N$_2$–80 % Ar mixture at atmospheric pressure. The gas flow rate is 500 sccm and the corresponding mean gas velocity is in the range 0.07–0.87 m/s (thus, nearly isobaric conditions prevail).

4.1. Wave-to-Plasma Power Transfer.

As the wave propagates, the wave power flow decreases along the discharge since the wave power is progressively absorbed by the plasma electrons, which dissipate this power in collisions with the gas particles. Thus, the energy transferred from the electrons to the gas particles is subsequently redistributed via numerous elementary processes among the translational (gas temperature) and internal (vibrational, rotational and electronic) degrees of freedom of the particles. Figure 3(a) shows

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**Figure 2.** Flow-chart of the model.
the spatial 2D distribution of the reduced electric field intensity $E/N$ in the discharge zone (up to about 6 cm axial distance from the launcher). The reduced electric field intensity achieves a maximum at the end of the plasma column plasma. The maximum reduced electric field intensity increases from about $6 \times 10^{-17} \text{ V cm}^2$ close to the launcher to about $1 \times 10^{-16} \text{ V cm}^2$ at the end of the discharge zone. The minimum reduced electric field intensity is observed at the wall. This minimum is almost constant, about $1 \times 10^{-17} \text{ V cm}^2$. The 2D map of the mean power needed to sustain an electron–ion pair, $\theta$ divided by total neutral density, is shown in figure 3(b). This quantity varies significantly in the radial direction, reaching a maximum at $r/a = \pm 0.5$. Close to the launcher, $\theta$ changes nearly by two orders of magnitude. A nearly one order of magnitude change in $\theta$ is observed in the axial direction ($10^{-12} \text{ W} - 10^{-11} \text{ W}$) in the central region. The changes of $\theta/N$ reflect the strong radial variations of both the electric field intensity and the neutral gas density, as a result of the radial variation in gas temperature, under isobaric conditions ($p = \text{const}$). In fact, the spatial variation of the mean absorbed power per electron essentially reflects that of the reduced electric field $E/N$ sustaining the discharge.

Figure 3. 2D ($r$–$z$) distribution of (a) reduced electric field $E_{total}/N$ and (b) $\theta/N$ ($p = 1 \text{ Atm}, P = 600 \text{ W}, 20 \% \text{ N}_2 - 80 \% \text{ Ar}$).
The 2D map of the gas temperature is shown in figure 4. The measured values of the wall temperature have been used as a boundary condition. There are strong variations of gas temperature both in the axial and radial directions. Maximum values of about 5500 K are observed in the discharge zone, close to the launcher. The gas temperature drops radially from about 5000 K at the axis to about 1000 K at the wall. The relatively small variation in gas temperature along the discharge is followed (at about 4 cm axial distance from the launcher) by a sharp drop in the post-discharge, where it decreases from 2000 K to nearly room temperature at the end.

**Figure 4.** 2D ($r$–$z$) distribution of the gas temperature ($p = 1$ Atm, $P = 600$ W, 20% N$_2$ – 80% Ar).

### 4.2. Charged Particles

The spatial density distribution of the electronic density is shown in figure 5. There are small axial changes in the discharge zone (up to about 6 cm axial distance) but, as expected, a rapid decrease of about two orders of magnitude occurs in the post-discharge region. Electron densities higher than $10^{13}$ cm$^{-3}$ are observed close to the launcher.

**Figure 5.** 2D ($r$–$z$) distribution of the electron density ($p = 1$ Atm, $P = 600$ W, 20% N$_2$ – 80% Ar).
Spatial distributions of the relative densities of the dominant positive ions Ar$^+$, N$^+_2$ and N$^+_3$ are shown in figures 6(a) to 6(c), respectively. As seen, the distributions of Ar$^+$ and N$^+_2$ have similar behaviours, showing almost no changes in the central zone of the discharge, but dropping very fast close to the tube wall and in the post-discharge region. According to the calculations, Ar$^+$ ions are the dominant positive ions (about 60 % of all ions) in the central zone of the discharge up to 6 cm axial distance. The main sources of Ar$^+$ ions are step-wise electron ionization processes from Ar metastables and pooling reactions between excited Ar atoms (see ref. 9). Positive N$^+_2$ ions constitute only about 35 % of the total ion density population in the discharge. These ions are principally created by associative ionization processes involving $N_2(\Lambda^3\Sigma_u^+)$ and $N_2(a^1\Sigma_u^-)$ metastables (see ref 9).

![Image](image1.png)

(a) ![Image](image2.png) (b) ![Image](image3.png) (c)

Figure 6. 2D ($r$–$z$) distributions of (a) Ar$^+$, (b) N$^+_2$ and (c) N$^+_3$ relative populations. ($p = 1$ Atm, $P = 600$ W, 20 % N$_2$ – 80 % Ar)

Close to the tube wall N$^+_3$ ions are the most populated. In the post-discharge, however, N$_4^+$ ions constitute over 70 % of the total ion population. This is a result of a strong increase in the relative contribution of associative ionization processes involving $N_2(\Lambda^3\Sigma_u^+)$ and $N_2(a^1\Sigma_u^-)$ metastables in this region. The contribution of this channel reaches values up to 70 % of the total positive ion yield.
Three-body recombination processes between Ar atoms and Ar$^+$ ions provide also significant amounts (up to 30\%) of Ar$^{+2}$ ions in the post-discharge.

4.3. Metastable and Vibrationally Excited Molecules
Microwave discharges containing nitrogen generate numerous particles in metastable states, which store energy and make it available for different processes such as ionization, chemical reactions and gas heating. Of particular importance is the triplet state $N_2(A^3\Sigma_u^+)$, which has a long radiative lifetime (about 2 s) and is usually highly populated. The spatial variation of the relative (to the total concentration of $N_2$) population of $N_2(A^3\Sigma_u^+)$ state is shown in figure 7(a). Close to the launcher, the $N_2(A^3\Sigma_u^+)$ relative population reaches levels higher than $10^{-4}$. The decrease in $E/N$ and electron density both axially and radially causes a decrease in the $N_2(A^3\Sigma_u^+)$ relative population. The $N_2(A^3\Sigma_u^+)$ population can be enhanced by the effective excitation transfer from Ar($^3P_0$, $^3P_2$) to N$^2$ yielding $N_2(C^3\Pi_u)$ via the fast radiative decay of $N_2(C^3\Pi_u)$ to $N_2(B^3\Pi_g)$ and the subsequent radiative and collisional transitions from this state to $N_2(A^3\Sigma_u^+)$. The decrease in $N_2(A^3\Sigma_u^+)$ population close to the wall and to the end of the plasma source is determined by the increase of neutral density in these regions. Under nearly isobaric condition, the decrease in temperature towards the wall and the column end results in a neutral density increase and, consequently, in an increase of the $N_2(A^3\Sigma_u^+)$ quenching rate by neutral particles. The spatial variation of the relative population of the N($^2P$) state is shown in figure 7(b). This atomic metastable state follows closely the behaviour of the molecular state $N_2(A^3\Sigma_u^+)$, and its relative population reaches values higher than $10^{-4}$ close to the launcher. These two metastable states are closely correlated: quenching of $N_2(A^3\Sigma_u^+)$ by nitrogen atoms is an important mechanism for the creation of N($^2P$) and $N_2(A^3\Sigma_u^+)$ is produced in collisions between N($^2P$) and vibrationally excited $N_2(X^1\Sigma_g^+,\nu)$ states, with $\nu = 9$ and 10.

![Figure 7](image-url)

**Figure 7.** Spatial distribution of the relative metastable (a) $N_2(A^3\Sigma_u^+)$ and (b) N($^2P$) population densities ($p = 1$ Atm, $P = 600$ W, 20\% N$_2$ – 80\% Ar).
At the high degrees of ionisation \(10^{-3} - 10^{-5}\) and reduced electric fields typical of microwave discharges, the calculated vibrational distribution functions (VDFs) are considerably “excited” and exhibit significant changes both radically and along the discharge length. Figures 8(a) and 8(b) show the axial and radial evolutions of the vibrational distribution function at the axis and at the gap, respectively. High vibrational excitation of the lower and intermediate vibrational levels is observed. There are small changes along the discharge region followed by a sharp decrease in the population of the higher and intermediate levels, with vibrational quantum numbers \(v > 5\), in the post-discharge plasma. This sharp decrease in the population density of the vibrational levels \((v > 5)\) is a consequence of the simultaneous effects of the decrease in degree of ionization and the higher \(V-T\) depopulation rates by \(N_2-N\) collisions due to the gas temperature decrease [13]. The observed increase in the population density, for levels up to 30, close to the wall is a consequence of the simultaneous effects of the increase in electric field and the decrease in gas temperature.

![Figure 8. VDF: (a) axial variation at the centre of the tube and (b) radial variation at the gap. \((p = 1\) Atm, \(P = 600\) W, 20 % \(N_2 - 80\%\) Ar, \(r/a = 0\))](image)

4.4. Nitrogen \([N(4S)]\) Atoms

The spatial distribution of the degree of dissociation, \(i.e.,\) of the \(N(4S)\) atom concentration relative to that of \(N_2\), is shown in figure 9. Direct electron impact dissociation is the main source channel of ground state atoms in the discharge zone up to about 5–6 cm axial distance. The decrease in electron density and reduced electric field causes a decrease of the dissociation degree towards the plasma column end as well as across the discharge. A smooth axial variation is observed in the discharge zone, which is followed by a sharp drop of nearly 3 orders of magnitude in the post-discharge. A high dissociation degree (higher than \(10^{-2}\)) is observed close to the launcher.

5. Conclusions

A 2D theoretical model for a microwave plasma torch driven by an azimuthally symmetric surface wave in \(N_2-Ar\) mixtures at atmospheric pressure has been developed. The model incorporates the description of both the discharge plasma, sustained by a pure \(TM_{00}\) surface mode, and the flowing afterglow. Maxwell’s equations, the electron Boltzmann equation and the rate balance equations for the most important species – \(N_2(X^3Σ_g^+, v)\) and \(N_2(A^1Σ_u^+, B^3Π_g, C^3Π_u, a^1Σ_u^-, a^3Π_u, w \Delta u)\) molecular states, \(Ar(3p^34s)\) and \(Ar(3p^34p)\) atomic states, \(N^+, N_2^+, N_4^+, Ar^+, Ar_2^+\) ions, and \(N(4S,3P,2D)\) atoms – were consistently solved to yield the species spatial distributions both in the radial and the axial directions. Strong spatial correlations are shown to exist between the density distributions of plasma electrons and electronically excited states of molecules and atoms. The model predicts high populations in
vibrational and metastable states of nitrogen molecules as well as high degree of nitrogen dissociation, of up to 5 %, in the discharge zone.

Figure 9. Spatial distribution of the degree of dissociation ($p = 1$ Atm, $P = 600$ W, 20 % N$_2$ – 80 % Ar).

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References
[1] Chen Z, Liu M, Tang L, Hu P and Hu X 2009 J. Appl. Phys. 106 013314
[2] Foster J, Tomas M and Neuber A A 2009 J. Appl. Phys. 106 063310
[3] Ricard A, Oseguera-Pena J E, Frank L, Michel H and Gantois M 1990 IEEE Trans. Plasma Sci. 18 940
[4] Henriques J, Tatarova E, Guerra V and Ferreira C M 2002 J. Appl. Phys. 91 5622
[5] Henriques J, Tatarova E, Dias F M and Ferreira C M 2002 J. Appl. Phys. 91 5632
[6] C M Ferreira, E Tatarova, V Guerra, B Gordiets, J Henriques, F M Dias and M Pinheiro 2003 IEEE Trans. Plasma Sci. 31 645
[7] Henriques J, Tatarova E, Dias F M and Ferreira C M 2008 J. Appl. Phys. 103 103304
[8] Guerra V, Dias F M, Loureiro J, Sá P A, Supiot P, Dupret C and Popov T 2003 IEEE Trans. Plasma Sci. 41 pp 542 – 552
[9] Henriques J, Tatarova E and Ferreira C M 2011 J. Appl. Phys. 109, 023301
[10] Ferreira C M, Tatarova E, Henriques J and Dias F M 2009 J. Phys. D: Appl. Phys. 42 194016
[11] Ferreira C M and Moisan M 1988 Physica Scripta 38 382
[12] Golant B E, Jilinski A P and Sakharov S A 1977 The Essentials of Plasma Physics (Moscow: Atomizdat)
[13] Guerra V, Tatarova E, Dias F M and Ferreira C M 2002 J. Appl. Phys. 91 2648
[14] Vereschchagin K A, Smirnov V V and Shakhatov V A 1997 Tech. Phys. 67 487
[15] Kabouzi Y, Graves D B, Castaños-Martínez E and Moisan M 2007 Phys. Rev. E 75 016402
[16] Tatarova E, Dias F M, Ferreira C M, Guerra V, Loureiro J, Stoykova E, Ghanashev I and Zhelyazkov I 1997 J. Phys. D: Appl. Phys. 30 2663