ON THE DESCRIPTION OF AN INDUCTIVELY COUPLED ARGON PLASMA


* Eindhoven, University of Technology
  Physics Department, P.O.Box 513
  5600 MB Eindhoven, The Netherlands

** Philips Research Laboratories, P.O.Box 80.000
  5600 JA Eindhoven, The Netherlands

† present at Philips Light Division, P.O.Box 80.000
  5600 JA Eindhoven, The Netherlands

ABSTRACT

A model of an inductively coupled argon plasma (ICP), based on a characterisation with the electron density and an off equilibrium parameter, is shown to be in good agreement with measurements in the analytical or passive zone of the ICP, if an extra recombination path is assumed. The most probable candidate for this fast recombination path which is effective at low electron densities is dissociative recombination.

1. INTRODUCTION

Inductively Coupled Plasmas (ICP) are widely used for spectrochemical analysis [1, 2] and recently also as a plasma source for chemical synthesis and plasma spraying [3, 4]. We aim at the development of a comprehensive description of the relevant processes in an ICP. The understanding of the excitation-deexcitation mechanisms may lead to an improved design which shows better performance with regard to power consumption, gas flows and excitation-ionisation of injected species.

Many researchers report on the determination of temperatures in such discharges [5-7]. The diversity of values of temperatures, determined with different techniques, has led many authors to the conclusion that the ICP deviates from Local Thermal Equilibrium (LTE).

Recently, it was stated that the electron density rather than the electron temperature must be used to describe the discharge [8, 9]. From the measured value of \( n_e \), an LTE value of \( T_e \): \( T_{e_{LTE}} \) can be calculated which can be proven to be very close to the actual value. We will call this line of thought the "close to LTE" approach.

As \( T_{e_{LTE}} \) is close to \( T_e \), one can substitute the value of \( T_{e_{LTE}} \) in the transport terms of the balance equations without appreciable error. The terms accounting for ionisation and excitation are much more sensitive to \( T_e \), whence in these terms an extra parameter, which accounts for the small deviation from equilibrium, has to be introduced. In a previous paper [8] we proposed that the overpopulation (\( \delta b_1 \)) of the
neutral argon ground state would be a suitable measure of the deviation from LTE. In this paper the formulation of mass and energy balances in terms of the parameter $\delta b_1$ and $n_e$ (or $T_e_{LTE}$) is discussed. Model calculations will be compared with measured profiles (absolute intensity measurements). We shall show that a fast recombination mechanism must be operative in the analytical zone of an ICP.

2. DESCRIPTION OF THE DISCHARGE IN THE "CLOSE TO LTE" APPROACH

We shall divide the discharge in a so-called active zone (in the load coil), where ionisation prevails, and in a passive zone where the net Joule heating is zero and net recombination occurs [9]. These zones are schematically depicted in Fig. 1.

![Fig. 1: Sketch of an ICP-plasma torch; after Boumans. The active zone is indicated by heavy shading, the recombining zone by light shading.](image)

In the active zone, the Joule heating causes the discharge to be ionising. The neutral argon ground state (density $n_1$) is overpopulated with respect to the Saha value ($n_1,S$) [8].

The overpopulation ($\delta b_1$) is defined as:

$$\delta b_1 = b_1 - 1 = (n_1/n_1,S) - 1$$  \hspace{1cm} (1)

In the passive zone, where Joule heating is absent, the situation may be reversed, i.e. there will be an under-population of the argon neutral ground state.

We now are in the position to formulate the mass and energy balances in terms of the parameters $n_e$, $T_e$ and $\delta b_1$. Note, that at given pressure $T_e$ is determined by $n_e$ and $\delta b_1$ through the Saha equation and is not an independent parameter.
In the stationary state the mass balance reads:

$$-\nabla \cdot n_e \mathbf{w}_+ = -\nabla \cdot n_e \mathbf{w}_- = -S_e + R_e$$  \hspace{1cm} (2)

where $\mathbf{w}_+$, $\mathbf{w}_-$ are the average velocities of ions and electrons and $n_e (= n_i)$ is the electron density. By using the principle of detailed balancing the net source term $(S_e - R_e)$ can be written as:

$$S_e - R_e = K_1 \delta b_1 n_1 S n_e - n_e^2 k_+ \Lambda_+$$  \hspace{1cm} (3)

where $K_1$ is the total depopulation rate from the ground level, $k_+$ the radiative recombination rate and $\Lambda_+$ the associated escape factor. In an ICP the latter has a value between .3 and .6.

Fig. 2 depicts the quantities $K_1(T_e^{\text{LTE}})$ and $S_1(T_e^{\text{LTE}}) = \frac{n_1 S}{n_e^2} = \frac{g_1}{2g_+} (2\pi m_e kT_e^{\text{LTE}}/h^2) \exp\left(\frac{E_1^{\text{e}}}{kT_e^{\text{LTE}}}\right)$ where $g_1$ and $g_+$ are the statistical weights of the neutral and ion ground state and $E_1^{\text{e}}$ is the ionisation energy. The dependence of these quantities on $T_e$ is rather strong; fortunately, the product is only a weak function of $T_e$ (see fig. 2). Since the deviations from LTE have been taken into account by $\delta b_1$ we may also interchange $T_e$ and $T_e^{\text{LTE}}$ in the source term without making an appreciable error. We can rewrite eq. (3) in terms of $n_e$ and $\delta b_1$ (where $c_{\text{coll}} \equiv S_1 K_1$):

$$n_e^2 \left(c_{\text{coll}} \delta b_1 n_e - k_+ \Lambda_+\right) = S_e - R_e$$  \hspace{1cm} (4)

Fig. 2 : Total excitation rate, $K_1$, the Saha function, $S_1$, and the product $K_1 S_1 = c_{\text{coll}}$ as functions of the electron temperature $T_e$. Also the product of $n_e c_{\text{coll}}$ is given for LTE conditions.
This result can be used to describe the decay of \( n_e \) above the load coil (passive zone).

Eq. 4 also gives information on the minimum value of \( T_e \) in the active zone. If a length of 2 cm, a flow velocity of 20 m/s, and an initial (arbitrarily low) electron density of \( 10^{16} \) m\(^{-3} \) are assumed, an ionisation rate of \( 10^4 \) s\(^{-1} \) is necessary to reach an electron density of \( 10^{21} \) m\(^{-3} \). This requires the value of the electron temperature in the active zone to be larger than 11000 K.

The second governing equation for the description of the discharge is the energy balance, which can be written as:

\[
\begin{align*}
\frac{2}{n_e} [K_1 s_{12} \beta_{12} n_e (E_i^1 + 5/2 kT_e) + C_{rad}] + 5/2 n_1 w_{12} \nabla kT_e \\
+ \nabla \cdot (\varepsilon_h + \varepsilon_e) = j \cdot E
\end{align*}
\]

In this equation \( \varepsilon_h \), \( \varepsilon_e \) are the conductive terms for heavy particles and electrons respectively and \( j \cdot E \) is the Joule input in the discharge. \( C_{rad} \) accounts for all radiative losses except free bound radiation to the ground state (which is incorporated in the first term between the brackets; \( E_i^1 \) is the ionisation energy in Joule). From the estimated magnitude of the ionisation rate in the active zone \( 10^4 \) sec\(^{-1} \) it can be deduced that \( j \cdot E \) must have a minimum value of \( 10^8 \) W/m\(^3 \).

If we assume the active region of the discharge to be a hollow cylinder with an inner radius of 0.5 cm, a length of 2 cm and an outer radius of 1 cm the power dissipating volume would be 5 cm\(^3 \). With a power input of 1 kW in the discharge the power density in the hot annulus will be \( 2 \times 10^8 \) W m\(^{-3} \), which is in close agreement with our estimate of the minimum value of \( j \cdot E \).

In the passive zone the \( j \cdot E \) term equals zero, and heat conduction (\( \nabla \cdot (\varepsilon_h + \varepsilon_e) \)) and convection are the governing terms. One can show that the inelastic term (\( \varepsilon_i \) [\( \cdots \) ]), is small even if ionisation is completely absent (\( \delta b_1 = -1 \)). Hence the balance in the passive region is determined by conduction and convection.

4. EXPERIMENTAL PROCEDURE AND RESULTS

The electron density has been measured in two ways. First, from \( H_\beta \) broadening a value of \( n_e \) is derived which is close to the maximum value at a certain height in the discharge. Second, Abel inverted absolute intensity measurements of several ArI transitions, yield radial electron density profiles. To the latter measurements the "close to LTE" concept has been applied. Deviations of 10% in the actual electron temperature lead to similar errors in \( n_e \), which is acceptable.

Fig. 3 depicts the density profiles for three heights in the discharge. One observes a flattening of the profile and a decrease of the line density (i.e. the total number of electrons per unit length : \( \int n_e r dr d\phi \)).
Fig. 3: Measured and calculated radial profiles of the electron density, $n_e$ for three values of the height above the load coil. Model calculations are performed with and without dissociative recombination.

5. COMPARISON WITH MODEL CALCULATIONS

From the mass balance the following equation can be deduced if we ignore the source term:

$$w_z \frac{\delta n_e}{\delta z} = \frac{1}{r} \frac{\delta}{\delta r} \left( r D_a \frac{\delta n_e}{\delta r} \right)$$

In words, the convective contribution equals the diffusive flow. Fig. 4 depicts the measured line density together with the values derived from eq. (6); in the numerical code, the (negligible) source terms have been included, but these had only a small influence. Obviously, the line density decreases much faster than what would be expected on the basis of our model. Hence, another loss mechanisms must be operative. A possible candidate is dissociative recombination of molecular ions (e.g. Ar⁺ or ArH⁺). In fact there is mass spectroscopic evidence for the presence of such molecules in the discharge [10, 11]. Dissociative recombination leaves the heavy particle
in an excited state which has to decay radiatively for the mechanism to be operative. If the excited state does not decay radiatively before ionisation occurs, the mechanism would not be effective. Hence dissociative recombination is only effective at low densities \( n_e < 10^{20-21} \text{ m}^{-3} \). If we assume a rate constant of \( 1.25 \times 10^3 \text{ s}^{-1} \) for the recombination process, then the model calculations show good agreement with the observed values. Fig. 3 depicts the calculated radial profiles. It is observed that the description with the ambipolar diffusion coefficient is reasonable. It can also be concluded that in the outer regions of the discharge the recombination mechanism must be more effective. This could be caused by the lower electron density or by the mixing of argon with ambient gases \( (\text{H}_2, \text{O}_2) \).

From the measured \( n_e \) profiles we have also determined the radial profiles of \( T_e \), cf. fig. 5. As stated, the actual electron temperature, \( T_e \), may deviate a 10% from \( T_e \) as a consequence of the deviation from LTE. The evolution of the...
$T_e$ profile with increasing height, $h$, has been calculated with eq. (5). A second calculation has been performed with an additional heat loss term, $10^{-13} n_e$ [J/m³], to account for energy losses associated with the molecular ion formation and dissociative recombination process. It is concluded that within the limited accuracy of the $T_e$-profiles the results can be explained, even without the additional loss process. The mass balance provides a more sensitive way to follow the evolution of the plasma, which proves again that the electron density is a better parameter than $T_e$ to characterize the plasma.

6. CONCLUSIONS

A novel description of the ICP discharge is offered. Since the discharge is close to LTE, one can take as a reasonable value for $T_e$ the equilibrium temperature $T_e^{\text{LTE}}$. The latter can be derived from a measurement of the electron density. An extra parameter ($\delta b_1$) accounts for the non-LTE population of the ground level of the Ar neutral system.

Mass and energy balances are formulated explicitly in terms of the interdependent parameters $\delta b_1$, $n_e$ and $T_e$.

Comparison of the model predictions with electron density measurements leads to the conclusion that an extra loss mechanism must be operative. We propose dissociative recombination from molecular ions (e.g. $\text{Ar}_2^+$ or $\text{ArH}^+$) to be the dominant recombination path in the ICP.

It should be possible to control the rate of this process, e.g. by admitting a molecular gas in one of the gas flows of the ICP. By controlling the radial and axial electron density profiles in this way one might be able to improve analytical performance.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the continuing support of dr. W.F. Knippenberg.

REFERENCES