Parametric study of thermo-flow fields in an inductively coupled RF plasma processing system for the production of single-walled carbon nanotubes

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Abstract:
In the present study, CFD simulations are carried out to investigate the effect of thermal conductivity of the reaction chamber’s graphite liners on the flow and the temperature fields in the induction thermal plasma processing system for the continuous production of single-walled carbon nanotubes (SWCNTs). The thermal conductivity of ten different graphite liners were measured at different temperatures and the thermal conductivity profiles were plotted versus temperature. These temperature-dependent profiles were then implemented into the CFD code and the temperature and flow fields were compared to our previous numerical simulations [1,4]. The results indicated that the thermal conductivity profiles of the graphite liners imposed slight variations on the flow and the temperature fields inside the reaction chamber.

Keywords: radio frequency (RF) induction thermal plasma, numerical modeling. Single-walled carbon nanotubes (SWCNTs)

1. Introduction
The novel synthesis of single-walled carbon nanotubes (SWCNTs) by radio-frequency (RF) induction thermal plasma is a promising process for large scale production of SWCNT for industrial and commercial applications. In this method, Fig.1, a mixture of carbon black and metal catalyst fine powders is introduced into the RF plasma torch. The powders are vaporized by the high temperature of argon-helium RF plasma at soft vacuum. The vapors enter the reaction chamber and under a controlled temperature gradient, carbon-metal clusters are formed which become potential sites for the nucleation and growth of SWCNTs. The reaction chamber includes a graphite liner, and a thermal insulator, which are employed for an active control over maximum achievable temperature, background temperature, and cooling rate. The high background temperatures and controlled cooling rates in the reaction chamber are very important for the synthesis of SWCNT and the presence of graphite liners in the reactor helps to produce and maintain such environment. In spite of the important role of the graphite liners, their effects on the thermo-flow field in the system are still poorly understood.

In this work, the RF plasma and the thermo-fluid equations were solved to model the plasma, temperature and flow fields in the RF plasma torch and the reactor. The temperature-dependent diffusivity profiles of ten different graphite liners, measured from the experimental instrument (LFA 457), were used to calculate the liner’s thermal conductivity as the functions of temperature. These data were then implemented into our 2D axisymmetric numerical model and the results were compared to our earlier simulations [1]. The changes in the temperature and flow field in the reaction chamber by varying the thermal conductivity profiles have been discussed.
2. Model Description

Plasma Model

A 2-dimensional, axi-symmetric model for simulations of plasma generation by an RF induction plasma torch has been developed based on the procedure described by Mostaghimi et al. [2] and Proulx et al. [3]. The following assumptions were considered in modeling the induction plasma: (i) two-dimensional, axisymmetric and steady-state flow; (ii) quasi-neutral and optically thin plasma in a local thermodynamic equilibrium (LTE) state; (iii) negligible displacement current and viscous dissipation; (iv) planar coils; (v) turbulent flow; (vi) consideration of the momentum and energy source terms due to the particle loading. Based on these assumptions, the plasma equations are described by steady-state conservation equations for the transport of mass, momentum, energy, and concentration of species along with the k-ε turbulence model coupled with electromagnetic field equations.

Plasma-Particle Model

In the induction thermal plasma process, the carbon precursor material is directly evaporated in the plasma plume, and therefore, the yield rate of SWCNT in the reactor can be affected by the evaporation efficiency of the injected particles. From previous studies [1,4] following assumptions were considered: (i) spherical particle; (ii) uniform temperature distribution within a particle; (iii) particle sizes were assumed to follow the Rosin–Rammler distribution function.

The Lagrangian approach was employed to predict particle trajectories within the plasma region as explained in [1].

Computational Domain and Operating condition

The geometry and operating conditions considered in the present work is shown in Fig. 2, and Table 1, respectively. The 2-D numerical simulations based on the above governing equations and assumptions were performed by the commercial code FLUENT [5]. The detailed dimensions, boundary conditions of the system, and the numerical schemes can be found in the previous studies [1,4].

<table>
<thead>
<tr>
<th>Net plasma power (kW)</th>
<th>Pressure (kPa)</th>
<th>Carrier gas (slpm)</th>
<th>Central gas (slpm)</th>
<th>Sheath gas (slpm)</th>
<th>Feed rate(g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>66</td>
<td>5 (Ar)</td>
<td>25 (Ar)</td>
<td>120 (He)</td>
<td>1.5 (CB/Ni-98%/2%wt)</td>
</tr>
</tbody>
</table>

Table 1, A typical operating condition employed in this study

All graphite liner samples were analyzed under the similar experimental condition and the diffusivity measurements were conducted by LFA 457 over the temperature range of about 150°C-1050°C. The data were then used to calculate the thermal conductivity profiles of the graphite liners. Fig. 3 shows the thermal conductivity profiles calculated for ten different graphite liner samples vs. temperature, used in our simulations. The graph of each graphite liner has been normalized by its thermal conductivity value at 150°C. For comparison, our previous simulation’s profile was plotted in red color.
3. Results and Discussion

Fig 4 compares the temperature and the carbon vapor concentration distributions of our current and previous simulation results [1,4]. In Fig. 4a, both simulation results presented the off-axis profiles of the high temperature zones, which mainly occurred inside the torch, as of the result of the skin depth effects. The injected powders cooled down the central region of the plasma jet close to the injection probe. From the entrance of the reaction chamber, the off-axis high temperature zone starts to vanish by the mixing and diffusion of the vapors in the reaction chamber. The presence of the graphite liners helps to preserve the temperatures of above 4000K within the first 50 cm of the reactor. In both cases, in the second half of the reactor, the zone with no graphite liners, the temperatures decrease rapidly to approximately 1,000 K due to the heat exchange with the water-cooled reactor walls. Fig. 4a illustrates that current simulations with the new temperature-dependent thermal conductivity profiles predicted much larger volume of the high temperature zone. This is mainly due to the larger values of thermal conductivity at higher temperatures in the previous model, which leads to more intensive heat exchange with the surroundings.

The axial temperature, velocity and the carbon vapor concentration values along the centerline for different graphite samples were also presented in Fig. 5. From Fig. 5a, the current simulations predicted that the maximum temperature along the centerline occurred near 0.337m with the value of 5500K which is about 11% higher than the maximum centerline temperature obtained from the previous simulations. The previous studies [6] suggested that the formation of SWCNTs is enhanced in the temperature range between 1800-2100 K. This can be explained by the formation of the metal catalyst of nickel in the liquid phase which is important in the nucleation and growth of SWCNTs. From Fig. 5a, the new thermal conductivity profiles indicated the longer centerline temperature profile within the 1800-2100K temperature regime, which is essential for the effective growth of SWCNTs.

The effect of the thermal conductivity profiles on the axial velocity has also been analyzed and the results are shown in Fig. 5b. The gas velocity controls the residence times of the feedstock material and the reaction products inside the reactor. In the reactor, in the high temperature region (>4000K), higher axial velocity facilitates the rapid transfer of the carbon vapors from the hot zone UV irradiation [7]. Fig. 5b demonstrated the relatively similar axial velocity profiles of our current and previous simulations. There is a minor difference between the profiles in the hot region where the previous simulation exhibited a slightly higher axial velocity.

Figures 4b and 5c show the distributions of the carbon mole fractions and the axial profile along the centerline inside the reactor system, respectively. The figures show a more rapid generation of the particle vapors by the new thermal conductivity profiles. In the new cases, the axial profiles of the carbon vapor reach their maximum values close to the entrance of the reaction zone (Z ~ 0.18-0.19 m),
while the generation of the carbon vapor in the previous simulation started slightly further down the axial position of \( Z = 0.2 - 0.21 \) m. The higher evaporation rate in the current simulations can be explained by the fast temperature rise at the entrance of the reactor.

4. Conclusion

The RF induction plasma technology has been extensively used in synthesis of SWCNTs at industrial scales. Although the presence of the graphite liners in the RF plasma system is essential to produce SWCNTs, their main role and effects on the flow field has been poorly understood. In this work, the empirical measurements of the temperature-dependent thermal conductivity for ten different graphite liners were implemented into our 2-D numerical simulations to study the effects of the liners on the thermo-fluid field and the results were compared with those from our previous simulations. Contrary to the numerical thermal conductivity used in our previous studies, the more accurate empirical thermal conductivity rates showed longer temperature contours along the centerline of the plasma jet. This behavior may be favorable for the formation of SWCNTs.

5. Acknowledgement

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References


