Numerical Modeling of Non-equilibrium Argon-Oxygen Induction Plasmas under Atmospheric Pressure

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Nobuhiko Atsuchi, Takayuki Watanabe.
Tokyo Institute of Technology, Research Laboratory for Nuclear Reactors, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550 Japan E-mail:watanabe@nr.titech.ac.jp

ABSTRACT

The purpose of this work is to develop chemically non-equilibrium modeling of induction thermal plasmas to investigate characteristics of thermal plasmas with chemically reactive gas. A non-equilibrium modeling of argon-oxygen induction thermal plasmas was performed without chemical equilibrium assumptions. The thermofluid and concentration fields were obtained by solving of two-dimensional modeling. Chemical reaction kinetics rates of the dissociation and recombination as well as the ionization were taken into account in this modeling. The transport properties were estimated using Chapman-Enskog method with higher order of Sonine polynomial expansion with collision integrals at each of the calculation step. As a result, the high-temperature region and particle distribution spread outside at the coil region in the chemically non-equilibrium model. Deviation from the Local Thermodynamic Equilibrium (LTE) assumption at the coil region is not negligible in argon-oxygen induction plasmas under atmospheric pressure.

KEYWORDS
Numerical modeling, Non-equilibrium, induction thermal plasma, argon-oxygen plasma

1. INTRODUCTION

The induction thermal plasma approach has been applied for many fields. Especially an attractive recent applications is treatment of harmful waste materials and recovery of useful material from waste (Sakano, et al., 1999, 2000). Another important application is production of high-quality and high-performance materials, such as synthesis of nanoparticles, deposition of thin films, and plasma spraying. Induction thermal plasmas offer unique advantages; these advantages include high enthalpy to enhance reaction kinetics, high chemical reactivity, oxidation and reduction atmospheres in accordance with required chemical reactions, and rapid quenching ($10^6$ K/s). These advantages increase the advances and demands in plasma chemistry and plasma processing. However, thermal plasmas have been simply used as high temperature source, because argon is typically used as the plasma gas. In certain applications, thermal plasmas with adding reactive gas are desirable to enhance the chemical reactivity of the plasma. Especially, plasmas under oxidation atmosphere are suitable for waste treatment.

Sophisticated modeling considering chemical reactions has been required for industrial application. However, thermal plasmas have been mainly treated as equilibrium conditions. The purpose of this work is to develop chemically non-equilibrium modeling of induction thermal plasmas. Some modeling works of induction thermal plasmas including chemical reaction kinetics have been proposed; Reactions between SiCl$_4$ and H$_2$ (Zhao, et al., 1990), dissociation of SiCl$_4$ (McKelliget, et al., 1988, 1990),
dissociation and recombination of finite-rate of diatomic gas in argon plasmas (Girshick, et al., 1990, 1993, Watanabe, et al., 1991, 1996, Desilets, et al., 1998, Sakano, et al., 1999, Tanaka and Sakuta, 2002), synthesis of ultra-fine powders through the decomposition of SiCl4 (Desilets, et al., 1997), ionization of argon (Nishiyama, et al., 1998). Recently, more sophisticated models are required, because estimation of thermodynamic and transport properties was oversimplified in previous works. The oversimplified estimation, such as use of equilibrium properties and use of the first-order approximation of the Chapman-Enskog method, would cause an error in the numerical results. In order to improve the accuracy of thermodynamic and transport properties, higher-order approximation of Chapman-Enskog method was used for estimation of the transport properties of oxygen plasmas (Watanabe and Sugimoto, 2004). They presented that the thermal conductivity and the electrical conductivity differ from that of the first-order approximation over 10000 K.

In this study, a non-equilibrium modeling of argon-oxygen induction thermal plasmas was developed without chemical equilibrium assumptions. This formulation including the finite-rates of dissociation and ionization is presented using higher-order approximation of Chapman-Enskog method for estimation of the transport properties. The non-equilibrium effect on argon-oxygen plasma characteristics will be discussed with comparison between the Chemically Non-equilibrium (CNE) and Chemically Equilibrium (CE) modeling. Characteristics of argon-oxygen plasmas will be also discussed.

2. NUMERICAL FORMULATION

2.1. Thermodynamic and transport properties

The transport properties of argon-oxygen plasmas were obtained from the Chapman-Enskog method. Up to now, numerical modeling of induction thermal plasmas has been performed with the first-order approximation of the Chapman-Enskog method for argon-oxygen plasmas because higher-order of Sonine polynomial expansion requires many kinds of collision integrals resulting in the complex formula (Hirschfelder, et al., 1964). The first-order approximation may cause an error especially for electrical conductivity and thermal conductivity of electron translational contribution at high
temperature. Therefore, higher-order approximation is used according to the required accuracy. The collision integrals were taken from Ref. (Mason, 1954, Monchick, 1959, Kihara, et al., 1960, Smith, et al., 1964, Devoto, 1967, Milloy, 1977, Aubreton, et al., 1986, Capitelli, et al., 2000) which provide intermolecular potential and fitting data. Detailed descriptions of the calculation method of viscosity, thermal conductivity and electrical conductivity are given by Ref. (Watanabe and Sugimoto, 2004). Figs. 1 and 2 demonstrate the temperature dependence of the viscosity and the thermal conductivity, respectively, for mixtures of argon and oxygen in seven different proportions. The thermal conductivity has high value where dissociation and ionization occur, and proportional to the composition of oxygen. In CNE model, the transport and thermodynamic properties are strongly related to the temperature and the composition of the plasma. Therefore, the transport and thermodynamic properties should be estimated considering the diffusion of species in the plasma at each calculation step until the convergence.

The thermodynamic properties, the enthalpy and the specific heat at constant pressure, were obtained from the equilibrium properties. This would be oversimplification, however, the exact estimation of the non-equilibrium thermodynamics properties is very complex with satisfying the self-consistent conditions. The radiative intensity of argon and oxygen was taken from Ref. (Krey, et al., 1970, Miller, et al., 1969).

2.2. Kinetic rate constants

From estimation of the equilibrium composition using FACT (Center for Research in Computational Thermochemistry), six species of O, O2, O+, Ar, Ar+, and e− were considered in this study.

The considered dissociation of oxygen is the following three kinds of three-body reactions.

\[
\begin{align*}
&O_2 + O_2 \leftrightarrow O + O + O_2 \\
&O_2 + O \leftrightarrow O + O + O \\
&O_2 + e^- \leftrightarrow O + O + e^-
\end{align*}
\]

(1) (2) (3)

The ionization of argon and oxygen atom was assumed to be the main ionization process in this study.

\[
\begin{align*}
&O + e^- \leftrightarrow O^+ + e^- + e^- \\
&Ar + e^- \leftrightarrow Ar^+ + e^- + e^-
\end{align*}
\]

(4) (5)

The dissociation and ionization rate of oxygen can be calculated with Eq. (6). The constants in Eq. (6) are presented in Table 1 taken from Ref. (Park, et al., 1989a, 1989b).

\[
k = a_i T^b \exp(-c_i / T)
\]

(6)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>(a_i)</th>
<th>(b_i)</th>
<th>(c_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(O_2 + O_2 \leftrightarrow O + O + O_2)</td>
<td>2×10^{21}</td>
<td>-1.5</td>
<td>59 500</td>
</tr>
<tr>
<td>2</td>
<td>(O_2 + O \leftrightarrow O + O + O)</td>
<td>1×10^{22}</td>
<td>-1.5</td>
<td>59 500</td>
</tr>
<tr>
<td>3</td>
<td>(O_2 + e^- \leftrightarrow O + O + e^-)</td>
<td>9.68×10^{22}</td>
<td>-2.0</td>
<td>59 500</td>
</tr>
<tr>
<td>4</td>
<td>(O + e^- \leftrightarrow O^+ + e^- + e^-)</td>
<td>3.91×10^{33}</td>
<td>-3.78</td>
<td>59 500</td>
</tr>
</tbody>
</table>
The ionization rate of argon can be calculated with Eq. (7). (Hoffert, et al., 1967)

\[
k = 3.75 \times 10^{-16} T^{1.5} \left( \frac{135300}{T + 2} \right) \exp \left( -\frac{135300}{T} \right)
\]  

(7)

The recombination rate constants were calculated using the equilibrium constant.

2.3. Model and assumptions

The geometry of calculation domain of induction plasma torch was shown in Fig. 3 and the operating conditions are summarized in Table 2. Plasma and sheath gas composition were mixtures of argon and oxygen (argon 50%). Carrier gas was not injected in this study. The plasma torch consists of a water-cooled quartz tube, and is surrounded by a water-cooled induction coil. The coil consists of three turns and applies the induction frequency at 4 MHz to the plasma. The actual power level was assumed to be 5 kW. Argon-oxygen mixture is injected as the plasma supporting gas (13 NL/min) and the sheath gas (20 NL/min). The sheath gas injected with swirl from outer slots protects the inner surface of the quartz tube.

The calculation are based on the following assumptions to derive the governing equations: (a) steady-state laminar flow; (b) axial symmetry; (c) optically thin; (d) negligible viscous dissipation in energy equation; (e) negligible displacement current in comparison with the conductive current; (f) negligible flow-induced electric field; (g) identical temperature of heavy particles and electrons.

Table 2 Torch characteristic dimensions and operational condition

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch power</td>
<td>5 kW</td>
</tr>
<tr>
<td>Work frequency</td>
<td>4 MHz</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>101.3 kPa</td>
</tr>
<tr>
<td>Coils radius</td>
<td>32 mm</td>
</tr>
<tr>
<td>Wall thickness of quartz tube</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Distance to frontal end of coil (L_1)</td>
<td>19 mm</td>
</tr>
<tr>
<td>Distance to rear end of coil (L_3)</td>
<td>65 mm</td>
</tr>
<tr>
<td>Insertion length of probe (L_2)</td>
<td>45 mm</td>
</tr>
<tr>
<td>Torch length (L_4)</td>
<td>190 mm</td>
</tr>
<tr>
<td>Outer radius of inner slot (r_1)</td>
<td>6.5 mm</td>
</tr>
<tr>
<td>Outer radius of outer slot (r_2)</td>
<td>21 mm</td>
</tr>
<tr>
<td>Inner radius of injection tube (r_3)</td>
<td>1 mm</td>
</tr>
<tr>
<td>Inner radius of quartz tube (r_4)</td>
<td>22.5 mm</td>
</tr>
<tr>
<td>Outer radius of injection tube (R_c)</td>
<td>4.5 mm</td>
</tr>
<tr>
<td>Flow rate of carrier gas (Q_1)</td>
<td>0 l/min</td>
</tr>
<tr>
<td>Flow rate of plasma gas (Q_2)</td>
<td>3 l/min</td>
</tr>
<tr>
<td>Flow rate of plasma gas (Q_3)</td>
<td>10 l/min</td>
</tr>
<tr>
<td>Flow rate of sheath gas (Q_4)</td>
<td>20 l/min</td>
</tr>
</tbody>
</table>

Fig. 3 Geometry of calculation domain of induction plasma torch
The effect of turbulence has been reported by (Chen and Boulos, 1994). They reported that most of the flow field in RF plasmas are laminar at the Reynolds number 625 at the gas inlet, while the turbulence effect is large at the Reynolds number 3125. As for the assumption (a), the flow field of the present RF plasmas can be considered as laminar, because the inlet Reynolds number is 350 in this study.

2.4. Governing equations and boundary conditions

The fields of flow, temperature and concentration in the induction thermal plasma were calculated by solving the two-dimensional continuity, momentum, energy and species conservation equations coupled with the Maxwell’s equations. Chemical reaction rates of the dissociation and recombination as well as the ionization were taken into account in this modeling.

Continuity:

\[ \nabla (\rho u) = 0 \]  

(8)

where \( \rho \) is the density and \( u \) is the velocity.

Momentum:

\[ \rho u \cdot \nabla u = -\nabla p + \nabla \tau + J \times B \]  

(9)

where \( p \) is the pressure and \( \tau \) is the viscous stress tensor. The last term in the right-hand side is due to the Lorentz force.

Energy:

\[ \rho u \cdot \nabla h = \nabla \cdot \left( \frac{\lambda}{C_p} \nabla h \right) + J \cdot E - q_r \]  

(10)

where \( h \) is the enthalpy, \( \lambda \) is the thermal conductivity, \( C_p \) is the specific heat at constant pressure, and \( q_r \) is the radiation loss per unit volume. The last term is due to the Joule heating.

Species:

\[ \rho u \cdot \nabla Y = \nabla (\rho D \nabla Y) + R_r \]  

(11)

where \( D \) is the diffusion coefficient, and \( R_r \) is the source term owing to the dissociation, recombination and ionization. In these equations, the condition current \( J \), the magnetic flux density \( B \), and the electric field intensity \( E \) were obtained from Maxwell’s equation.

The electromagnetic (EM) field in this study was analyzed on the basis of the two-dimensional modeling approach with the electric field intensity as the fundamental EM field variable (Chen and Pfender, 1991). Maxwell’s equations are expressed in terms of the electric field intensity as follows

\[ \nabla^2 E - \xi \sigma \frac{\partial E}{\partial t} = 0 \]  

(12)

where \( \xi \) is the magnetic permeability and \( \sigma \) is the electrical conductivity. The associated boundary
conditions for the EM fields are identical to Ref. (Chen and Pfender, 1991).

The boundary conditions along the centerline were set to insure axial symmetry. At the wall of the plasma torch, no slip conditions are maintained for the velocity, and the concentrations have zero gradient. The temperature at the inside wall of the plasma torch was calculated assuming the outside wall was maintained at 300 K by water cooling. The injection tube was assumed to be at 500 K. The outflow boundary conditions at the torch were assumed that gradient of the variables are zero. The sheath gas has swirl velocity component. Each gas stream has constant axial velocity with zero radial velocity having temperature at 300 K.

The CE model is based on thermal equilibrium composition, therefore species conservation equation is not calculated. Transport properties were estimated in the same way of CNE model.

2.5. Calculation procedure

The governing conservation equations were solved using SIMPLER (Semi-Implicit Method for Pressure Linked Equation Revised) algorithm (Patanker, 1980). The governing equations and the electric field intensity equation and the associated boundary conditions were discretized into finite difference from using the control-volume technique. Non-uniform grid points 30 by 30 were used for radial and axial directions, respectively. Grids are made finer close to the center and the coil region. Thermodynamic and transport properties were calculated from the temperature and compositions at each position in the calculation domain at each iteration step as described in Sec. 2.1.

3. CALCULATION RESULTS

The calculated isotherms, streamlines and concentration contours of oxygen atom are shown in Figs. 4-6, respectively. Computations were performed for argon-oxygen plasmas (argon 50%) operated under atmospheric pressure by comparing of the CNE and CE models.

![Fig. 4 Comparison of isotherms of chemical equilibrium and non-equilibrium models for an argon-oxygen plasma at 4 MHz and 5 kW. All isotherms are divided by 1000 K.](image)
Fig. 5 Comparison of streamlines of chemical equilibrium and non-equilibrium models for an argon-oxygen plasma at 4 MHz and 5 kW. All streamlines are divided by 0.1.

Fig. 6 Comparison of oxygen atom concentration contours of equilibrium and chemical non-equilibrium models for an argon-oxygen plasma at 4 MHz and 5 kW. All contours are divided by 0.05.
The calculated temperature fields were presented in Fig. 4. The high-temperature region in the torch in the argon-oxygen plasma is wide, therefore, the radial temperature gradient near the wall is steep in both CNE and CE model. This is attributed to oxygen dissociation around 4000 K, because higher heat capacity including the dissociation leads to a decrease in the temperature around the high-temperature region. From the comparison between the CNE and CE calculation, the CNE model indicates the temperature-region over 4000 K is radially wider than that of the CE model at the coil region, although the high-temperature region over 9000 K with the CNE model is smaller than the CE model. This is because the radial diffusion of the dissociated O atom, containing higher enthalpy.

The flow field with the CNE model in Fig. 5 exhibits the characteristic recirculation caused by the radial Lorentz force above the coil region. The radial expanded high-temperature region in the CNE calculation causes strong recirculation above the coil region.

The corresponding concentration profiles of oxygen atom in Fig. 6 show that high-concentration region of oxygen atom almost coincides with the high-temperature region. Effect of chemical reaction kinetics and diffusion on species distribution at the center and the rear end of the coil in an argon-oxygen plasma were presented in Fig. 7 and Fig. 8, respectively. Fig. 7 shows radial particle-distribution of the CNE model has a peak outside compared to the CE model. Fig. 8 shows the CNE models simulate wider radial distribution profiles than the CE model. That is, the existence region of O, O⁺ and Ar⁺ is expanded to the wall.
Effect of chemical reaction kinetics and diffusion on the degree of dissociation of oxygen was presented in Fig. 9. The complete dissociation region of the CNE model is also expanded to the wall compared to the CE model. The diffusion effect in the coil region is not negligible, however argon-oxygen induction plasmas can be partially treated as equilibrium. Strong non-equilibrium near the wall in nitrogen plasmas was reported by Ref. (Tanaka and Sakuta, 2002). Strong non-equilibrium in nitrogen plasmas results from higher nitrogen dissociation energy of 9.1 eV compared to oxygen of 5.1 eV. Therefore, oxygen can more easily dissociate than nitrogen, and the chemically non-equilibrium model are almost the same with those of fully equilibrium model at the high-temperature region of argon-oxygen plasmas.

4. CONCLUSIONS

Chemically non-equilibrium modeling for argon-oxygen induction thermal plasmas was developed considering effects of diffusion and finite reaction rates without LTE assumption.

The degrees of dissociation and ionization with non-equilibrium model are almost the same with those of fully equilibrium model at the high-temperature region of argon-oxygen plasmas. This indicates argon-oxygen induction plasmas can be partially treated as equilibrium, but the diffusion effect in the coil region is not negligible. The diffusion effect of the CNE model is as follows; Radial temperature-distribution is wider than that of the CE model at the coil region, and oxygen atoms exist in radially wider area with almost maximum-concentration of oxygen atom at the coil region. As a result, Radial particle-diffusion leads to the transport of higher enthalpy, then this causes temperature deviation between CNE and CE model.

Therefore, the present modeling including chemically non-equilibrium would give the guidance for the rational design of new material processing.
REFERENCES

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