Finite element simulation of the effects of process parameters on deposition uniformity of chemical-vapor-deposited silicon carbide

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ARTICLE INFO

ABSTRACT

A two-dimensional model was developed to simulate chemical vapor deposition process for preparing SiC coating by MTS + H_2 system in a vertical hot-wall reactor. The effects of process parameters, including deposition temperature, the flux of mixed gases, the ratio of H_2 and Ar, and the volume ratio of MTS and mixed gases, on deposition uniformity of SiC coating were calculated by finite-element method. The CVD process was optimized by an orthogonal $L_9(3)^4$ test to deposit uniform SiC coating. The results show that the deposition uniformity of SiC is influenced greatly by the deposition temperature and the ratio of H_2 and Ar, and little by the flux of mixed gases and the volume ratio of MTS and mixed gases. The optimal deposition uniformity of SiC can be obtained under the operating condition as follows: deposition temperature 900 °C, the flux of mixed gases 0.6 l/min, H_2: Ar = 1:0, and the volume ratio of MTS and mixed gases 1:10. Part of calculated results is validated by corresponding experimental data, which implies that this model is valid and reasonable to characterize CVD process of SiC coating.

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1. Introduction

SiC is the preferred and foundational anti-oxidation material for advanced C/C and C/SiC composites due to its excellent performance at high temperatures and good oxidation resistance [1–4]. Chemical vapor deposition (CVD) process is widely used to fabricate SiC coating [5–8]. Since a number of large and complex applications are expected to be coated simultaneously in a CVD reactor, deposition uniformity is seemed to be very important for the preparation of high-quality coating. It has been proved that coating thickness has obvious influence on its oxidation protective ability for carbon based composites [1,9,10]. The coating with too big or too small thickness will degrade its oxidation resistance. In addition, the well-controlled uniformity will reduce cost and duration of the applications. Therefore, a systematic study on deposition uniformity of SiC coating by CVD process is necessary.

Besides elaborate experimental works, modeling and numerical simulations have been regarded as powerful tools for deep understanding of CVD process. A number of works on modeling of CVD process were reported [11–20]. Most of these works deal with the effects of process parameters on the growth rate of deposition products. However, deposition uniformity is seldom concerned.

In this paper, a two-dimensional model was implemented by the finite-element method to simulate numerically CVD process of SiC coating in a vertical reactor. The effects of process parameters on deposition uniformity of CVD-SiC were calculated and analyzed, and the CVD process was optimized by an orthogonal $L_9(3)^4$ test to deposit uniform SiC coating. The corresponding experiments were carried out to validate the model.

2. Model development

In this work, MTS as precursor material, hydrogen and argon as carrier gas and diluting gas are pumped into CVD reactor, and deposition of SiC occurs on the surface of C/C composites. In fact, SiC deposition process is very complex with gas phase reactions resulting in the formation of many Si- and C-bearing gas species. Since a sufficiently thorough knowledge of MTS pyrolysis chemistry is lacking, the overall chemical reaction is taken:

$$Cl_3SiCH_3 \rightarrow SiC + 3HCl \tag{1}$$

The reactor in the model is a vertical hot-wall reactor [21]. The structure of the reactor means that it can be reduced from a 3D model to a 2D axisymmetric problem. The modeling domain is

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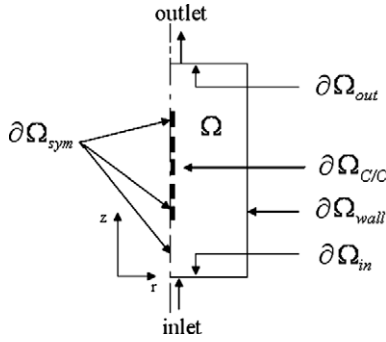*E-mail address:* lihejun@nwpu.edu.cn (H. Li).

Fig. 1. The model geometry.

shown in Fig. 1. The height and the diameter of the reactor are 600 and 40 mm, respectively, with $z = 0$ located at the inlet and $z = 600$ at the outlet. Five samples with diameter of 5 mm and length of 20 mm are arranged along the axis of reactor from $z = 210$ and distributed at intervals of 20 mm.

2.1. Assumption

Primary assumptions about reactor condition and physical properties of gases are taken in modeling as follows:

(1) Compressibility of gases is neglected and gas flow is regarded as laminar flow.
(2) Heat generation by chemical reaction is neglected and temperature in the reactor is a constant.
(3) Chemical reaction is regarded as an isothermal irreversible first-order reaction.
(4) The reaction is independent of the time. So, the steady state for the governing equations is adopted.
(5) All of gases are considered as ideal gases and obey the state equation of perfect gas.

2.2. Governing equations

Because of axial symmetry of geometry, the governing equations are formulated in cylindrical coordinates for a 2D system (r and z) [22]. In Fig. 1, the domain is bounded by the walls of the reactor ($\partial\Omega_{wall}$), the inlet ($\partial\Omega_{in}$), the outlet ($\partial\Omega_{out}$), the symmetry line ($\partial\Omega_{sym}$) and the C/C composite ($\partial\Omega_{C/C}$). In addition, the domain includes a subdomain, the free fluid subdomain (Ω). Number the samples from top to bottom as S1, S2, S3, S4 and S5. Coating thickness of five samples in the reactor can be calculated through the model. The difference of coating thickness between S5 and S1 (ΔD) is used to characterize coating uniformity, as coating thickness at the middle of S3 is deposited to 50 μm.

The assumptions mentioned above in combination with the chemical reaction for the deposition process make it possible to define the equation system. The momentum balance and the continuity equations for laminar flow in cylindrical coordinates are described as

$$\frac{\partial}{\partial z}\left(-\eta r\frac{\partial u}{\partial z}\right) + \frac{\partial}{\partial r}\left(-\eta r\frac{\partial u}{\partial r}\right) + \rho r u\frac{\partial u}{\partial z} + \rho r v\frac{\partial u}{\partial r} + \frac{\partial p}{\partial z} = 0 \quad \text{in } \Omega \tag{2}$$

$$\frac{\partial}{\partial z}\left(-\eta r\frac{\partial v}{\partial z}\right) + \frac{\partial}{\partial r}\left(-\eta r\frac{\partial v}{\partial r}\right) + \frac{\eta}{r}v + \rho r u\frac{\partial v}{\partial z} + \rho r v\frac{\partial v}{\partial r} + \frac{\partial p}{\partial r} = 0 \quad \text{in } \Omega \tag{3}$$

$$r\left(\frac{\partial u}{\partial z} + \frac{\partial v}{\partial r}\right) + v = 0 \quad \text{in } \Omega \tag{4}$$

where η is viscosity (kg m^{-1} s^{-1}), ρ is density (kg m^{-3}), u is velocity vector in the z-direction (m s^{-1}), v is velocity vector in the r-direction (m s^{-1}), p is gas pressure (Pa).

The mass balance equations in cylindrical coordinates are defined by the following equation in the free fluid subdomain:

$$\frac{\partial}{\partial z}\left(-Dr\frac{\partial c}{\partial z}\right) + \frac{\partial}{\partial r}\left(-Dr\frac{\partial c}{\partial r}\right) + ru\frac{\partial c}{\partial z} + rv\frac{\partial c}{\partial r} + rkS_a c = 0 \quad \text{in } \Omega \tag{5}$$

where D is diffusion coefficient (m^2 s^{-1}), c is MTS molarity (mol m^{-3}), k is the first-order reaction rate (m s^{-1}), S_a is effective deposition area on substrate per unit volume (m^2 m^{-3}).

2.3. Boundary conditions and initial conditions

The system of equations defined above is solved by using the proper boundary conditions. In laminar flow no-slip conditions for the surface of the reactor wall and the C/C composite are

$$(u, v) = (0, 0) \quad \text{at } \partial\Omega_{wall} \ \& \ \partial\Omega_{C/C} \tag{6}$$

In addition, at the axis of symmetry:

$$v = 0 \quad \text{at } \partial\Omega_{sym} \tag{7}$$

The last three conditions for the momentum balance and continuity equations are

$$u = u_0 \quad \text{at } \partial\Omega_{in} \tag{8}$$
$$v = 0 \quad \text{at } \partial\Omega_{in} \tag{9}$$
$$p = p_0 \quad \text{at } \partial\Omega_{out} \tag{10}$$

For the mass balance equations there is

$$\left(-D_z^i\frac{\partial c}{\partial z} - D_r^i\frac{\partial c}{\partial r}\right) \cdot n = 0 \quad \text{at } \partial\Omega_{wall}, \partial\Omega_{sym} \ \& \ \partial\Omega_{C/C} \tag{11}$$

where D^i is diffusion coefficient in the free fluid. This equation implies that there is no flux perpendicular to these boundaries. At the inlet, the composition of the gas yields:

$$c = c_0 \quad \text{at } \partial\Omega_{in} \tag{12}$$

At the outlet, it is assumed that the transport of species takes place mainly by convection, and the concentration gradients perpendicular to this boundary is neglected:

$$\left(-D\frac{\partial c}{\partial z}, -D\frac{\partial c}{\partial r}\right) \cdot n = 0 \quad \text{at } \partial\Omega_{out} \tag{13}$$
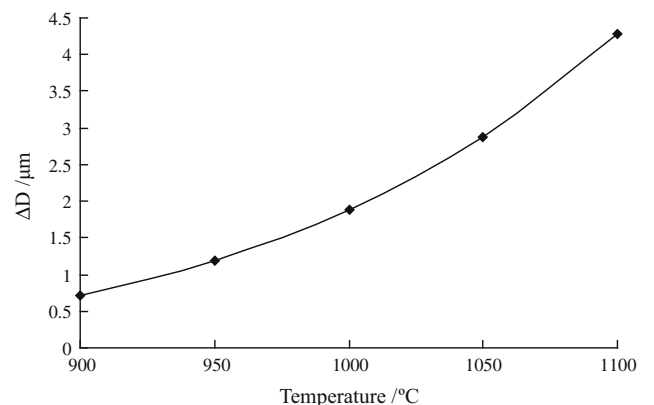

Fig. 2. Effect of deposition temperature on coating uniformity.