INFLUENCE OF GAS FLOW RATE AND PRESSURE UPON NON CHEMICAL-EQUILIBRIUM COMPOSITION IN N₂ THERMAL ICP

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Abstract

A two-dimensional hydrodynamic model for N₂ inductively coupled thermal plasma (ICTP) under high-pressure condition was developed using 18 reaction rates without the chemical equilibrium (CE) assumption. Using this model, the effects of the total gas flow rate and pressure upon the particle composition distribution in the ICTP were investigated.

1. Introduction

The inductively coupled thermal plasma (ICTP or thermal ICP) at the atmospheric pressure has been widely adopted in various technology fields such as materials processing, plasma waste destruction and plasma spraying because of its high temperature and high reaction activity [1]. Up to now, numerical modeling of the high pressure ICTP has been made to understand the flow and temperature fields in the ICTP on the assumption of local thermal equilibrium (LTE) [2]. However, further detailed understanding of the reactions and particle density distributions in the ICTP has greatly been required for advanced material processing without LTE assumption.

In the present paper, for the first step, a two-dimensional model for N₂ ICTP was developed considering the effect of reaction rates, convection and diffusion on the particle density distribution under non chemical equilibrium (non-CE) condition. First, a plasma model and the governing equations used were interpreted. Secondly, the gas flow and temperature fields and particle composition in the two-dimensional space were calculated by solving the mass conservation equation of each of particles in N₂ ICTP. Thirdly, by using the model, the influence of the total gas flow rate and the pressure upon the N atom distribution was investigated. Finally, the deviation from CE in the distribution of the particle composition was estimated by comparing CE calculation result.

2. Modelling of N₂ ICTP

2.1 Hypothesis

In the present calculation, it was assumed that N₂ ICTP is under the following conditions: (i) All the temperature for the translation, excitation, rotation and vibration motions of the electron and heavy particles are identical. (ii) The plasma has an axisymmetric structure. (iii) The optically thin assumption was established, and thus the effect of light
absorption is negligible. (iv) The gas flow is laminar. (v) Pressure in the ICTP is around the atmospheric pressure. (vi) There are only five particles \( \text{N}_2, \text{N}_2^+, \text{N}, \text{N}^+ \) and electron in \( \text{N}_2 \) ICTP.

2.2 Governing equations

On the basis of the assumption mentioned in the previous section, the ICTP behavior can be expressed by the following conservation equation of the dependent variable \( \phi \):

\[
\frac{\partial (\rho \phi)}{\partial t} + \nabla \cdot (\rho u \phi - \Gamma_\phi \nabla \phi) = S_\phi
\]

(1)

where \( u \) the vector of gas flow velocity, \( \rho \) the mass density, \( \Gamma_\phi \) diffusion coefficient of \( \phi \), \( S_\phi \) the source term of \( \phi \). For example, \( \phi=1 \) leads Eq.(1) to the mass conservation, \( \phi=u \) and \( v \) mean the momentum conservations, and \( \phi=h \), which is the enthalpy, corresponds to the energy conservation equation. For the conservation of chemical species, Eq.(1) can be rewritten by:

\[
\frac{\partial (\rho Y_j)}{\partial t} + \nabla \cdot (\rho u Y_j - \rho D_j \nabla Y_j) = m_j \sum_{\ell} (\beta_{j\ell}^r - \beta_{j\ell}^i) x_{k\ell} \prod_{k=1}^N n_k^i k_{j\ell}^i
\]

(2)

\( Y_j \), \( m_j \), \( n_i \) and \( D_j \) are the mass fraction, mass, number density and effective diffusion coefficient of species \( j \), respectively, \( \beta_{j\ell}^r \), \( \beta_{j\ell}^i \) stoichiometric number, \( \alpha_i \) reaction rate for reaction \( i \). Solving this equation enables us to obtain the particle density distribution considering diffusion, convection and reaction rates. The reaction rate \( \alpha_i \) for forward direction was given by Arrhenius' law \( \alpha_i = a_i T^b \exp(-c_i/T) \), where \( a_i \) and \( c_i \) are constants and \( T \) is the temperature. In this calculation, eighteen reactions including three body-recombination, association and ionization reactions and their backward reactions were taken into account.

The values of \( a_i \) and \( c_i \) were given by Dunn [3]. The reaction rates \( \alpha_i \) for the backward direction were calculated by the relationship \( \alpha_i = k(T) \alpha_i \) where \( K(T) \) is the equilibrium constant. Adding to the conservation equations, the equation of state, Maxwell equations for vector potential were simultaneously solved.

2.3 Thermodynamic and transport properties

Thermodynamic and transport properties of \( \text{N}_2 \) plasma were obtained by the following procedure. Mass density \( \rho \) was calculated by the equation of state at each of calculation step using calculated composition. Effective diffusion coefficient \( D_j \) for species \( j \) was given at each step by [4]

\[
D_j = \frac{1 - Y_j}{\sum_{k \neq j} x_k D_{jk}}
\]

(3)

where \( x_k \) is the molar fraction of species \( k \). The quantity \( D_{jk} \) is the diffusion coefficient between species \( k \) and \( j \), which can be written by
\[ D_{jk} = \frac{\kappa T}{p} \frac{1}{\Delta_{kj}^{(1)}} \]  

\[ \frac{1}{\Delta_{kj}^{(1)}} = \frac{3}{8} \pi \kappa T (m_k + m_j) \frac{1}{\pi \Omega_{kj}^{(1,1)}} \]  

where \( \pi \Omega_{kj}^{(1,1)} \) is the momentum transfer cross section of species \( k-j \), \( \kappa \) is the Boltzmann constant. The electrical conductivity \( \sigma \) was computed at each step by

\[ \sigma = \frac{e^2}{4 \pi \varepsilon_0 \kappa T} \sum_{j \neq e} n_j \Delta_{ej}^{(1)} \]  

where \( \varepsilon_0 \) is the permittivity of vacuum, and \( e \) is the electronic charge. The other properties such as the enthalpy \( h \), specific heat \( C_p \), thermal conductivity \( \lambda \), viscosity \( \eta \) and radiation loss \( P_{\text{rad}} \) were given by the equilibrium value as functions of temperature and pressure for simplicity.

### 2.4 Calculation space and boundary conditions

Figure 1 show the calculation space and boundary conditions. The calculation was performed in the \( r-z \) two-dimensional cylindrical space. This space was divided into 31 x 61 grids. The plasma torch has an 82 mm inner diameter and 161 mm length. A three-turn induction coil with a radius of 70mm is located at \( z=39, 59 \) and 79 mm. The cold N\(_2\) gas with the temperature 300 K is supplied along the inside quartz tube from the area \( (r,z) = (0,37)-(0,41) \) with a total gas flow rate \( Q_{\text{tot}} \) of 100-500 slpm. The input power into the plasma was set to 30 kW, and the frequency of the coil current was fixed to 1.67 MHz. The other boundary condition was set to the same manner of ref.[2]. The SIMPLE method [5] after Patankar was adopted to solve the governing equations described in the previous section.

\[ \lambda \frac{\partial T}{\partial r} = 0, \quad w = 0 \]  

\[ \frac{\partial \rho u}{\partial r} + \frac{\partial \rho v}{\partial z} = v = 0 \]  

\[ \frac{\partial h}{\partial r} = 0, \quad \frac{\partial h}{\partial z} = 0 \]  

\[ \Delta_{ab} = \Delta_{ba} = 0 \]  

Fig.1 Calculation space.

Fig.2 Gas flow and temperature field in N\(_2\) ICP at 0.1MPa.
3. Calculation results
3.1 Gas flow rate effect

Figures 2 (a), (b) and (c) indicate the stream lines and isothermal contours for N\textsubscript{2} ICTP at total gas flow rates $Q_{\text{tot}}$ of 100, 200 and 500 slpm, respectively. As seen in Fig.2 (a), the gas flow has a vortex around $(r,z)=(15,18)$. This is because the Lorentz force accelerates the gas flow in the radial direction around the second coil. The temperature has a local maximum value above 8000 K around $(r,z)=(12,60)$ where the electromagnetic field strength is largest. As $Q_{\text{tot}}$ increases, the gas flow is concentrated along the wall, while the flow through the high temperature area was decreased. On the other hand, the maximum temperature of the ICTP is a magnitude around 8000 K irrespective of $Q_{\text{tot}}$. Figures 3 (a), (b) and (c) show the N atom number density distribution for $Q_{\text{tot}}=100$, 200 and 500 slpm, respectively. The N atom has high density around $7 \times 10^{23}$ m\textsuperscript{-3} by the dissociation of N\textsubscript{2} due to the high temperature. This value hardly changes by increasing $Q_{\text{tot}}$. It is also important to know how the mass flow of active N atom can be taken from the torch outlet from the viewpoint of the material processing. Figure 4 indicates the mass flow of N atom. From this figure, the mass flow decreases rather with the increase of $Q_{\text{tot}}$. This arises mainly from the reduction of the gas flow through high temperature.

3.2 Pressure effect

Figures 5 (a), (b) and (c) demonstrate the stream lines and isothermal contours for a pressure $P$ of 0.05, 0.1 and 0.2 MPa, respectively. Decreasing $P$ raises the gas flow through the high temperature area, whilst declines the temperature because of the rising radiation loss. At $P=0.2$ MPa, the maximum temperature reaches around 7000 K. Figures 6 (a), (b) and (c) show the mass fraction of N atom.

At $P=0.05$ MPa, the maximum mass fraction of N atom has a high value of 0.7, which means the high dissociation degree. However, at $P=0.2$ MPa, that is only 0.2. This is attributed to the fact: increasing $P$ declines the temperature, and shifts the reaction equilibrium to the direction
of the association N+N->[N2] according to the Le Chatelier's law. Figure 7 shows the mass flow of N atom versus P. Rising P decreases the mass flow because of low dissociation degree.

4. Comparison with chemical equilibrium calculation

In the similar procedure, CE calculation was also made for comparison with non-CE calculation. Figure 8 shows the ratios $n_n/n_N^{eq}$ where $n_N^{eq}$ and $n_N$ are the N number densities obtained with or without CE assumption, respectively. As seen in this figure, especially near the wall, $n_N$ is over 10 times higher than $n_N^{eq}$. Figure 9 shows the radial distribution of particle composition around the second coil. It should be noted that radial distribution of particles, particularly N, is plainer than those obtained from CE calculation. This arises mainly from the following fact: the area near the wall has low temperatures around 300 K and thus extremely low reaction rate. In

Fig.6 Mass fraction of N atom in N2 ICTP at gas flow rate of 100 slpm.

Fig.5 Gas flow and temperature field in N2 ICTP at gas flow rate of 100 slpm.

Fig.7 Mass flow of N atom from N2 ICTP at gas flow rate of 100 slpm versus pressure.
addition, the gradient of the particle density is considerably high around this position. As a result, the large effect of the diffusion rather than the convection causes the plainer density distribution and then higher density near the wall than those from CE calculation.

5. Conclusions
A two-dimensional hydrodynamic model for N\textsubscript{2} inductively coupled thermal plasma (ICTP) under high-pressure condition was developed using reaction rates without the chemical equilibrium (CE) assumption. The effects of the total gas flow rate and pressure on the particle density distribution were investigated. The developed model will be useful for the detailed understanding in such the plasma processing fields.

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References