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Ion densities in a high-intensity, low flow nitrogen–argon plasma

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The plasma density in an expanding thermal plasma was determined using planar Langmuir probe measurements. The arc plasma was operated at low flow (500 standard cm^3 per minute). It is shown that the decrease of density with increasing distance from the nozzle of the arc in an argon plasma can be explained by diffusion away from the expansion axis. The determined decay length is 10 cm. In the case that nitrogen is injected in the arc, the plasma density is lowered considerably due to charge exchange and dissociative recombination in the expansion. Because of the low electron density (10^{17} m^{-3}) at a partial nitrogen flow larger than 10%, the dissociative recombination becomes slow. The main loss process of N_2^+ ions in this case is diffusion away from the plasma axis. The effective decay length found in the nitrogen plasma is 9 cm.

I. INTRODUCTION

High-density plasmas are commonly used in a variety of industrial applications. Some of these sources are used as downstream sources, where the plasma production is separated from the treatment region. One such source is the expanding thermal arc under investigation at the Eindhoven University of Technology. In a previous report, the electron and ion densities in the expanding nitrogen plasma were investigated. Because in many industrial applications pump capacity is limited, the question arose to modify the plasma source to work at lower flows [total flow smaller than 500 standard cm^3 per minute (sccm)]. Initial investigations creating argon plasmas in this regime are reported by van de Sanden. In the current paper we extend the investigation of the ion densities in the nitrogen expanding plasma to the low flow regime. A model for the gas phase reactions involving ions after the expansion of the plasma will be presented and compared to measurements.

II. EXPERIMENTS

A. Cascaded arc plasma

The plasma source used is the cascaded arc [Fig. 1(a)]. The current can be varied but is set to 36 A in the experiments described here. The voltage drop depends on the gas flow rate and gas composition and ranges from 50–100 V. No magnetic field was applied in this study. Details of the operation of the cascaded arc can be found in Ref. 6. The argon gas is injected at the cathode side and is ionized in the arc channel. The plasma is then let to expand supersonically into a low-pressure chamber [Fig. 1(b)]. Normally this plasma is operated at high flow rates, typically of the order of several standard liters per minute. To be able to use this plasma at flow rates in the range of 100–500 standard cm^3 per minute (sccm), the bore of the copper plates was varied. It was found that operation was most reliable if six plates were used with bores varying between 4 and 1 mm. The fourth plate, with a bore of 2 mm contains a seeding channel, through which nitrogen can be flowed into the arc.

An overview of all relevant parameters during the experiments is given in Table I.

B. Planar probe

The Langmuir probe used to determine the plasma density is a tungsten disk with a radius of 2 mm. The backside and edges of the probe are shielded off by a ceramic (Al_2O_3) tube. The probe is more extensively described in Ref. 7. The probe is placed on the expansion axis of the plasma with the normal to the probe surface parallel to the expansion. The probe can be controlled by a movable arm to measure at different positions in the plasma.

III. THEORY

In the expanding plasma under investigation, the densities are of the order 10^{17}–10^{18} m^{-3} and the electron temperature is 0.1–0.3 eV. The Debye length therefore, is of the order 10^{-5} m. This means that the sheath formed around the probe due to the absorption of charged particles is much smaller than the probe dimensions. The mean-free paths are of the order 10^{-1}–10^{-3} m, much larger than the sheath dimensions. This means that no collisions inside the sheath have to be taken into account. The electron saturation current I_{es} for this case is given by

\[ I_{es} = \frac{1}{4} n_{e0} \bar{v}_e e A_s, \]

with \( n_{e0} \) the electron density of the undisturbed plasma, \( \bar{v}_e \) the electrons’ mean velocity, \( e \) the electron charge, and \( A_s \) the sheath surface. Because the Debye length is very small compared to the probe radius and because the edges of the probe are shielded from the plasma, the sheath surface may be approximated by the probe surface. The velocity distribution is assumed to be Maxwellian so that \( \bar{v}_e = \sqrt{(8/\pi)}(kT_e/m_e) \), with \( k \) Boltzmann’s constant, \( T_e \) the electron temperature, and \( m_e \) the electron mass. In the ex-

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Expanding plasma the ion temperature is approximately equal to the electron temperature. The ion and electron saturation current are therefore related through
\[ I_{\text{es}} = I_{\text{is}} = \frac{5}{A} \frac{m_i}{m_e} \]
with \( m_i \) the mass of the ions. Because \( T_e \approx T_i \), the Bohm criterion \( 9 \) is automatically satisfied.

**IV. ARGON PLASMA**

A pure argon plasma was created with a total flow of 500 standard cm\(^3\) min\(^{-1}\) (sccm). Because extensive research has been carried out on the expanding argon jet,\(^2,5,10,11\) this plasma can be used as a means of calibrating the probe measurements\(^12\) and investigate the workings of the arc under the conditions of low flow. The electron density was measured by the Langmuir probe, as a function of distance from the nozzle. The results are shown in Fig. 2. The background pressure in the vessel is 7 Pa, the electron temperature behind the shock is approximately 0.2 eV.\(^13\)

The decrease of electron density as a function of distance from the nozzle is caused by recombination and diffusion. The three-particle recombination,
\[ \text{Ar}^+ + e^- + e \rightarrow \text{Ar} + e \]
has (with \( T_e = 0.2 \) eV) a rate of \( k_1 = 0.1 - 2 \times 10^{-36} \) (m\(^3\) s\(^{-1}\)).\(^10\) The decrease of electron density through recombination can be calculated as a function of distance from the nozzle:
\[ \frac{\partial n_e}{\partial z} = -n_e^2 k_1 \frac{v_d}{v_d^2} \]
with \( v_d \) the forward drift velocity, which is assumed to be constant.

With the initial condition \( n(z=0) = n_{e0} \), this is solved to
\[ n_e(z) = \left( \frac{2 k_1 z}{v_d} + 1 \right) \frac{n_{e0}}{v_d^2} \left( \frac{n_{e0}}{v_d} \right)^{-1/2} \]

With the plasma parameters given above, a drift velocity \( v_d \) of 600 m/s (see, for example, Ref. 2), and an initial density \( n_{e0} \) of \( 10^{19} \) m\(^{-3}\), the density is reduced to \( 0.5 n_{e0} \) at \( z = 4.5 \) m. It is clear from these calculations that recombination cannot explain the observed decrease in electron density on the axis of this argon plasma. This means that the loss of electron density on the axis is dominated by diffusion toward the walls.

The mass balance in steady state, neglecting recombination, is given by
\[ -\nabla \cdot (D_a \nabla n_e) + \nabla \cdot (n_e \nabla v_d) = 0, \]
with \( D_a \) the ambipolar diffusion coefficient. This equation can be solved analytically in several different ways, each with its own set of assumptions. Although the different methods lead to slightly different axial density profiles they all have a typical decay length (1/e length) of approximately

![FIG. 1. Cascaded arc (a) and expanding thermal arc setup (b).](image)

**TABLE I. Overview of experimental conditions.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar flow</td>
<td>500–100 sccm</td>
</tr>
<tr>
<td>N(_2) flow</td>
<td>0–400 sccm</td>
</tr>
<tr>
<td>Arc current</td>
<td>36 A</td>
</tr>
<tr>
<td>Downstream (z&gt;10 cm):</td>
<td></td>
</tr>
<tr>
<td>Chamber pressure</td>
<td>7 Pa</td>
</tr>
<tr>
<td>Electron density</td>
<td>(10^{17}–10^{19}) m(^{-3})</td>
</tr>
<tr>
<td>Electron temperature</td>
<td>0.1–0.3 eV</td>
</tr>
</tbody>
</table>

![FIG. 2. Measured (■) and fitted (dashed line) electron densities in an argon plasma, as a function of the distance from the nozzle.](image)
\[ l_{\text{decay}} = \frac{R_0^2 v_d}{4D_a}, \]  

(6)

where \( R_0 \) is the plasma radius, which is almost constant for the downstream plasma (\( z > 10 \) cm); see for example, Ref. 14. The decay length of the electron density can be estimated, using the ambipolar diffusion coefficient, \( D_a \):

\[ D_a = \left(1 + \frac{T_i}{T_e}\right) \frac{kT_e}{m_i} \tau_{ia}, \]  

(7)

where \( \tau_{ia} \) is the ion–atom collision time. With \( T_i = T_e = 0.2 \) eV, a gas temperature of 500 K and pressure \( p = 7 \) Pa, the collision time \( \tau_{ia} \) is approximately \( 10^{-6} \) s, according to Ref. 15. This leads to a diffusion coefficient \( D_a \approx 1 \) m² s⁻¹. An estimated plasma radius of 3 cm and a drift velocity of 600 m s⁻¹ result in a decay length for the electron density of approximately 14 cm. For \( r = 0 \), an exponential fit to the measured data is shown as the dashed line in Fig. 2. The effective decay length fitted is 10 cm. Taking into account the uncertainty in several of the parameters used in estimating the rate of decay, it is possible to conclude that the observed decay can be explained through diffusion.

An extrapolated initial density \( n(0,0) \approx 9.4 \times 10^{18} \) m⁻³ is found. This can be compared to results in the high flow regime (flow > 3500 sccm) by van de Sanden et al., 2 who found that the ion density scales approximately linearly with arc current and background pressure. Extrapolating their results (as an example, arc current = 45 A, background pressure = 40 Pa, initial ion density = \( 5 \times 10^{19} \) m⁻³) to the settings used here predicts an initial density of \( 5 \times 10^{18} \) m⁻³. The initial density in the plasma under investigation in this paper is a factor of 2 higher. This may be attributed to a relatively higher pressure inside the arc caused by the smaller bore of the central plates [see Fig. 1(a)] used when operating at lower flow.

V. NITROGEN PLASMA

The results found in argon can now be used as a basis for understanding the results in the nitrogen/argon mixtures. Some extra considerations have to be made because, as will be shown, reactions in the gas phase are no longer negligible. Inside the arc the temperatures are high (\( T_i \approx T_e \approx 1 \) eV) as well as the electron density (\( n_e \approx 10^{22} \) m⁻³). Therefore, the relative abundance of the ions can be calculated using pLTE considerations. The ions will be atomic ions only and their relative density is given by

\[ \frac{n_{N^+}}{n_{Ar^+}} = \frac{g(N^+)}{g(Ar^+)} \frac{N_{\text{flow}}}{N_{\text{flow}} e^{[(E_{Ar^+} - E_{N^+})/T_e]}, \]  

(8)

with \( n_{N^+}, n_{Ar^+} \), the density of \( N^+ \) and \( Ar^+ \), \( g(\ldots) \) the statistical weights of the different particles, and \( E_\ldots \) the ionization energy for each atom. For the purpose of modeling and understanding the reactions taking place in the expansion, it is assumed that the relative density given by Eq. (8) still exists just after the shock in the expansion. This assumption seems justified because the compression of the atomic ions in the shock will be smaller than a factor of 4 (Ref. 2) and direct association will still be negligible. The influence of varying the relative flow of the gases into the arc on the electron density and relative ion densities downstream is investigated. The results of the Langmuir probe measurements are shown in Figs. 3 and 4(a). In Fig. 3, the electron density on the expansion axis, at a distance of 15 cm from the nozzle, is shown as a function of relative nitrogen flow. In Fig. 4(a) the ratio of electron to ion saturation current is shown. The ratio of electron to ion saturation current is equal...
to the square root of the mass ratio of electrons to ions, according to Eq. (2), and is therefore a measure for the relative ion densities.

To understand these results, it is necessary to incorporate recombination reactions in the mass balance equation [Eq. (5)]. The dissociated and ionized gas coming from the arc expands into a background of neutral argon and molecular nitrogen formed on the vessel walls. The following reactions will determine the densities of the different species.

- Charge exchange,
  \[ \text{Ar}^+ + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2^+ \text{, rate } k_1, \]
  \[ \text{N}^+ + \text{N}_2 \rightarrow \text{N} + \text{N}_2^+ \text{, rate } k_2. \]

- Recombination,
  \[ \text{N}_2^+ \rightarrow e + \text{N}^+ + \text{N}, \text{ rate } k_3. \]

At \( T_e \approx 0.2 \text{ eV} \), the charge exchange rates \( k_1 \) and \( k_2 \) are estimated to be \( 7 \times 10^{-17} \) (Ref. 16) and \( 1 \times 10^{-16} \text{ m}^3 \text{ s}^{-1} \) (Ref. 17), respectively. The rate of the dissociative recombination, \( k_3 \), is estimated at \( 10^{-13} \text{ m}^3 \text{ s}^{-1} \) (Ref. 18). With a drift velocity of 600 m/s and the rates given above, diffusion away from the expansion axis is negligible compared to charge exchange and recombination for a relative nitrogen flow above approximately 1% and electron densities larger than \( 10^{17} \text{ m}^{-3} \). This is also shown by the dashed line in Fig. 3. Equation (5) can now be rewritten as a set of rate equations:

\[
\begin{align*}
\frac{\partial n_{\text{Ar}^+}}{\partial z} & = -k_1 n_{\text{Ar}^+} n_{\text{N}_2} \frac{1}{v_d}, \\
\frac{\partial n_{\text{N}^+}}{\partial z} & = -k_2 n_{\text{N}^+} n_{\text{N}_2} \frac{1}{v_d}, \\
\frac{\partial n_{\text{N}_2^+}}{\partial z} & = k_1 n_{\text{Ar}^+} n_{\text{N}_2} \frac{1}{v_d} + k_2 n_{\text{N}^+} n_{\text{N}_2} \frac{1}{v_d} - k_3 n_{\text{N}_2^+} n_e \frac{1}{v_d},
\end{align*}
\]

where \( n_e = n_{\text{Ar}^+} + n_{\text{N}^+} + n_{\text{N}_2^+} \) follows from quasineutrality. These equations are solved numerically.

Allowing some variations in the rate constants, a fit to the measured data is shown as the solid line in Fig. 3. The rates used to obtain a good fit are \( k_1 = 2 \times 10^{-16} \text{ m}^3 \text{ s}^{-1} \), \( k_2 = 1 \times 10^{-16} \text{ m}^3 \text{ s}^{-1} \), and \( k_3 = 0.5 \times 10^{-13} \text{ m}^3 \text{ s}^{-1} \). The absolute value of these rates depends linearly on the drift velocity. The fitted values for the rates \( k_1 \) and \( k_2 \) also depend on the neutral gas temperature. Within the uncertainties introduced by these dependencies, the values fitted compare reasonably to the theoretical values given above. The same rate constants are used to calculate the ion to electron mass ratio in the plasma. This is shown in Fig. 4(b). Although the experimentally determined ratios [Fig. 4(a)] and the calculated ones differ in absolute value, the trend toward lighter ions is visible. The difference in absolute values is possibly caused by small offsets in the measuring circuitry, which has a great influence on the ion saturation current and therefore on the current ratio.

The model predicts that at seeding percentages of nitrogen larger than approximately 10%, the plasma will consist of predominantly \( \text{N}_2^+ \) ions. The plasma density downstream drops to below \( 10^{17} \text{ m}^{-3} \). At these low electron densities the dissociative recombination becomes small. If a total ion loss rate, \( A_{\text{ion}} \), is defined as

\[ A_{\text{ion}} = \frac{1}{n_e} \frac{\partial n_e}{\partial t}, \]

it is possible to distinguish between the loss rate due to recombination and the loss rate due to diffusion. This is shown in Fig. 5, where the loss rates are shown as a function of nitrogen seeding, at a distance of 15 cm from the nozzle. From these calculations it follows that at a nitrogen seeding of more than 10% the main loss process is diffusion toward the wall. The plasma density as a function of distance from the nozzle with a nitrogen seeding of 80% is shown in Fig. 6, where the solid line is an apparent linear fit resulting in a 1/e decay length of 9 cm. This decay length is comparable to the one found in argon since the \( \text{N}_2^+ \) ions have a resonant charge exchange with the \( \text{N}_2 \) in the background, similar to \( \text{Ar}^+ \) in argon. The diffusion coefficient of \( \text{N}_2^+ \) is expected to

![FIG. 5. Total ion loss rate, \( A_{\text{ion}} \), due to diffusion (dashed line) and due to recombination (solid line) as a function of nitrogen seeding.](image)

![FIG. 6. Measured (■) and modeled (dashed line) electron densities as a function of the distance from the nozzle.](image)
be higher by a factor of \( \frac{401}{19} \) (the mass ratio), but this will be partly compensated by a higher drift velocity.

The results obtained here with the plasma in the low flow regime can be compared to results found by Dahiya et al.\(^4\) in a similar plasma at much higher flow (>1000 scc/min). Although the same (charge exchange and dissociative recombination) reactions are taking place, the dominant ion found in the mass spectrometer by Dahiya et al. is \( \text{N}^+ \). This is due to the fact that the ion densities at higher flow rates are higher, typically of the order of \( 10^{18} \text{ m}^{-3} \) at a distance of 20 cm from the nozzle.

VI. CONCLUSIONS

It was shown that the decrease of the plasma density as a function of the distance to the nozzle in a low flow (500 sccm) argon plasma can be explained by diffusion away from the expansion axis. The decay length is 10 cm. In the case that nitrogen is seeded into the arc plasma the plasma density is lowered considerably due to charge exchange and dissociative recombination. At nitrogen flows larger than 10%, the plasma density at 15 cm from the nozzle is slightly less than \( 10^{17} \text{ m}^{-3} \) and does not decrease further with higher partial nitrogen flow. The dominant ion in this case is molecular ion \( \text{N}_2^+ \). Because of the low electron density at high percentages of nitrogen, the dissociative recombination becomes slow. The main loss process of ions in this case is diffusion away from the plasma axis. The effective decay length found is 9 cm.

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1See, for example, M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Material Processing (Wiley, New York, 1994).