The Induction Plasma Chemical Reactor: Part I. Equilibrium Model

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A mathematical model is presented for the numerical simulation of the flow, temperature, and concentration fields in an rf plasma chemical reactor. The simulation is performed assuming chemical equilibrium. The extent of validity of this assumption is discussed. The system considered is the reaction of SiCl_4 and NH_3 for the production of Si_3N_4 .

KEY WORDS: Induction plasma; modeling; chemical equilibrium; silicon nitride synthesis.

1. INTRODUCTION

RF induction plasma reactors offer a high enthalpy and pure medium free of electrode contamination for plasma chemistry. Due to these features, they have found a number of applications involving chemical synthesis. A better understanding of the chemical processes involved includes full modeling of the transport processes in these reactors. The modeling of fluid flow, temperature, and concentration fields in rf plasmas has greatly advanced in recent years. However, the models have been restricted to cases where no chemical synthesis occurred in the torch.

The present paper represents one step toward the full modeling of fundamental processes involved in the use of the induction plasma as a chemical reactor. The assumptions involved are essentially similar to those used in previous works,^(1,2) aiming at the calculation of the flow, temperature, and concentration fields in an inductively coupled rf plasma. These are:

—steady-state, laminar flow with negligible viscous dissipation,

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- local thermodynamic equilibrium,
- optically thin plasma,
- two-dimensional, rotationally symmetric flow, and temperature and concentration fields with one-dimensional electromagnetic fields.

In addition, three other assumptions were necessary in this work, these are:

- The Lewis number is equal to unity for all species.
- The diffusion coefficients for all species are equal and are calculated from the mixture thermal conductivity data by setting the Lewis number of the mixture equal to unity.
- The plasma is in chemical equilibrium.

The third assumption is particularly important since it implies that the reacting system involved has chemical reaction kinetics that are considerably faster than the associated heat and mass transfer processes.

While this assumption might not be true for many reacting systems, the principal contribution of this work lies in the development of the proposed approach as a first approximation to the considerably more complex case of chemical reactor modeling.

The latter case is fully dealt with in the second part of this paper where a comparison is made between the predictions of the equilibrium model and that of a model taking into account the kinetic rates of all of the chemical reactions involved. It should be underlined that the chemical equilibrium model offers a relatively simple means of studying the mixing in a plasma reactor.

The numerical simulation of rf plasma reactors has so far received little attention. Harada *et al.*⁽³⁾ performed a simple numerical simulation of the flow inside a reactor. Yoshida *et al.*⁽⁴⁾ calculated the thermodynamic equilibrium compositions for a Si_3N_4 plasma reactor. Zhao and Zhu⁽⁵⁾ also considered the flow in a Si_3N_4 plasma chemical reactor under typical operating conditions. This calculation, however, did not consider the chemical reactions. Oxidation of titanium chloride in a turbulent chemical reactor was considered by Zhao *et al.*⁽⁶⁾. The plasma torch was not, however, included in this model.

In this study a mathematical model is presented for the numerical simulation of the flow, temperature, and species concentrations fields in a radio-frequency plasma chemical reactor for the synthesis of Si_3N_4 ultrafine powder with argon as the plasma gas and SiCl_4 and NH_3 as reactants. The model is based on the rotationally symmetric continuity, momentum, energy, and species conservation equations along with the one-dimensional electromagnetic field equations. Particular attention is given to the determination of the species concentrations. Assuming chemical equilibrium, the species concentration is determined by minimizing the Gibbs free energy. The model

is applied to an rf plasma reactor with a small water-cooled stainless steel tube inserted into it. A study of the effects of the operating conditions on the flow, temperature, and species concentration fields is carried out.

2. GOVERNING EQUATIONS

A schematic of the torch geometry is shown in Fig. 1. The governing equations used in the model are the continuity, momentum, energy, and

Fig. 1. Schematic of the torch geometry and the system of coordinates.

species conservation (diffusion) equations along with the one-dimensional electromagnetic field equations. They are as follows:

Continuity:

$$\frac{\partial}{\partial z}(r\rho u) + \frac{\partial}{\partial r}(r\rho v) = 0 \quad (1)$$

Momentum:

$$\rho \left(u \frac{\partial u}{\partial z} + v \frac{\partial u}{\partial r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left[r\mu \left(\frac{\partial u}{\partial r} + \frac{\partial v}{\partial z} \right) \right] + \frac{\partial}{\partial z} \left(2\mu \frac{\partial u}{\partial z} \right) - \frac{\partial p}{\partial z} + \rho g \quad (2)$$

$$\begin{aligned} \rho \left(u \frac{\partial v}{\partial z} + v \frac{\partial v}{\partial r} - \frac{w^2}{r} \right) &= \frac{1}{r} \frac{\partial}{\partial r} \left[2r\mu \frac{\partial v}{\partial r} \right] - \frac{2\mu v}{r^2} \\ &\quad + \frac{\partial}{\partial z} \left[\mu \left(\frac{\partial u}{\partial r} + \frac{\partial u}{\partial z} \right) \right] - \frac{\partial p}{\partial r} + F_r \end{aligned} \quad (3)$$

$$\rho \left(u \frac{\partial w}{\partial z} + v \frac{\partial w}{\partial r} + \frac{vw}{r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left[r^2 \mu \frac{\partial}{\partial r} \left(\frac{w}{r} \right) \right] + \mu \frac{\partial}{\partial r} \left(\frac{w}{r} \right) + \frac{\partial}{\partial z} \left(\mu \frac{\partial w}{\partial r} \right) \quad (4)$$

where u , v , and w are the velocity components in the z , r , and θ directions, respectively, p is pressure, ρ and μ are density and viscosity, ρg is the gravity force, and F_r is the Lorentz electromagnetic force (see Eq. (17)) acting on the plasma gas in the discharge region.

Energy:

$$\rho \left(u \frac{\partial H}{\partial z} + v \frac{\partial H}{\partial r} \right) = \frac{1}{r} \left[\frac{\partial}{\partial z} \left(r \frac{k}{c_p} \frac{\partial H}{\partial z} \right) + \frac{\partial}{\partial r} \left(r \frac{k}{c_p} \frac{\partial H}{\partial r} \right) \right] + P - Q_r \quad (5)$$

where H is the total enthalpy, k the thermal conductivity, c_p the specific heat of the mixture at constant pressure, P the volumetric rate of heat generation due to Joule heating, and Q_r the radiative power loss per unit volume.

Diffusion:

$$\begin{aligned} \rho \left(u \frac{\partial C_i}{\partial z} + v \frac{\partial C_i}{\partial r} \right) &= \frac{1}{r} \left[\frac{\partial}{\partial z} \left(r\rho D_i \frac{\partial C_i}{\partial z} \right) + \frac{\partial}{\partial r} \left(r\rho D_i \frac{\partial C_i}{\partial r} \right) \right] + \dot{W}_i, \\ i &= 1, 2, \dots, N_e \end{aligned} \quad (6)$$

where C_i , ρD_i , $\dot{W}_i$, and N_e are the mass fraction, the diffusion coefficient, the mass rate of formation/destruction of species i , and the number of species, respectively. The assumption of equality of diffusion coefficients for all species, along with the chemical equilibrium assumption, enables us to considerably simplify the calculation of the concentration fields. Under these assumptions, it is more convenient to utilize the element mass fraction

K_j , rather than the species mass fraction C_i , since K_j is a conserved quantity. The quantity k_j is related to the species mass fraction C_i by

$$K_j = \sum_{i=1}^{Ne} \alpha_{ji} C_i, \quad j = 1, 2, \dots, M \quad (7)$$

where the coefficient α_{ji} is the mass of the j th element in one unit mass of the i th species, while M is the number of the elements. Since $\rho D_i = \rho D$, we can multiply Eq. (6) by α_{ji} and sum it over $i = 1 \rightarrow Ne$; the result is

$$\rho \left(u \frac{\partial K_j}{\partial z} + v \frac{\partial K_j}{\partial r} \right) = \frac{1}{r} \left[\frac{\partial}{\partial z} \left(r \rho D \frac{\partial K_j}{\partial z} \right) + \frac{\partial}{\partial r} \left(r \rho D \frac{\partial K_j}{\partial r} \right) \right] \quad (8)$$

Such a formulation eliminates the chemical source term $\dot{W}_i$. The calculation procedure is as follows. The element concentration field equations for Ar, Si, H, N, and Cl are solved along with the continuity, momentum, energy, and electromagnetic field equations. Once the element concentrations and the enthalpy have been obtained, the species concentrations are calculated. The equilibrium compositions are obtained using a penalty method for minimizing the Gibbs free energy G ,

$$G = \sum_{j=1}^{M_c} G_j^0 n_j + \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} n_{ij} [G_{ij}^0 + RT \ln \{\bar{f}_{ij}/f_{ij}^0\}] \quad (9)$$

under the following conditions:

i. *Chemical equilibrium:*

$$\sum_{j=1}^{M_c} A_{lj} n_j + \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} A_{li} n_{ij} = b_l, \quad l = 1, 2, \dots, N_e \quad (10)$$

ii. *Phase equilibrium:*

$$\sum_{j=1}^{N_p} n_{ij} = n_{it}, \quad i = 1, 2, \dots, N_c \quad (11)$$

ii. *Nonnegativity constraints:*

$$\begin{aligned} n_{ij} &\geq 0, & i = 1, 2, \dots, N_c, & j = 1, 2, \dots, N_p \\ n_j &\geq 0, & j = 1, 2, \dots, M_c \end{aligned} \quad (12)$$

where M_c represents the number of components present as condensed phases, N_p the number of phases, N_c the number of components in mixed phases, n_{ij} the number of moles of component i in phase j , n_j the total number of moles in phase j , G_j^0 and G_{ij}^0 the partial Gibbs energy at the reference state, R the gas constant, T the absolute temperature, $\bar{f}_{ij}$ the partial fugacity of species i in phase j , f_{ij}^0 the fugacity of species i in phase

$$\frac{dH_z}{dr} = -\sigma E_\theta \cos \chi \quad (14)$$

$$\frac{d\chi}{dr} = \frac{\sigma E_\theta}{H_z} \sin \chi - \frac{\mu_0 \omega H_z}{E_\theta} \cos \chi \quad (15)$$

where E_θ , H_z , and χ are the circumferential electric intensity, the axial magnetic field intensity, and the phase difference between the two fields, respectively, μ_0 the magnetic permeability of vacuum, and ω the oscillator angular frequency ($2\pi f$). The quantities F_r and P in Eqs. (3) and (5) can be written as

$$P = \sigma E_\theta^2 \quad (16)$$

$$F_r = \sigma \mu_0 E_\theta H_z \cos \chi \quad (17)$$

3. BOUNDARY CONDITIONS

The boundary conditions for Eqs. (1)–(5), (8), and (13)–(15) are as follows:

i. *Inlet conditions* ($z = 0$):

$$\begin{aligned} 0 < r < R_{11} \quad u &= Q_1 / \pi R_{11}^2 \\ v &= w = 0 \\ C_{\text{SiCl}_4} &= 1 \\ T &= 350 \text{ K} \end{aligned} \quad (18)$$

$$\begin{aligned} R_{12} < r < R_2 \quad u &= Q_2 / \pi (R_2^2 - R_{12}^2) \\ v &= 0 \\ w &= 25 \text{ m/s} \\ C_{\text{Ar}} &= 1 \\ T &= 350 \text{ K} \end{aligned} \quad (19)$$

$$\begin{aligned} R_2 < r < R_0 \quad u &= Q_3 / \pi (R_0^2 - R_2^2) \\ v &= w = 0 \\ C_{\text{Ar}} &= 1 \\ T &= 350 \text{ K} \end{aligned} \quad (20)$$

ii. *Centerline* ($r = 0$) *conditions*:

$$v = w = \partial u / \partial r = \partial H / \partial r = \partial C_i / \partial r = 0 \quad (21)$$

iii. *Conditions on the inner wall of the plasma confinement tube:*

$$u = v = w = \partial C_i / \partial n = 0 \quad (22)$$

$$k \partial T / \partial n = k_c (T - T_{w0}) / \delta_w \quad (23)$$

where $T_{w0} = 375$ K, is the external surface temperature of the quartz tube, and k and k_c are the thermal conductivity of the gas and the quartz tube, respectively. The wall temperature of the small stainless steel tube was assumed to be 350 K.

iv. *Side wall ($L_2 < z < L_2 + DH$) inlet conditions:*

$$u = 0$$

$$v = -Q_4 / (2\pi R_0 DH) \quad (24)$$

$$C_{\text{NH}_3} = 1.0$$

$$T = 350 \text{ K}$$

v. *Exit ($z = L_2 + L_3$) conditions:*

$$\partial u / \partial z = \partial v / \partial z = \partial w / \partial z = \partial C_i / \partial z = \partial H / \partial z = 0 \quad (25)$$

vi. *Boundary conditions for the electromagnetic field equations (13)–(15):* These are set at $r = 0$ and $0 < z < L_2$, which are

$$\chi = \pi/2, \quad d\chi/dr = 0$$

$$E_\theta = 0, \quad dE_\theta/dr = -\mu_0 \omega H_z/2 \quad (26)$$

$$H_z = H_c, \quad dH_z/dr = 0$$

here

$$H_c = \frac{NI}{2L_c} \left[\frac{L_0 + L_c - z}{[R_c^2 + (L_0 + L_c - z)^2]^{1/2}} + \frac{L_0 - z}{[R_c^2 + (L_0 - z)^2]^{1/2}} \right]$$

the electric current I is not specified, rather the total power input to the plasma P_0 is known. This is set as an integral-type boundary condition

$$P_t = \int_0^{L_2} \int_0^{R_0} 2\pi r P dr dz \quad (27)$$

and if $P_t \neq P_0$, a correction factor for the electric and magnetic fields is found, $\alpha_c = \sqrt{P_0/P_t}$; multiplying the electromagnetic fields by α_c ensures the condition for the specified dissipated power.

4. CALCULATION OF PHYSICAL PROPERTIES

The thermal conductivity, enthalpy, and viscosity for argon are obtained from Ref. 10. The radiation properties and electrical conductivity of atmospheric argon are from Refs. 11 and 12, respectively. It is assumed that in the discharge region, the plasma gas is composed of pure argon, and thus the radiative and electrical properties used are those of pure argon. The viscosity of NH_3 , HCl , N_2 , SiCl_4 , etc. are obtained from Ref. 13, and their conductivity and diffusion coefficients are calculated from viscosity data, assuming a Prandtl number equal to 1. The viscosity μ and thermal conductivity k of the gas mixture are calculated by a simple linear relation, i.e.,

$$\Phi_{\text{mixture}} = \sum_{i=1}^M X_i \Phi_i \quad (28)$$

here X_i is the mole fraction of species i in the gas mixture, and $\Phi = \mu$ or k . The enthalpy and specific heat of all species except Ar are from Ref. 7, and the enthalpy and specific heat of the mixture are calculated by Ref. 7,

$$\begin{aligned} H &= \sum_{i=1}^{Ne} C_i (h_i + h_i^D) \\ h_i &= \int_{298}^T c_p dT \\ c_p &= \sum_{i=1}^{Ne} C_i c_{pi} \end{aligned} \quad (29)$$

where h_i^D is the formation enthalpy of species i . The density ρ for the mixture is given by

$$\rho = (p/RT) / \left(\sum_{i=1}^{Ne} C_i Z_i / M_i \right) \quad (30)$$

here the summation extends over all gaseous species; M_i is the molecular weight of species i and Z_i is the compressibility.

5. SOLUTION PROCEDURE

The electromagnetic field equations (13)–(14) are solved using a fourth-order Runge–Kutta method. Equations (1)–(5) and (8) are solved by using the SIMPLER algorithm,⁽¹⁴⁾ which is a general algorithm for the solution of elliptic fluid flow, heat transfer and diffusion problems, and is based on a scheme developed by Patankar and Spalding. The details of the solution procedure are the same as in Ref. 1. The number of grid points used is 60×30 in the axial and radial directions, respectively.

Table I. Operating Parameters for the Eight Cases Considered

Case	P_0 (kW)	Q_1 (SiCl ₄) (liters/min STP)	Q_4 (NH ₃) (liters/min STP)
1	7.5	1.0	10.0
2	10.0	1.0	10.0
3	15.0	1.0	10.0
4	20.0	1.0	10.0
5	10.0	1.0	5.0
6	10.0	1.0	20.0
7	10.0	2.0	10.0
8	10.0	2.0	20.0

6. TORCH GEOMETRY AND OPERATING CONDITIONS

The torch geometry considered here is shown in Fig. 1. SiCl₄ is introduced inside the torch by the central flow Q_1 . The central tube is assumed to be water-cooled and is inserted down to the downstream end of the induction coil. NH₃ is introduced circumferentially and is depicted in Fig. 1 as Q_4 . Special attention is paid to the determination of the effects of variation in the power and SiCl₄ and NH₃ flow rates. As shown in Table I, eight cases were considered. The parameters not shown in Table I were kept constant throughout the computation and are given in Fig. 1. The operating pressure is atmospheric and argon is the predominant gas species.

7. RESULTS AND DISCUSSION

We regard case 2 as the basic case for our study. Figure 3 shows the isotherms, flow, field, and the swirl isocontours. The maximum temperature occurs in the discharge zone and is about 11,000 K. The temperature remains above 2000 K in regions close to the centerline. While the streamlines are essentially parallel throughout the reactor, three recirculation zones are noticed. The first one is caused by the electromagnetic pumping, the second one is due to the finite thickness of the central tube, while the third one is caused by the side injection of NH₃. Figure 3 also shows that the inlet swirl drops rather fast.

The concentration fields of different species are presented in Fig. 4. Due to the high temperatures close to the injection points of SiCl₄ and NH₃, they dissociate as soon as they are introduced into the reactor. It is also seen that the dissociation products mix rather well with the other species present. Si₃N₄(s) starts forming close to the injection point of NH₃, indicating fast radial diffusion of Si. The maximum concentration Si₃N₄(s)

Fig. 3. Flow and temperature fields, giving the swirl velocity isocontours (left), streamlines (center), and temperature isotherms (right) for a plasma operating at $P_0 = 10.0$ kW, $Q_1 = 1.0$ liters/min (SiCl_4), and $Q_2 = 10.0$ liters/min (NH_3).

occurs at regions where the temperatures favor the formation of such species. These are shown to be close to the wall and also close to the centerline in the downstream section of the reactor. We emphasize that these results are obtained under the assumption of chemical equilibrium. At higher temperatures, this assumption is more likely to be true. Therefore, one could think that since the reactants are introduced in the high-temperature regimes, their dissociation may occur close to equilibrium, and the predicted concentrations could be realistic, whereas at lower temperatures this might not be the case.

Figures 5 and 6 show the effect of power on the centerline temperature and velocity profile. As expected, the higher powers correspond to higher temperatures and also higher velocities. The latter will cause a reduction in the species residence time in the reactor.

Fig. 4. Concentration fields for the same conditions as given in Fig. 3.

Fig. 5. Effect of power on the axial temperature profiles along the centerline of the reactor, cases (1-4).

The effect of the power on the centerline concentration profiles of SiCl_4 , Si_3N_4 , $\text{Si}(\text{v})$, and $\text{Si}(\text{l})$ is shown in Figs. 7 and 8. As shown, the heating up and dissociation of SiCl_4 is extremely fast for all power levels considered, and Si_3N_4 forms earlier in the torch for lower powers. These results can easily be explained in terms of the equilibrium concentration profiles of Fig. 2 and the axial temperature variation of Fig. 5.

Figures 9 and 10 show the centerline temperature and velocity profiles for cases 5-8 (Table I). In these cases, the input power is kept constant at 10 kW, while the flow rate of the reactants is varied. The maximum temperature difference occurs between cases (5) and (8), where case (8) corresponds to the maximum reactant flow rate and thus lower temperatures. On the other hand, the maximum centerline velocity difference is between cases (6) and (7) (Fig. 10). Figures 11 and 12 show the concentration along the centerline for SiCl_4 , Si_3N_4 , $\text{Si}(\text{v})$, and $\text{Si}(\text{l})$ for these four cases. As expected, case (8) has the highest yield of Si_3N_4 .

8. SUMMARY AND CONCLUSIONS

A mathematical model is proposed for the calculation of the flow, temperature, concentration, and electromagnetic fields in an rf induction

Fig. 6. Effect of power on the axial velocity profile along the centerline of the reactor, cases (1-4).

Fig. 7. Centerline concentration profiles for SiCl_4 and Si_3N_4 , cases (1-4).

Fig. 8. Centerline concentration profiles for $\text{Si}(\text{v})$ and $\text{Si}(\text{l})$, cases (1-4).

Fig. 9. Effect of the reactant flow rates on the centerline temperature profile, cases (5-8).

Fig. 10. Effect of the reactant flow rates on the centerline velocity profile, cases (5-8).

Fig. 11. Centerline concentration profiles for SiCl_4 and Si_3N_4 , cases (5-8).

Fig. 12. Centerline concentration profiles for $\text{Si}(\text{v})$ and $\text{Si}(\text{l})$, cases (5-8).

plasma reactor. This model should be considered as a preliminary step toward the full modeling of such reactors. In the next stage of this work, the assumption of chemical equilibrium will be removed. It is understood that under typical conditions in these reactors, this assumption will not hold in the low-temperature regions.

The results of this study indicate that for the torch geometry considered here, the SiCl_4 and NH_3 heats up and dissociates rapidly once they are introduced inside the torch. This is due to the presence of high temperatures close to the injection points. The effect of variations of the input power and the flow rates of SiCl_4 and NH_3 is also discussed.

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