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Modeling of gas phase diffusion transport during chemical vapor infiltration process①

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[Abstract] In order to improve the uniformity of both the concentration of gaseous reagent and the deposition of matrix within micro-pores during the chemical vapor infiltration (CVI) process, a calculation modeling of gas phase diffusion transport within micro-pores was established. Taken CH_3SiCl_3 as precursor for depositing SiC as example, the diffusion coefficient, decomposing reaction rate, concentration within the reactor, and concentration distributing profiling of MTS within micro-pore were accounted, respectively. The results indicate that, increasing the ratio of diffusion coefficient to decomposition rate constant of precursor MTS is propitious to decrease the densification gradient of parts, and decreasing the aspect ratio *(L/D)* of micro-pore is favorable to make the concentration uniform within pores.

[Key words] Chemical vapor infiltration; modeling; diffusion transport; composites
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1 INTRODUCTION

The chemical vapor infiltration (CVI) method is one of the most practical and promising process for fabrication of ceramic/carbon matrix composites reinforced by long fibers. In the course of matrix depositing, there is competition between gaseous reagents consume requirements of deposition chemical reaction and gas phase transport rate. The effect of pore net structure within preform on gas phase transport rate and matrix densification tenor is very important. For most parts fabricated by CVI method, the matrix rapidly deposits on the outer surface of the preform, because where has a higher gaseous precursor concentration than the pores located in the interior of the preform. It leads to block the entrance of pore, consequently, the micro-pores can not be perfectly filled in. The rapid and perfect densification of micro-pore is one of the key issues for lower cost fabrication of desired composites. Tai and Lackey et al[1, 2] made some theoretical investigates. In present work, taking deposition of SiC from CH_3SiCl_3(MTS) precursor as an example, both modeling of gas phase diffusion transport and algebra equations of CVI process are established. The effect factors on gas phase diffusion in CVI process were studied in a numerical calculation method.

2 MODELING OF GAS PHASE DIFFUSION TRANSPORT

In CVI process, in order to deposit a solid coating on the surface of pore within the porous preform, an additional gas-phase diffusion step needs to occur, namely gaseous reagents diffuses from the surface of preform into the interior pores. Such diffusion is driven by a concentration gradient in isobaric CVI. Consider a straight, cylindrical pore of initial diameter D and length L, as depicted in Fig. 1, exposed to a gaseous mixture undergoing decomposition at a uniform temperature T. As solids deposit on the inside walls of the pore, the pore diameter, D, will decrease as a function of time, t and of the axial position, Z. The relationship between concentration profile, C_{MTS} (Z), of MTS precursor along the pore and the initial concent-

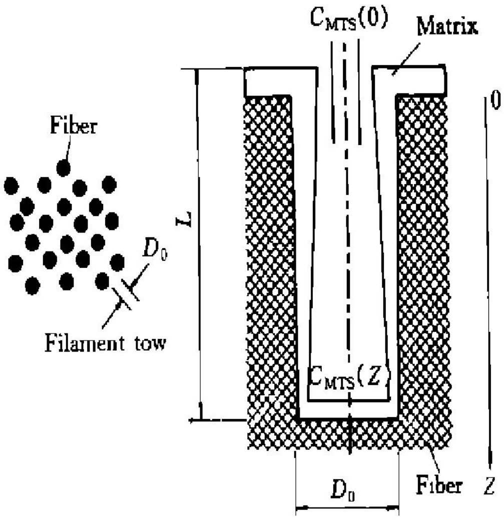

Fig. 1 Schematic of gas diffusing into long pore space

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ration, $C_{MTS}(0)$, on the entrance of pore can be described as follows[3]:

$$\frac{C_{MTS}(z)}{C_{MTS}(0)} = \frac{\cosh[(1-z/L)\theta]}{\cosh\theta} \tag{1}$$

where L is the length of pore, z is the axial position, and θ is the Thiele modulus which can be expressed as follows:

$$\theta = (k_S L^2 / D_e D)^{0.5} \tag{2}$$

where k_S is the first-order reaction rate of MTS decomposition reaction on the surface of pore, $\mathrm{cm \cdot min^{-1}}$, and D_e is the diffusion coefficient of the multi-component gas mixture, MTS+ H_2, $\mathrm{cm^2 \cdot min^{-1}}$.

2.1 Diffusivity

The diffusion coefficient in the vapor deposition process varies with temperature, pressure, and pore diameter. The effective diffusivity, D_e of gas phase transport in a porous body includes the Fickian diffusivity, D_f and the Knudsen diffusivity, D_k[4]. It is hardly to precisely depict the complex pore size distribution, so it is necessary to add a correct item, ε/τ. The relationship about them can be typically described by

$$D_e = \varepsilon/\tau(1/D_f + 1/D_k)^{-1} \tag{3}$$

where ε is the porosity of a porous body, and τ is the tortuosity factor. According to Ref. [5], the experimentally determined value of τ is usually between 2 and 6, although slightly larger and smaller values have also been observed. An alternate empirical correlation for τ is[6]

$$\tau = 1/\varepsilon \tag{4}$$

When the pore radius r is much larger than the molecular mean free path λ, namely $2r \gg 100\lambda$, the Knudsen diffusivity D_k can be ignored for the purposes of obtaining the desired estimate because the molecules collide mostly with each other. The Fickian diffusivity D_f can be calculated using the Chapman-Enskog relationship[2] given for MTS in H_2 by

$$D_f = 0.001858 \frac{T^{3/2}}{p\sigma^2\Omega_d}\sqrt{\frac{M_{MTS} + M_{H_2}}{M_{MTS} W_{H_2}}} \tag{5}$$

where T is the temperature, K; p is the pressure 1.01×10^5 Pa, the molecular weights for H_2 (M_{H_2}) and MTS (M_{MTS}) are 2 and 149.5 $\mathrm{g \cdot mol^{-1}}$, respectively, the overall hard shell diameter, σ is an average between the H_2 (2.827 Å) and the MTS (5.114 Å), and the collision integral for diffusion, Ω_d is estimated from the Leonard-Jones potential of H_2 and MTS to be 0.8099. At 1.01×10^5 Pa and 1373.5 K, the diffusion coefficient, D_f is therefore estimated to be 5.12 $\mathrm{cm^2 \cdot s^{-1}}$.

Eqn. (5) can be simplified further as follows[7]:

$$D_f = K_M T^{3/2} / p \tag{6}$$

For MTS diluted by H_2, the K_M approximates to be 0.0107 ($\mathrm{cm^2 \cdot kPa \cdot s^{-1} \cdot K^{-3/2}}$). At 1.01×10^5 Pa and 1373.5 K in the system, D_f is therefore estimated to be 5.38 $\mathrm{cm^2 \cdot s^{-1}}$. From the equations (5) and (6), note that the diffusion coefficient, D_f is inversely proportional to pressure and increases with temperature according to a power law with an exponent 1.5.

When $2r \leqslant \lambda$, the gas molecules collide mostly with the walls of the pore and the flow is in the Knudsen or molecular regime. As the concentration of the vapor increases, the frequencies of a molecule colliding with other molecules or with pore wall become comparable. Therefore, the diffusion coefficient can be determined from both molecular diffusion and Knudsen diffusion. The Knudsen diffusivity D_k can be denote[2] as

$$D_k = \frac{2r}{3}\left(\frac{8RT}{\pi M_{MTS}}\right)^{0.5} \tag{7}$$

At $2r = 10\ \mu\mathrm{m}$ and $T = 1373.5$ K, D_k is estimated to be 1.323 $\mathrm{cm^2 \cdot s^{-1}}$. From Eqns. (3) ~ (7), D_e approximates to be $4.07\varepsilon^2$ ($\mathrm{cm^2 \cdot s^{-1}}$).

2.2 MTS decomposition rate

The decomposition rate, k_S ($\mathrm{cm \cdot min^{-1}}$) is defined as the dissipation rate of MTS of unit area on the interior surface of pore. It is difficult in direct measuring the value. According to the mass conservation law, the relationship between the decomposition rate k_S of MTS and the deposition rate R_d of SiC on the interior surface of pore can be deduced as follows:

$$k_S = (R_d \rho_{SiC} M_{MTS}) / (M_{SiC} \rho_{MTS(g)}) \times 10^{-4} \tag{8}$$

where the densities for SiC (ρ_{SiC}) and gas-phase MTS ($\rho_{MTS(g)}$) are 3.12 and $6.672 \times 10^{-3}\ \mathrm{g \cdot cm^{-3}}$, respectively, and the molecular weights for MTS (M_{MTS}) and SiC (M_{SiC}) are 149.5 and 40 $\mathrm{g \cdot mol^{-1}}$, respectively. At $R_d = 0.43\ \mu\mathrm{m \cdot min^{-1}}$, k_S is calculated to be 0.075 $\mathrm{cm \cdot min^{-1}}$.

2.3 MTS concentration in reaction chamber

In order to calculate the MTS concentration $C_{MTS}(0)$ under kinetic equilibrium state in the reaction chamber, it is necessary to compute the resident time τ, which can be expressed as[8]

$$\tau = 273\, Vp / 101\,325\, FT \tag{9}$$

where V denotes volume of reaction chamber, $\mathrm{cm^3}$, F denotes gas flow rate, $\mathrm{mL \cdot min^{-1}}$, and T and p are temperature (K) and pressure (Pa) in chamber, respectively.

So the MTS concentration $C_{MTS}(0)$ in the chamber can be deduced as

$$C_{MTS}(0) = C\rho F\tau / M_{MTS} V \tag{10}$$

where C and ρ denote the volume fraction of MTS in overall mixture gas and the density of MTS vapor ($6.672 \times 10^{-3}\ \mathrm{g \cdot cm^{-3}}$), respectively.

Unite Eqns. (9) and (10), $C_{MTS}(0)$ can also be expressed as follows:

$$C_{\mathrm{MTS}}(0) = \frac{C\rho}{M_{\mathrm{MTS}}} \cdot \frac{273}{T} \cdot \frac{p}{101\,325} \qquad (11)$$

$C_{\mathrm{MTS}}(0)$ is calculate to be 1.69×10^{-6} mol•cm^{-3} on the condition that the flow rates of H_2, MTS and Ar are 600, 210 and 300 mL•min^{-1}, respectively, T is 1 373.5, K; and p is 1.01×10^5 Pa.

3 EFFECT FACTORS ON GAS-PHASE DIFFUSION IN MICRO-PORE

3.1 Ratio of D_e and k_S

Fig. 2 denotes the relationship between value of $C(z)/C(0)$ and axial position z under different ratio of gas efficient diffusivity D_e and reaction rate k_S of MTS decomposition reaction, on a determinate length of pore L, the MTS concentration within the pore and therefore the deposition rate of SiC will be more uniform, the larger the gas-phase diffusivity D_e compared to the reaction rate k_S. On the other hand, MTS concentration in location of Z within pore ($C(Z)$) will increase with increasing ratio D_e/k_S. At the same temperature, that $C(Z)$ tends to equate $C(0)$ predicts SiC matrix deposition rate within pore space to be more uniform. So it is in favor of making the density of SiC matrix composites part uniform to both increase the gas diffusion coefficient D_e and decrease MTS decomposition reaction rate k_S. In CVI process, a relative lower deposition temperature is usually used to improve the uniformity of part density, which not only decreases k_S, but also increases the uniformity of MTS concentration within pore space. On the other hand, to decrease pressure in the system can be adopted to increase the diffusion coefficient D_e therefore to quicken gas phase transport rate[9].

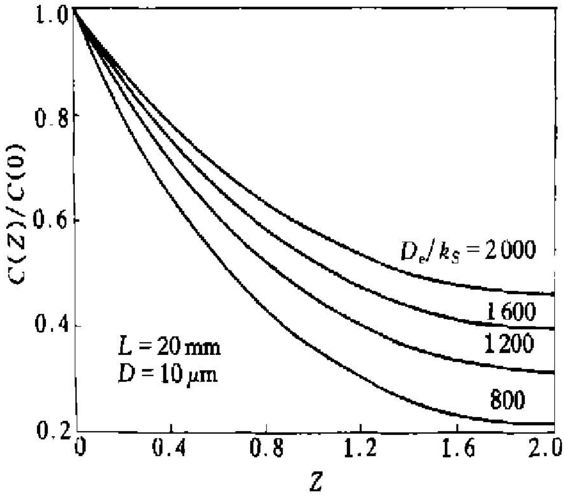

Fig. 2 Calculated values of $C(Z)/C(0)$ with different ratios of D_e to k_S

3.2 Initial length and diameter of pore

As shown in Fig. 3, the smaller the aspect ratio L/D is propitious to make MTS concentration $C(Z)$ within pore tend to equal the concentration $C(0)$ on the entrance of pore. For example, at $D_e/k_S = 1\,600$ and $D = 10$ μm, MTS concentration $C(Z)$ within any location of pore is equal to $C(0)$ when the ratio L/D is 20, namely the length of pore is 200 μm, which only equal the thickness of one layer carbon cloth or carbon tow. In other word, the densification of matrix is uniform when the length of pore is just equal to the thickness of one layer carbon cloth. Based on this, the authors bring forward an improved CVI method to change the course into that first to braid a preform and then to deposit matrix in CVI method, and adopt a course that both stacking of carbon cloth and deposition of matrix are conducted in simultaneity. It leads to both densification of micro-pore and weave of preform are synchronously accomplished. In this improved CVI method, the length of micro-pore is greatly shorten, therefore, a more uniform part can be rapidly fabricated compared to traditional CVI methods. More details about this improved CVI method were reported[10-12].

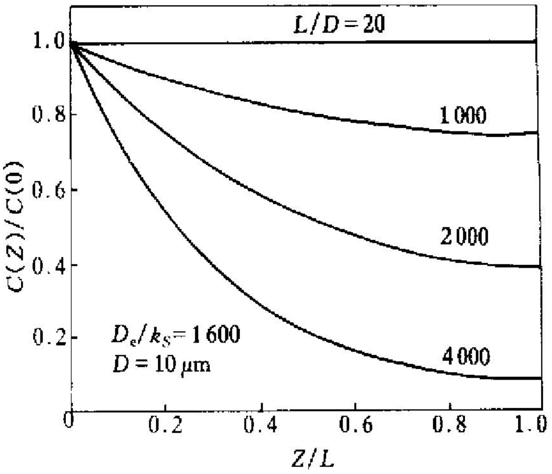

Fig. 3 Relationship between distributing curves of concentration in pores and L/D

4 CONCLUSION

Taking the deposition of SiC using CVI process as an example, the modeling of gas phase diffusion transport with micro-pores of the preform was established. The calculation results indicated that MTS gas-phase concentration within the pore and therefore the deposition rate of SiC matrix will be more uniform, both the larger the gas efficient diffusivity D_e compared to the reaction rate of MTS decomposition reaction k_S and the smaller the aspect ratio L/D.

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