Mathematical model for precursor gas residence time in isothermal CVD process of C/C composites

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Abstract: In the chemical vapor deposition (CVD) process of C/C composites, the dynamics and mechanism of precursor gas flowing behavior were analyzed mathematically, in which the precursor gas was infiltrated by the pressure difference of the gas flowing through felt. Differential equations were educed which characterized the relations among the pressure inside the felt, the pressure outside the felt of the precursor gas and the porosity of the felt as a function of CVD duration. The gas residence time during the infiltration process through the felt was obtained from the differential equations. The numerical verification is in good agreement with the practical process, indicating the good reliability of the current mathematical model.

Key words: chemical vapor deposition; residence time; mathematical model

1 Introduction

Several decades ago, BOKROS and PRICE [1] found that the deposition of pyrocarbon on graphite plate in fluidized bed for manufacturing carbon/carbon (C/C) composites was generated in a sequence of laminar, columnar, dense isotropic and porous isotropic from the upstream of fluidized bed (air inlet) to downstream (air outlet). This result implies that there should be a close relationship between the structure of pyrocarbon and the residence time of the gas in reaction furnace at a given reaction temperature and other conditions [2−7]. It is well known that during CVD process, with the increasing thickness of deposition, it becomes harder for the gas to pass through the pores of the deposited materials and therefore longer time is needed to pass through the entire furnace with deposition. The decomposition of precursor gas into pyrocarbon is composed of complex reactions including addition, polymerization and dehydrocyclization reactions to the optimum intermediate structure of benzene or six-membered cyclic derivative that can deposit into high textured pyrocarbon [8−9]. The residence time of the precursor gas plays an important role in forming the intermediate structure, small molecules or linear hydrocarbons form readily in a short resident time, while carbon soot forms easily from high aromatic polymer during a long resident time [10]. Therefore, it is worthwhile to study the relationship between the pyrocarbon structures and precursor resident time.

The gas residence time in most of the researches [11−13] is considered to be the duration consumed when the gas passes through the free space of furnace or the precursor gas is renewed inside of the chamber. In the later case, the gas residence time could be expressed as

$$\tau = \frac{V T_0 P}{Q T P^0}$$  \hspace{1cm} (1)

where $\tau$ is the gas residence time; $V$ is the volume of furnace chamber; $Q$ is the total flux of both precursor gas and carrier gas; $T_0$ and $P^0$ are the environmental temperature and pressure; $T$ and $P$ are the temperature and pressure inside furnace, respectively.

Some researches consider that the gas residence time is the precursor gas residence time only, and $P$ in Eq. (1) should be replaced by the partial pressure of precursor gas. However, in an actual CVD process, if carrier gas exists inside the furnace, its flow and pressure

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could not be neglected. In addition, there must be a prerequisite for Eq. (1), the gas flow is preceded via laminar flowing [14]. With the development in CVD technique, gas flowing driven by a pressure difference between the inlet and outlet of the chamber has been introduced into both thermal gradient and isothermal CVD process. Therefore, it is necessary to reconsider the gas residence time in the current new processes. Simulation on the traditional CVD process was carried out systematically by McALLISTER and WOLF [15], in which the influences of factors such as temperature and duration, on the CVD process were discussed in detail. However, the theoretical analysis on gas residence time was not given. In this study, a mathematical model for the precursor gas residence time during isothermal CVD process was introduced for the first time. It was considered that current research could provide a useful and scientific basis in both industry and research.

2 Hypotheses of mathematical model

Before CVD process, annular carbon fiber felts are piled up together, and the chamber formed from the inner space of the felts is covered by graphite plate on the top as shown in Fig. 1. The round gas inlet and outlet are located in the middle of the top and the bottom of the furnace chamber, respectively. Precursor gas enters the furnace chamber from the inlet at the bottom of the CVD furnace chamber. Because of the resistance of the felt on the precursor gas flowing, pressure difference is generated inside and outside the felts, which drives the precursor gas to infiltrate into the fine pipes inside the felt wall and to deposit on the inner surface of the fine pipes.

It is supposed that the precursor gas enters the furnace chamber at a constant flow rate, when it passes through the fine pipes inside the felt wall, the precursor gas encounters resistance from the felt wall, and the deposition of pyrocarbon takes place on the inner surface of the pipes. During deposition, the diameter of the pipes inside the felt wall becomes finer gradually, and the resistance on the precursor gas from the felt wall becomes higher with increasing pressure difference between the inside and outside of the felt. In order to simplify the problem, complex thermal-motions of gas, such as the turbulence, are not considered, the main hypothesis taken into account are listed as follows: 1) when the precursor gas flows through pipes inside the felt wall, the felt is not compressed from the pressure difference, and the squeezing effect of gas is neglected; 2) since the duration of each gas atom passing through the pipes inside the felt wall is thought to be very short, it is presumed that the temperature of flowing gas inside the furnace chamber is uniformly distributed or constant in this research; 3) in the CVD process of C/C composites, both the precursor gas and carrier gas have to infiltrate through the felt pipes, while the volume variation of the gas due to the reaction inside the felt is neglected in a short period; 4) the pyrocarbon formed from the decomposition of the precursor gas is thought to be evenly distributed inside the furnace chamber and the concentration of pyrocarbon in the entire CVD process is a fixed value; 5) there is a good thermal conductivity in both the furnace wall and the felt body, and they are connected to the thermostat which can keep the temperature constant inside the entire furnace chamber; 6) the precursor gas infiltrates from the furnace inlet at a constant flow velocity; and 7) the molecular viscous force on the furnace wall and felt wall is neglected.

3 Analysis of vapor infiltration process in felt

There are numerous corrugated pipes which distribute uniformly inside the felt, and the precursor gas infiltrates through the pipes at a constant flow velocity as shown in Fig. 2(a). For a simplification in calculation, the pipes are supposed to be straight and perpendicular to the felt wall, in which the precursor gas flows in a direction normal to the felt wall as shown in Fig. 2(b). Since the total number of the pipes is considered to be comparable to the number of carbon fiber, and the porosity of initial felts is generally in a range of 65%–70%, therefore, the theoretical diameter of the pipes is considered to be about 1–1.5 times of the initial diameter of the fibers (6–8 μm) based on the supposition that these pipes are uniformly distributed inside the felts.

From Pioseuille law in fluid dynamics [14–16], the average flow rate of gas in a straight pipe can be
Fig. 2 Schematic diagrams of felt wall consisting of numerous fine pipes (a) and idealized straight fine pipes within felt wall (b) expressed as:

\[ Q_v = \frac{\pi(p_1 - p_2)}{8 \eta L} r^4 \]  

(2)

where \( p_1 \) and \( p_2 \) are the pressures inside \( V_1 \) and \( V_2 \), respectively; \( r \) is the radius of the felt. The gas flow velocity \( u_i \) in each pipe can be expressed as:

\[ u_i = \frac{(p_1 - p_2)}{8 \pi \eta L} s^2 \]  

(3)

where \( u_i \) is the gas flow velocity in each pipe (suppose that the pipes have the same diameter); \( \eta \) is the viscous coefficient of precursor gas of the inlet, which is assumed to be a constant in the deposition process; \( s \) is the cross-sectional area of the pipe and \( s = \pi r^2 \).

\[ N = \frac{kV_m}{L s} \]

where \( N \) is the total number of pipe inside the felt; \( V_m \) is the volume of felt and \( k \) is the porosity of the felt, therefore, the gas flow rate \( u \) can be expressed as:

\[ u = Nu_i = \frac{kV_m}{L s} \frac{(p_1 - p_2)}{8 \pi \eta L} s^2 = \frac{kV_m(p_1 - p_2)s}{8 \pi \eta b^2(d_2 - d_1)^2} \]  

(4)

where \( u_i \) is the flow rate of the precursor gas flowing into chamber \( V_1 \); \( b \) is the ratio between the average length \( L \) of pipes and the thickness of felt \( (d_2 - d_1) \); \( d_1 \) and \( d_2 \) are the inner and outer diameter of the annular felt, respectively. Since the pipes inside the felt are actually flexure and complicated, the average length of the pipes is thought proper to be calculated by \( L = b(d_2 - d_1) \).

Suppose that the precursor gas in the whole system is in an equilibrium state, therefore, from the ideal gas law \( PV = nRT \), it is obtained that the variation in the amount of precursor gas \( \Delta n_1 \) inside the chamber \( V_1 \) in time \( \Delta t \) satisfies the following equation:

\[ \Delta n_1RT = (p_0u_1 - p_1(t)u(t))\Delta t \]  

(5)

Therefore, after duration \( t \), the amount of gas in \( V_1 \) satisfies

\[ p_1(t)V_1 + \Delta n_1RT = p_1(t + \Delta t)V_1 = (p_1(t) + \Delta p_1)V_1 \]  

(6)

Let \( \theta_1 = 8 \pi \eta_{L_1} \), Eq. (6) can be simplified by Eq. (4) into

\[ p_0u_1 \Delta t = \frac{p_0u_1(k(t)V_m(p_1(t) - p_2(t)))s(t)}{\theta_1 b^2(d_2 - d_1)^2} \Delta t = \Delta p_1 V_1 \]  

(7)

That is

\[ \frac{V_1 \Delta p_1}{\Delta t} = \frac{p_0u_1}{V_1} \frac{k(t)V_m s(t)}{\theta_1 b^2(d_2 - d_1)^2} p_1(t)(p_1(t) - p_2(t)) \]  

(8)

Let \( t \to 0 \),

\[ \frac{dp_2(t)}{dt} = \frac{p_0u_1}{V_1} \frac{k(t)V_m s(t)}{V_1 \theta_1 b^2(d_2 - d_1)^2} p_1(t)(p_1(t) - p_2(t)) \]  

(9)

If it is supposed that the volume of the furnace chamber outside the felt is \( V_2 \), similar to Eq. (5), it is obtained

\[ \Delta n_2RT = (p_2(t)u(t) - p_2(t)u_2(t))\Delta t \]  

(10)

where \( u_2 \) is the amount of gas inside the chamber \( V_2 \).

Therefore, two independent situations were considered in the current research, the infinitely thin furnace wall and the furnace wall \( D \).

If the furnace wall is infinitely thin at the gas outlet: \( L \to 0 \), the gas pressure difference between inside and outside the felt \( (p_1 - p_2) \to 0 \). Then \( \Delta n_2V_2 = 0 \), which means \( \Delta n_2 = 0 \). Eq. (10) implies that \( pu_2 = p_2u_2 \), where \( u_2 \) is the gas flow rate at outlet and considered to be constant in a specific time unit since the process is very short. So \( u_2(t) = u(t) \), where \( V \) is the total volume and \( V = V_1 + V_2 + V_{p,k} \), where \( V_{p,k} \) is the volume of gas inside felt pore. So,

\[ \tau_1(t) = \frac{Vp}{R(t)u(t)} \]  

(11)

Suppose that the outlet is a cylindrical tube, the thickness is \( D \) and its area is \( A \). The two end pressures of the tube are \( p_2(t) \) and \( p_1(t) \), respectively. Therefore,

\[ \frac{dp_2(t)}{dt} = \frac{1}{V_2} \frac{k(t)V_m s(t)}{\theta_1 b^2(d_2 - d_1)^2} p_1(t)(p_1(t) - p_2(t)) - \frac{A^2}{\theta_1 D} \frac{p_2(t)(p_2(t) - p_1(t))}{p_2(t) - p_1(t)} \]  

(12)

where \( u_2 \) changes with time, the time of gas residence time \( \tau_2 \) can be obtained by the following formula:

\[ \int_{t}^{t+\tau_2} u_2(t)\,dt = V \]  

(13)
4 Analysis of dynamic CVD progress of pyrocarbon

On the basis of analyzing the relation among \( V_1, V_2 \) and the pressure that change in the fine pipes inside the felt, the dynamic CVD process of pyrocarbon, the change of porosity \( k \) and the pipe area \( s \) during the deposition are considered in this section.

Name the deposited pyrocarbon contained in a mol gas is \( c \) (kg/mol), then the pyrocarbon quality \( q \) that flows in the pipe is expressed as:

\[
q = Nc = \frac{pu c}{RT} \tag{14}
\]

where \( u \) is the overall gas flow in pipe. If it is supposed that the precursor gas in the pipe is incompressible, and the average gas flow velocity of precursor gas in each pipe is \( v = \frac{u}{s} \), then the pyrocarbon through \( \Delta x \) in the pipe is:

\[
\Delta q(x) = q(x + \Delta x) - q(x) = -\alpha q(x) \sqrt{\frac{\Delta t}{v}} \frac{\Delta x}{v} \tag{15}
\]

Hence,

\[
\frac{\Delta q}{\Delta x} = p \frac{u \alpha c(x) \sqrt{s(t)}}{RT} \frac{\Delta x}{v^2} \tag{16}
\]

Let \( \Delta x \to 0 \), it is obtained

\[
\frac{dc}{dx} = \frac{\alpha c s^{5/2}(t)}{u_i^2} \tag{17}
\]

Suppose the initial concentration of precursor gas is \( c_0 \) [17–18], thus

\[
c(x) = c_0 \exp[-\alpha s^{5/2}(t) x / u_i^2] \tag{18}
\]

Therefore, the variable quantity of \( c \) throughout the pipe is

\[
\Delta c = c(L) - c_0 = c_0 \exp[-\alpha s^{5/2}(t) L / u_i^2] - 1 \tag{19}
\]

If the first order approximation is taken, it is obtained

\[
\Delta c \approx -c_0 \frac{\alpha s^{5/2}(t) L}{u_i^2} \tag{20}
\]

If it is supposed that the pyrocarbon deposits uniformly in the pipes, \( s(t) \) is evenly distributed in the entire pipe.

Suppose that \( \mu \) is the volume of deposited pyrocarbon per unit time in the pipe, thus \( \mu = \Delta c p \mu u_i \). Let \( \beta \) be the positive proportion coefficient among \( \mu, s(t) \) and flow and deposition volume per unit time, it is obtained as:

\[
\Delta s(t) = \mu \Delta t = \beta p \mu u_i \Delta c = -\beta c_0 \frac{p s^{5/2}(t) L}{u_i} \Delta t \tag{21}
\]

Let \( \Delta t \to 0 \), by substation using the following equation:

\[
u_i(t) = \frac{p_1(t) - p_2(t)}{\theta_i L} s^2(t) \tag{22}
\]

it is obtained as:

\[
\frac{ds(t)}{dt} = -\beta c_0 p_1(t) \frac{\theta_i L \sqrt{s(t)}}{p_1(t) - p_2(t)} \tag{23}
\]

where \( N \) is a constant and \( k_0 \) is the initial value of porosity of the C/C composite, so

\[
k_0 V_m = \frac{k(t) V_m}{L s_0} \tag{24}
\]

and the porosity at time \( t \) is

\[
k(t) = \frac{k_0}{s_0} s(t) \tag{25}
\]

Substitute Eq. (11) into Eq. (7), it is obtained as

\[
\frac{dp_1(t)}{dr} = \frac{p_0 u_1}{V_1} - \frac{k_0 V_m s^2(t)}{\theta_i s_0 V_m L^2} p_1(t)(p_1(t) - p_2(t)) \tag{26}
\]

So the time of gas flowing through the pipe is

\[
\tau_2 = \frac{L}{v} = \frac{L s(t)}{u_i} \tag{27}
\]

From the above result, if the furnace wall of gas outlet is infinitely thin, and combine Eqs. (23) and (26), a simple model is obtained as:

\[
\frac{dp_1(t)}{dr} = \frac{p_0 u_1}{V_1} - \frac{k_0 V_m s^2(t)}{\theta_i s_0 V_m L^2} p_1(t)(p_1(t) - p_2(t)) \tag{28}
\]

Therefore, the gas residence time through the pipe could be obtained as:

\[
\tau_1 = \frac{V_p}{p_1 u_i} - \frac{k_0 V_m s^2(t)}{s_0} p_1(t)(p_1(t) - p_2(t)) \tag{29}
\]

and the infiltration time of the precursor gas in a specific process is
\[
\tau_2 = \frac{b^2 (d_2 - d_1)^2}{\theta_1} \frac{(p_1(t) - p) s(t)}{(p_1(t) - p_2(t))}
\]

By combining Eqs. (23), (26) and (12), an improved model is obtained as:

\[
\begin{align*}
\frac{dp_1(t)}{dt} &= p_0 \frac{b^2 d_0}{V_0} \left( \frac{k_0 V_0 s^2(t)}{\theta_1 b^2 V_1 (d_2 - d_1)^2} p_1(t)(p_1(t) - p_2(t)) \right) \\
\frac{dp_2(t)}{dt} &= \frac{k(t) V_0 s(t)}{\theta_1 b^2 V_2 (d_2 - d_1)^2} p_1(t)(p_1(t) - p_2(t)) - \\
&+ \frac{A^2}{\theta_1 V_2^2 D} \left( p_2(t)(p_2(t) - p) \right) \\
\frac{ds(t)}{dt} &= -\beta k_0 \left( p_1(t) \frac{\theta_1 L}{p_1(t) - p_2(t)} \right)
\end{align*}
\]

Thus, \( \tau_1 \) meets

\[
\int_0^{\tau_1} \frac{p_2(t) - p}{\theta_2 D} A^2 dt = V.
\]

Similarly,

\[
\tau_2 = \frac{b^2 (d_2 - d_1)^2}{\theta_1} \frac{(p_1(t) - p_2(t)) s(t)}{(p_1(t) - p_2(t))}
\]

5 Numerical verification

On the base of the data in actual CVD process of C/C composites as tabulated in Table 1, numerical verifications are carried out using Runge-Kutta method impeded in MATLAB software by summarizing the above equations. The results regarding the felt porosity, pressure difference between \( V_1 \) and \( V_2 \), duration of gas flow through pipes and gas residence time through the chamber are plotted as a function of CVD duration in Figs. 3(a)−(d), respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of CVD oven ((H))/mm</td>
<td>1 600</td>
</tr>
<tr>
<td>Diameter of CVD oven ((d))/mm</td>
<td>680</td>
</tr>
<tr>
<td>Height of felt ((R))/mm</td>
<td>1 000</td>
</tr>
<tr>
<td>Outside diameter of felt ((d_1))/mm</td>
<td>237</td>
</tr>
<tr>
<td>Inside diameter of felt ((d_2))/mm</td>
<td>438</td>
</tr>
<tr>
<td>Void ratio of felt ((k_0))/%</td>
<td>70</td>
</tr>
<tr>
<td>Mean length of pipes ((L))/mm</td>
<td>121</td>
</tr>
<tr>
<td>Gas flow in (V_1) ((u_1))/cm(^3)·s(^{-1})</td>
<td>533.3</td>
</tr>
<tr>
<td>Viscosity coefficient of inlet gas ((\eta_1))/Pa·s·cm(^3)·g(^{-1})</td>
<td>0.090 3</td>
</tr>
<tr>
<td>Viscosity coefficient of outlet gas ((\eta_2))/Pa·s·cm(^3)·g(^{-1})</td>
<td>0.090 0</td>
</tr>
<tr>
<td>Wall thickness of air-out/mm</td>
<td>11</td>
</tr>
<tr>
<td>Outside diameter of air-out/mm</td>
<td>23</td>
</tr>
<tr>
<td>Pressure in (V_1) ((p_1))/Pa</td>
<td>1 000</td>
</tr>
<tr>
<td>Pressure in (V_2) ((p_2))/Pa</td>
<td>600</td>
</tr>
<tr>
<td>Outside pressure of air-out ((p))/Pa</td>
<td>400</td>
</tr>
</tbody>
</table>

Fig. 3 Variations of felt porosity (a), pressure difference between \( V_1 \) and \( V_2 \) (b), time of gas flow through pipes (c) and gas residence time (d) through whole chamber in CVD process.
Figure 3(a) shows the variation of felt porosity calculated during CVD process. Felt porosity decreases sharply at the beginning of deposition for 300 s, and then becomes to vanish, indicating gradual densification of the felts during CVD process. With the decrease in felt porosity or increase in densification, the pressure difference between the outside and inside of the felt which can accelerate the gas flow rate through the pipe in the felt wall increases evidently when the pressure of $P_2$ is kept to be a fixed value (Fig. 3(b)). Although the gas flow rate reduces, the gas flow velocity through pipe decreases obviously (Fig. 3(c)). But the gas residence time through the whole CVD chamber becomes longer when the felt porosity reduces to a certain value (Fig. 3(d)).

Figure 4 shows the variation of the specific porosity volume of the carbon felt during specific CVD process, the specific porosity volume is a generally used parameter because it is an easy measurement and has a proportional relation to that of the porosity factor. It can be seen that the whole variation shapes in the curves in Figs. 3(a) and 4 are very similar indicating that the current mathematic model is reliable. However, because the influence of temperature in CVD deposition rate was not considered in the current model, the time scales are not in good agreement in both figures. Therefore, a consideration in the influence of temperature or the deposition rate as a function of temperature is necessary in the future research.

![Fig. 4 Specific porosity volume during CVD process](image)

### 6 Conclusions

1) Precursor gas is infiltrated by pressure difference through the felt. The dynamics and mechanism of the precursor gas in the chemistry vapor deposition furnace are analyzed, and differential equations are deduced which characterize the relationship among the pressure inside the felt, the pressure outside the felt and the porosity of the felt.

2) Numerical verification is accordant to the practical CVD process, indicating the rationality and reliability of the current mathematical model.

### References


等温 CVD 制备炭/炭复合材料过程中
气体滞留时间的数值分析

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摘 要：在化学气相沉积(CVD)制备炭/炭复合材料的过程中，对采用强制通过毛坯的特定装炉方式下的碳源气体的流动动力学及其反应机理进行系统的理论分析。在一系列的计算基础上，得到毛坯内部空腔压强、毛坯外部空腔压强和毛坯的孔隙度随时间变化的微分方程模型，求出气体在炉体的滞留时间以及渗透毛坯的时间。该理论计算所得的 CVD 过程中毛坯孔隙度变化与实际生产过程中的孔隙度变化趋势一致，表明该研究理论分析结果具有较高的可信度。

关键词：化学气相沉积；滞留时间；微分方程

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