Investigation of silicon nanoparticles synthesis in the downstream region of a DC non-transferred arc plasma torch by three-dimensional modelling

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Abstract: In this paper, we report on modelling of silicon nanoparticle synthesis in a DC non-transferred arc torch coupled with a conical reaction chamber. A computational approach is adopted to describe plasma thermo-fluid dynamics, electromagnetic field, precursor trajectories and thermal histories, and nanoparticle nucleation and growth, being the latter modelled using the method of moments.

Keywords: Thermal plasmas, Nanoparticle synthesis, Modelling

1. Introduction

DC non-transferred arc plasmas are commonly used for nanoparticle production at commercial and laboratory scale. Plasma high temperature (around 10000 K) offers the possibility to vaporize a wide range of different precursors and to obtain very high cooling rates for the production of metal, oxide or composite nanoparticles. The typical approach in DC non-transferred arc torches is to inject solid, liquid or gaseous precursor materials in the tail of the plasma discharge, resulting in the formation of a vapour that is transported in a reaction chamber downstream the plasma torch. Nanoparticle nucleation occurs when vapour reaches the supersaturated state in colder regions in the reaction chamber, where additional quenching gas can be injected to control particle formation and to prevent nanoparticle deposition on the walls.

In order to optimize the plasma synthesis process for a specific material, a series of issues must be addressed, such as: reduction of the fraction of non-vaporized precursor, reduction of precursor and nanoparticle deposition on the walls, identification of suitable quench injection conditions to obtain targeted nanoparticle.

In this work, a 3D model of the DC non-transferred arc synthesis of Si nanoparticles has been developed that includes plasma flow in a conical reaction chamber with annular inlets for quench gases, trajectory and thermal history of radially injected solid Si precursor, and transport of the nucleated nanoparticles using the Method of Moments (MOM). Plasma flow and temperature field at the chamber inlet are obtained by means of the Elenbaas-Heller equations for a 250 kW plasma column of Ar-H₂ gas mixture, to simulate the outflow of a DC non-transferred torch without including it in the domain. Computations have been done for different precursor size distributions and for different quench injection conditions. Variation on the precursors particle size distribution is shown to have an important effect on the amount of non-vaporized precursors and vapour concentration field, whereas nanoparticle deposition on the reactor walls depends strongly on the flow patterns generated by the quenching gases. Optimal operating conditions can be identified that allow maximizing nanoparticle production while reducing material deposition on chamber walls.

2. Modelling approach

A 3-D model for synthesis of silicon nanoparticles in the reaction chamber downstream a DC non-transferred arc torch has been implemented in the ANSYS FLUENT® environment. The model include the following hypothesis:

- Plasma is in local thermodynamic equilibrium (LTE);
- Combined diffusion approach of Murphy is used to model the diffusion in a mixture of argon and hydrogen;
- Turbulent effects are taken in account through standard k-ε model;
- Plasma is optically thin and radiative losses are taken in account considering only the presence of argon in the mixture; resonance lines are neglected in the computation of radiative losses;
- Composition is computed taking in account six species: Ar, Ar⁺, H₂, H, H⁺ and electrons.

Mass, momentum and energy equations are solved as in [4] taking into account energy losses due to radiation and plasma-precursor interaction. Precursor trajectory and thermal histories have been modelled using a Lagrangian approach, with the final aim of calculating precursor evaporation. The generated precursor vapours have been tracked by means of an additional an advection-diffusion equation for the vapour mass fraction, considering no influence of the vapours on the plasma properties. The nucleation, growth and transport of nanoparticles have
been modelled using the method of moments (MOM) methods for the solution of the General Dynamics Equation (GDE) for aerosols.

In MOM, the aerosol GDE is mathematically reformulated in order to obtain a system of equations that is easier to solve; the first three moments of the nanoparticle size distribution function are handled. The zero-th moment represents the total concentration of the generated nanoparticles, while the first moment corresponds to their total volume. Transport equations for the first three moments are solved, assuming a log-normal shape of the particle size distribution and including turbulent effects in the diffusion term of transport equations, as done in [4,5].

The 3-D domain analysed in this work include a conical reaction chamber with a single carrier gas injection point for precursor injection and with an annular quench gas inlet, schematically shown in Fig. 1. Argon gas is supplied to the reaction chamber as quench gas and carrier gas for precursor.

Boundary conditions for temperature at reaction chamber inlet, which correspond to the DC torch outlet, have been calculated solving the 1-D Elenbaas-Heller equations

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \left( \frac{h}{C_p} \sigma E_z^2 - P_r \right) \right) = 0
\]

where \( h \) is the enthalpy, \( \kappa \) is the thermal conductivity, \( C_p \) is the specific heat, \( \sigma \) is the electrical conductivity, \( E_z \) is the axial electric field and \( P_r \) represents the radiation energy losses. The electric field in the torch has been set in order to obtain a total current of 500 A.

Velocity inlet boundary condition has been calculated solving the 1-D Navier-Stokes equation with a fixed axial pressure drop to obtain a total flow rate of 1000 slpm. The computed power at DC torch outlet is 250 kW.

A no-slip boundary condition is applied on all the internal walls, while a 300 K temperature has been fixed at the internal walls of the chamber.

The chamber operating pressure has been fixed at 100 kPa. The precursor is set to be solid micrometric silicon characterized by a particle size distribution with mean diameter equal to 15 \( \mu \)m and 30 \( \mu \)m and by a feed rate equal to 20 g/min. Other chamber parameters are listed in table 1.

Table 1. Reaction chamber operating conditions for different cases

<table>
<thead>
<tr>
<th>Case</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor feed rate [g/min]</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Carrier gas flow rate [slpm]</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Precursor mean diameter [( \mu )m]</td>
<td>15</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Quench gas flow rate [m³/h]</td>
<td>0</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

3. Results

The temperature field in the reaction chamber for different cases has been reported in figure 1. For case 1, which has no quench gas injection, a strongly deflected plasma jet has been obtained, whereas for the cases with quench gas injection the temperature field is almost axi-symmetrical.

![Fig. 1 Schematic of the computational domain (in mm).](image)

![Fig. 2 Temperature field on the plane yz for different cases](image)

As can be seen in figure 3, the precursor injected laterally from a single point is dragged by the plasma flow towards the outlet of the reaction chamber; precursor
particles are heated by the plasma and partially evaporated: particles smaller than 10 μm are fully evaporated, whereas particles with higher diameter reach the chamber outlet before complete evaporation. For this reason, cases with smaller precursor mean diameter (cases 1 and 2) result in higher evaporation rate (see table 2). Precursor deposition on the walls shows similar values for all the considered cases (1-2 g/min) and it is mainly due to particles with diameter lower than 10 μm that are deflected towards reaction chamber walls by turbulent eddies. The evaporation of the precursor occurs mainly close to the precursor injection point, as can be seen from the iso-surfaces of vapour concentration at high values (10-30 μg/cm³) reported in figures 3.

Table 2. Precursor, vapour and nanoparticle mass balance [g/min]

<table>
<thead>
<tr>
<th>Case</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor feed rate</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Precursor evaporation rate</td>
<td>15</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>Precursor deposition on the walls</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Precursor flow rate at outlet</td>
<td>4</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Vapour flow rate at outlet</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Nanoparticle production rate</td>
<td>9</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>Nanoparticle deposition on the walls</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Nanoparticle flow rate at outlet</td>
<td>6</td>
<td>9</td>
<td>7</td>
</tr>
</tbody>
</table>

The generated Si vapour is subsequently transported downstream by the convective effect of the plasma flow and radially by turbulent diffusion. When vapour reaches regions with temperature lower than about 3000 K, nucleation of nanoparticles occurs, as can be seen from nanoparticle concentration iso-surfaces reported in figure 3.

![Fig. 3 Precursor trajectory and diameter, vapour concentration iso-surfaces and nanoparticle mass concentration iso-surfaces for different cases.](image)

The vapour conversion to nanoparticles is highest for case 2 with quench gas injection and smaller precursor (see table 2). For case 1 with no quench gas most of the vapour is flowing at the chamber outlet before conversion to nanoparticles. In case 3, the lower evaporation due to
bigger precursor size leads to a lower nanoparticle production rate, but the ratio between the vapour generated and the nanoparticle production rate (72%) is higher than for case 1 (60%). The higher vapour to nanoparticle conversion rate of cases 2 and 3 is mainly due to the quenching of the plasma plume. The vapour concentration at outlet for case 1 without quench gas injection is higher than for the cases with quench gas injection (see figure 4).

Nanoparticle conversion occurs in the fringes of the plasma plume, as shown in figure 5, where the field of vapour consumption rate has been reported. In case 1, the plume is deflected and the nucleation occurs mostly on the side of precursor injection. For cases 2 and 3, vapour is consumed all around the plasma plume but maximum values for vapour consumption rate are located on the side of precursor injection. As a consequence, the nanoparticle concentration has a maximum which is off-axis and on the side of precursor injection for all the cases investigated (see figure 6). Nanoparticle deposition rate on the chamber wall is almost the same for the cases considered (see table 2), whereas the same trend reported for nanoparticle production has been obtained for nanoparticle flow rate at outlet.

![Fig. 5 Rate of vapour consumption due to nucleation and condensation processes on the plane yz for different cases.](image)

![Fig. 6 Nanoparticle mass concentration field on the plane yz for different cases.](image)

4. Conclusions

A model for the silicon nanoparticle synthesis in the downstream region of a DC non-transferred arc torch has been developed that takes into account plasma thermo-fluid dynamics, precursor evaporation and nanoparticle nucleation and growth. This model can be used to compare different system geometries and operating conditions with a design-oriented approach.

References