

Rapid chemical vapor infiltration of C/C composites

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Abstract: With liquid petrol gas (LPG) as carbon source, carbon felt as porous preform and hydrogen as diluent, C/C composites were fast fabricated by using a multi-physics field chemical vapor infiltration (MFCVI) process in a self-made furnace. A set of orthogonal experiments were carried out to optimize parameters in terms of indices of density and graphitization degree. The results show the optimal indices can be achieved under the conditions of temperature 650 °C, LPG concentration 80%, gas flux 60 mL/s, total pressure 20 kPa, infiltration time 15 h. The verification experiment proves the effectiveness of the orthogonal experiments. Under the optimal conditions, the graphitization degree of 75% and bulk density of 1.69 g/cm are achieved with a uniform density distribution. At the same time, a new structure is obtained.

Key words: C/C composites; chemical vapor infiltration(CVI); graphitization degree; bulk density; orthogonal experiment

1 Introduction

Carbon fiber-reinforced carbon matrix composites, carbon-carbon (C/C) composites, typically made by chemical vapor infiltration (CVI), are attractive materials to be used at elevated temperatures in inert atmosphere and ablative environments for aviation and aerospace applications. But the high manufacture cost of C/C composites restrains applications. At present, thousands of hours are needed for the C/C composites manufacture of full cycle large-scale isothermal chemical vapor infiltration(ICVI). Nevertheless, by the rapid densification technologies, the cost can be greatly lowered[1–3]. Therefore, many countries have been focusing their studies on rapid CVI technology[3–7] including an improved ICVI[8–10]. A rapid densification technology, multi-physics field CVI (MFCVI) was developed[11]. In this work, orthogonal experiments were designed and carried out to evaluate the novel technique for scale production. High density and high graphitization degree are the most important for high temperature applications. These two parameters were employed as orthogonal indices to weigh the

performance of C/C composites[12].

2 Experimental

C/C composites were fast fabricated by MFCVI in a self-made furnace[11]. Schematic diagram of infiltration is presented in Fig.1 with liquid petrol gas (LPG) as carbon source, polyacrylonitrile-based carbon felt with dimensional sizes of 280 mm×40 mm×20 mm and an initial density of about 0.2 g/cm³ as porous preform and hydrogen as diluent gas. A set of orthogonal experiments $L_{16}(4^5)$ were designed to optimize the density and graphitization degree[13–14]. The temperature varied between 650 °C and 950 °C, LPG concentration changed from 50% to 80%, gas flux was in the range of 40–100 mL/s and consequently total pressure increased from 5 kPa to 20 kPa. The factor-level configuration is shown in Table 1.

The density of C/C composites was measured by Archimedes principle. The graphitization degree of C/C composites was obtained after high temperature treatment at 2300 °C for 2 h. The Rigaku-D/2550VB X-ray diffractometer was employed to scan the (002) peak of the composites. According to Franklin model, the

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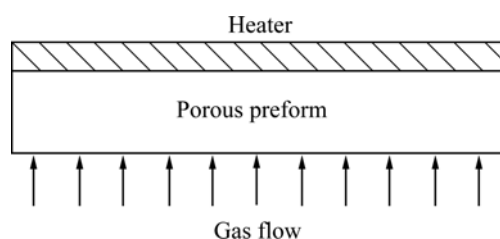


Fig.1 Schematic diagram of CVI process in cold-wall reactor

Table 1 $L_{16}(4^5)$ factor-level configuration

Level	A $\theta/^{\circ}\text{C}$	B $C/\%$	C $v/(\text{mL}\cdot\text{s}^{-1})$	D p/kPa	E t/h
1	650	50	40	20	6
2	750	60	60	15	9
3	850	70	80	10	12
4	950	80	100	5	15

diffraction angle corresponding to (002) peak, gravity center and median value of full width at half maximum (FWHM) were collected to calculate the graphitization degree (g). g value of the C/C composites in the present work was the average of the three calculated values. Polarized optical microscopy (PLM) was used to

characterize the texture of the different pyrolytic carbons on a Leica MeF3A microscope. Scanning electron microscopy (SEM) was performed on JSM6360LV microscope.

3 Results and discussion

Table 2 shows the results of the orthogonal experiments.

3.1 Density

As shown in Table 2, the mean optimal parameters for density are 650 $^{\circ}\text{C}$, 70%, 100 mL/s, 10 kPa and 15 h. It is clear that a wider range of one factor leads to a greater influence on indices while the level of the factor is varied reversely. The factors are in the order $R_A > R_B > R_C > R_D = R_E$, indicating an increasing effect on indices. The variance analysis was carried out to evaluate the influence of factor and the obtained data are listed in Table 3. The F -test results show $F_A > F_{99}(3, 6) = 9.78$, indicating that both A and B are predominant at level of 0.01. The best level should be accessible if the level can be selected on the basis of low cost and easy operation. Therefore, the best level combination is $A_1B_3C_4D_3E_4$ according to above analysis.

Table 2 Results of $L_{16}(4^5)$ LPG-hydrogen experiments

Experiment No.	A	B	C	D	E	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$g/\%$
1	650	50	40	20	6	1.58	68.5
2	650	60	60	15	9	1.61	70.1
3	650	70	80	10	12	1.74	73.7
4	650	80	100	5	15	1.71	77.1
5	750	50	60	10	15	1.58	45.6
6	750	60	40	5	12	1.50	51.2
7	750	70	100	20	9	1.66	62.3
8	750	80	80	15	6	1.59	67.5
9	850	50	80	5	9	1.57	41.3
10	850	60	100	10	6	1.54	57.7
11	850	70	40	15	15	1.63	56.3
12	850	80	60	20	12	1.59	71.2
13	950	50	100	15	12	1.50	32.8
14	950	60	80	20	15	1.42	42.1
15	950	70	60	5	6	1.52	56.5
16	950	80	40	10	9	1.50	58.3
Mean ρ/g	I	1.66/72.4	1.56/47.1	1.55/58.6	1.56/61.0	1.56/62.6	
	II	1.58/56.7	1.52/55.3	1.58/60.9	1.58/56.7	1.59/58.0	
	III	1.58/56.6	1.64/62.2	1.58/56.2	1.59/58.8	1.58/57.2	
	IV	1.49/47.4	1.60/68.5	1.60/57.5	1.58/56.5	1.59/55.3	
Range		0.17/25.0	0.12/21.4	0.05/4.7	0.03/4.5	0.03/7.3	

Table 3 Results of variance analysis on density

Factor	Sum of partial squares	Freedom	<i>F</i> ratio	<i>F</i> critical value	Predominance
A	0.060	3	30.000		**
B	0.033	3	16.500	($\alpha=0.10$)3.29	**
C	0.005	3	2.500	($\alpha=0.05$)4.76	
D	0.002	3	1.000	($\alpha=0.01$)9.78	
E	0.002	3	1.000		
Error	0.00	6			

Note: ** means the predominant factor at level 0.01

Table 4 Results of variance analysis on graphitization degree

Factor	Sum of partial squares	Freedom	<i>F</i> ratio	<i>F</i> critical value	Predominance
A	1 284.763	3	25.328		**
B	1 021.873	3	20.145	($\alpha=0.10$)3.29	**
C	47.503	3	0.936	($\alpha=0.05$)4.76	
D	53.948	3	1.064	($\alpha=0.01$)9.78	
E	113.813	3	2.244		
Error	101.45	6			

3.2 Graphitization degree

The mean optimal condition for graphitization degree is 650 °C, 80%, 60 mL/s, 20 kPa and 6 h. The factor is in the order of $R_A > R_B > R_E > R_C > R_D$.

Variance analysis results are listed in Table 4. The *F*-test results show $F_A > F_{99}(3, 6)=9.78$, demonstrating that both A and B are predominant at level 0.01. Thus, the best level combination is $A_1B_4C_2D_1E_1$.

3.3 Integrative comparison of cross table

In order to find the conditions that meet the relevant parameters of density and graphitization degree, an integrative comparison of cross table was undertaken and shown in Table 5.

Table 5 Integrative comparison

Factor	A	B	C	D	E
Density	A_1	B_3	C_4	D_1	E_4
Predominance	**	**			
Graphitization degree	A_1	B_4	C_2	D_1	E_1
Predominance	**	**			
Comparison results	A_1	B_4	C_2	D_1	E_4

Form the cross table analysis (Table 5), $A_1B_4C_2D_1E_4$ is the optimum condition; and based on the experiment results, it can be seen that the five characteristic values in the experiments do not conflict with each other. After analysis, the optimum conditions do not appear in orthogonal experiments. Therefore, it is necessary to carry out the verification experiments.

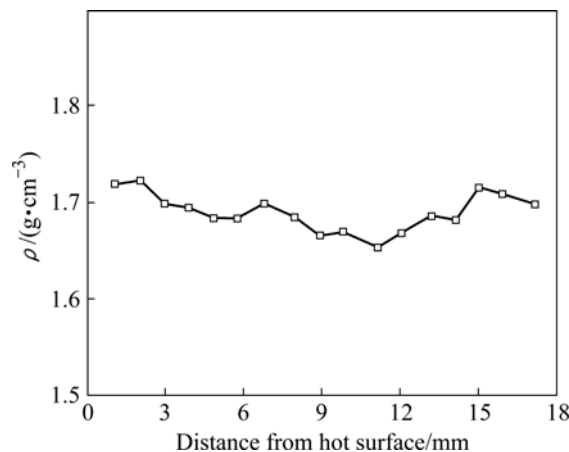
3.4 Verification experiment

The verification experiment was performed under

the conditions shown in Table 5, temperature 650 °C, LPG concentration 80%, gas flux 60 mL/s, total pressure 20 kPa and infiltration time 15 h. The corresponding density and graphitization degree are 1.69 g/cm³ and 75%, respectively, which conform the analysis and the availability of the experiments.

3.5 Density distribution

In order to measure the density distribution of the C/C composites fabricated by MFCVI, the obtained sample was cut into small pieces (30 mm×30 mm×20 mm) along the thermal gradient direction. After polishing every 500 μm of the thickness of pieces, the mass of the remained piece was measured. The cycle was repeated until the piece was used up. The density distribution along the thickness direction was calculated according to the mass, as shown in Fig.2. It is clear that the density distribution of the C/C composites fabricated by MFCVI

**Fig.2** Density distribution of C/C composites

is quite uniform. The middle part has a lower density, which is attributed to the gas diffusion limitation. It is supposed that the low gradients of thermal diffusion and magnetic field, and the cooling effect of the fast flowing gas all cause the temperature of the exterior part substantially lower than that of the hot surface. As a result, the open pores on surface can further be infiltrated. The results indicate that the density distribution of the fabricated materials can meet the requirement of most applications.

3.6 Microstructure analysis

PLM performed on the matrix exhibits a novel structure of pyrolytic carbon (Fig.3(a)). There are no obvious Maltese-cross and extinction angle with deep blue and orange colors. Meanwhile, it is noticeable that a lot of huge cones grow from the matrix.

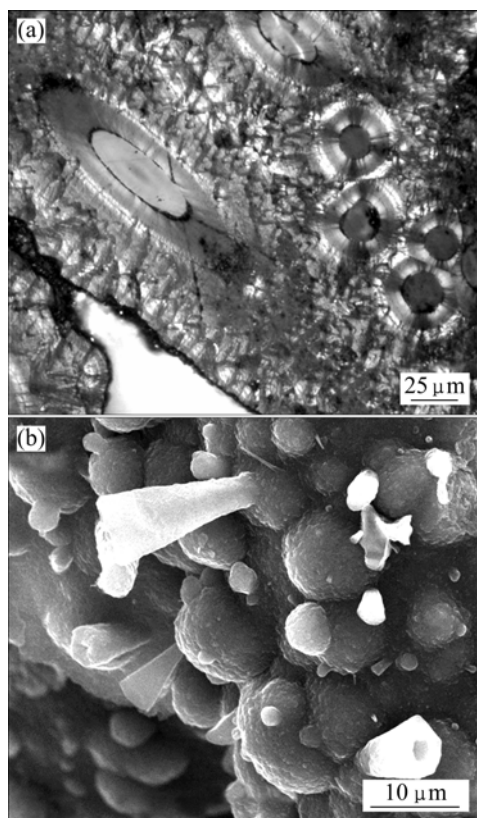


Fig.3 Microstructure of pyrocarbon of C/C composites: (a) PLM image; (b) SEM image

SEM measurements show there are a large amount of nodular textures and hollow cones on the surface of this pyrolytic carbon up and down while the fracture surface is RL-like layers with a certain angles. Energy disperse spectrum (EDS) results show that no catalytic element exists in the materials except carbon. The XRD pattern also displays the presence of identical structures. At the same time, its graphitization degree is higher. This

pyrolytic carbon has a new structure.

4 Conclusions

1) Orthogonal experiments demonstrate that the optimal parameters for C/C composites via MFCVI are temperature 650 °C, LPG concentration 80%, gas flux 60 mL/s and total pressure 20 kPa within 15 h.

2) The density is 1.69 g/cm and graphite degree is 75% under optimal conditions. and the density distribution is uniform.

3) PLM and SEM images show the possibility of the existence of a novel pyrocarbon structure with a high graphitization degree.

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