Mechanical properties of C_f/ Si-O-C composites prepared by hot-pressing assisted pyrolysis of polysiloxane [①]

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Abstract: Silicon oxycarbide composites reinforced by three-dimensional braided carbon fiber (3D-B C_f/ Si-O-C) were fabricated via precursor infiltration and pyrolysis of polysiloxane, and the effects of processing variables on mechanical properties and microstructures of 3D-B C_f/ Si-O-C composites were investigated. It is found that the mechanical properties and densities of 3D-B C_f/ Si-O-C composites can be increased if the first pyrolysis cycle is assisted by hot-pressing. Pyrolysis temperature has great effects on mechanical properties and microstructures of 3D-B C_f/ Si-O-C composites. The composite, which is hot-pressed at 1 600 ℃ for 5 min with pressure of 10 MPa in the first pyrolysis cycle, exhibits high mechanical properties: bending strength 502 MPa and fracture toughness 23. 7 MPa•$m^{1/2}$. The high mechanical properties are mainly attributed to desirable interfacial structure and high density.

Key words: silicon oxycarbide; continuous carbon fiber reinforcement; mechanical property; microstructure; precursor infiltration and pyrolysis; hot-pressing; ceramic matrix composite

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1　INTRODUCTION

Continuous fiber reinforced ceramic matrix composites(CFRCMCs) show great talent for overcoming the brittleness of monolithic ceramics and are attractive materials for applications requiring low mass, high strength and toughness at elevated temperatures. Generally, there are several methods to fabricate CFRCMCs, such as chemical vapor infiltration(CVI), slurry infiltration combined with hot-pressing, reaction bonding, and polymer-infiltration-pyrolysis(PIP).

The PIP route has gained increasing attention in recent years for its advantages such as low processing temperature, controllable ceramic compositions, and near-net-shape technologies. Many different preceramic polymers have been discovered since their original development by Yajima et al[1]. Of all the precursors for PIP, polysiloxane(PSO) has attracted more attention in recent years[2]. It is not only commercially available but also very cheap, and its derived silicon oxycarbide(Si-O-C) (in Ar or N_2) and silicon oxynitride(Si-N-O) (in NH_3) ceramics have been demonstrated to possess improved properties such as creep resistance and microstructural stability over those of many conventional silicate ceramics[3, 4]. Therefore, PSO is considered a desirable precursor for low-cost CFRCMCs with high performance.

The mechanical properties of CFRCMCs are determined by their microstructures. Interfacial structure and density are the two most important factors that have effects on mechanical properties of PIP-derived CFRCMCs. To get desirable interfacial structure, fiber coatings have been employed. At the same time, many methods have been employed to densify PIP-derived CFRCMCs because there are a lot of pores and microcracks in composites resulted from the evolution of gaseous products and volume shrinkage during precursor pyrolysis. Besides repeating infiltration-pyrolysis cycle[5] and incorporating suitable filler into precursor[6], hot-pressing is another effective method to densify composites. In the study by Nakano et al[7], three-dimensional carbon fiber reinforced polycarbosilane-derived SiC composites were hot-pressed after eight cycles of vacuum infiltration and pyrolysis under atmospheric pressure. Open porosity was reduced to less than 3% by hot-pressing densification, however, severe fiber deterioration and strong fiber/ matrix bonding were observed. As a result, the mechanical properties were decreased. In their subsequent study[8], temperature and pressure were optimized, and the mechanical properties were increased because of the desirable interfacial structure and high density.

In this study, hot-pressing is performed in the first pyrolysis cycle, and the effects of processing variables on mechanical properties and microstructures of polysiloxane-derived three-dimensional braided car-

bon fiber reinforced Si-O-C composites (3D-B C_f/ Si-O-C) are investigated.

2 EXPERIMENTAL

Colorless transparent liquid polysiloxane(PSO), containing 1. 4% (mass fraction) hydrogen, was selected as precursor for Si-O-C ceramics. Divinylbenzene(DVB) (light yellow transparent liquid) was selected as cross-linking reagent for PSO. Chloroplatinic acid(H_2PtCl_6), dissolved in anhydrous ethanol, was used as catalyst. The cure and pyrolysis of DVB/PSO were reported earlier[9, 10].

Carbon fibers with tensile strength of 3 GPa and elastic modulus of 210 GPa were selected for this study. Fiber volume fraction ratio in x, y, z directions of three-dimensional braided carbon fiber preform (3D-B C_f) was 8: 1: 1.

Carbon fiber preform was infiltrated with PSO/DVB solution under vacuum for 1 h, then cured at 120 ℃ for 6 h. The first pyrolysis was carried out under three processing conditions, and three samples which were denoted as A, B, and C respectively were fabricated. The detailed processing parameters of sample A, B, and C are presented in Table 1. In order to elucidate the effects of hot-pressing process on microstructures and mechanical properties of 3D-B C_f/ Si-O-C composites, another two samples, denoted as HR and PT, were also fabricated, and their detailed processing parameters are also presented in Table 1. In all cases high purity flowing N_2 was used as protective atmosphere.

The bulk densities of the resulted composites were measured according to Archimede's principle with deionized water as immersion medium. Each data point was an average over eight values. The bending strength was tested by a three-point ben-

ding method with the span/ height ratio of 15 and a cross-head speed of 0. 5 mm/ min. The fracture toughness was determined by the single edge notched beam(SENB) method with a cross-head speed of 0. 05 mm/ min and the span/ height ratio of 4. The ratio of notch depth to specimen height was 0. 50. For mechanical properties tests, three specimens were measured for each composite. After the flexure tests, scanning electron microscopy (SEM) was employed to observe the fracture surface of the composites.

3 RESULTS AND DISCUSSION

The mechanical properties and densities of samples A, B, C, HR and PT are presented in Table 2. The mechanical properties and densities of samples B and C are superior to those of sample A, demonstrating that the mechanical properties and densities can be increased if the first pyrolysis cycle was assisted by hot-pressing.

The density of the matrix is measured to be 1. 90 g/ cm^3. The density of carbon fiber is 1. 76 g/ cm^3. Fiber volume fractions of samples A, B and C are 40%, 43% and 48%, respectively.

Figs. 1 – 3 show the fracture surfaces of samples A, B and C. In Fig. 1, sample A shows little fiber pull-out and the pull-out length is very short, indicating that fiber/ matrix bonding is very strong. In the SEM image of sample B (Fig. 2), many pulled-out fibers are observed, and the pull-out length is much longer than that in sample A, indicating that fiber/ matrix bonding of sample B is weaker than that of sample A. However, it can be found that there are some matrix debris adhering to pulled-out fibers, indicating that fiber/ matrix bonding is still strong. Of three samples, sample C(Fig. 3) illustrates the most extensive fiber pullout and the longest pull-out

Table 1 Processing parameters in each cycle of samples fabricated by PIP

Cycle No.	Sample	Heating rate/ (℃·min^{-1})	Pyrolysis temperature/ ℃	Pyrolysis time/ min	Pressure/ MPa	Pressing time/ min
1	A	1	1 000	60	0	0
	B	30	1 300	30	10	30
	C	30	1 600	5	10	5
	HR	30	1 000	60	0	0
	PT	30	1 600	5	0	0
2 – 7	A	1	1 000	60		
	B	1	1 000	60		
	C	1	1 000	60		
	HR	1	1 000	60		
	PT	1	1 000	60		

Table 2 Mechanical properties and densities
of samples A, B, C, HR and PT

Sample	Bending strength/ MPa	Fracture toughness/ (MPa·m$^{1/2}$)	Density/ (g·cm^{-3})	Theoretical density/ (g·cm^{-3})
A	246.2	9.4	1.728	1.844
B	388.9	16.7	1.742	1.840
C	502.0	23.7	1.780	1.833
HR	173.9	–	–	–
PT	173.4	–	–	–
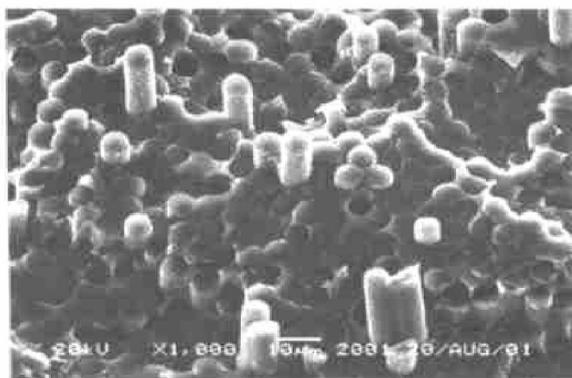
Fig. 1 SEM image of fracture surface of sample A

Fig. 2 SEM image of fracture surface of sample B

Fig. 3 SEM images of fracture surfaces of sample C
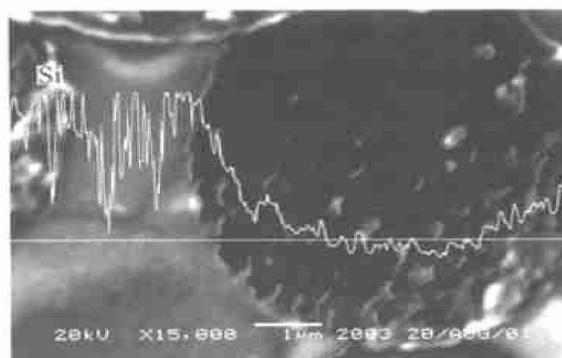
Fig. 4 Characteristic X-ray profile of Si element in sample A
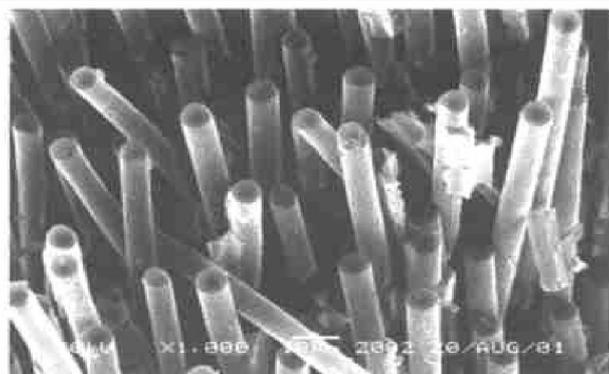
length. In addition, obvious interfacial debonding and smooth fiber surface are observed in Fig. 3, indicating that fiber/matrix bonding is weak.

For CFRCMCs, in-situ strength of fibers dominates the bending strength and interfacial bonding determines the fracture toughness. In sample A, the diffusion of Si atoms into carbon fibers are observed as shown in Fig. 4. How the Si atoms in matrix diffuse into or react with carbon fibers is not clear so far, but it has been well demonstrated that the atoms in matrix can diffuse into or react with carbon fibers during pyrolysis to create strong fiber/matrix bonding and a great reduction in fiber strength[7, 11, 12]. According-
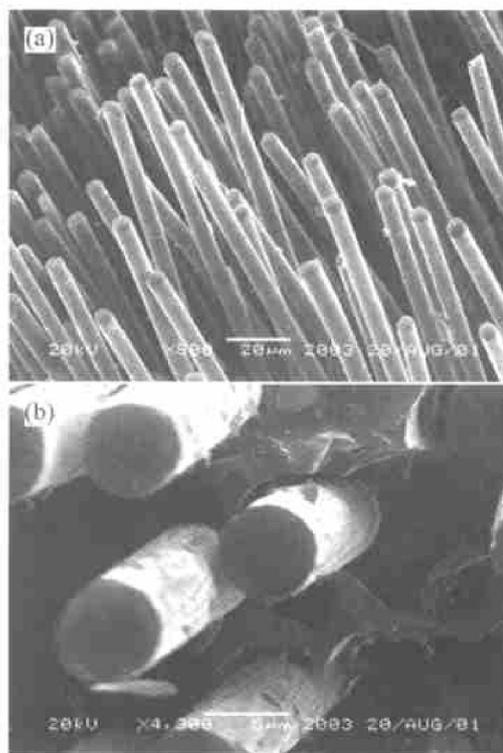
ly, sample A exhibits low bending strength and fracture toughness. The interphase due to the diffusion of Si atoms into carbon fibers consists of Si, C and O in which oxygen atoms are derived from surface sizing of carbon fibers and Si-O-C matrix.

As shown in Table 2, when the heating rate of the first pyrolysis cycle increased from 1 ℃/min to 30 ℃/min, the bending strength of the resultant sample HR is inferior to that of sample A, indicating that increasing the heating rate of the first pyrolysis cycle can not enhance bending strength. Fig. 5 shows the fracture surface of sample HR. It is noted that sample HR exhibits flat fracture surface with very short fibre pull-out, demonstrating strong interfacial bonding. The diffusion of Si atoms into carbon fibers, as shown in Fig. 4, is also observed in this sample, which is responsible for the strong fiber/matrix bonding.
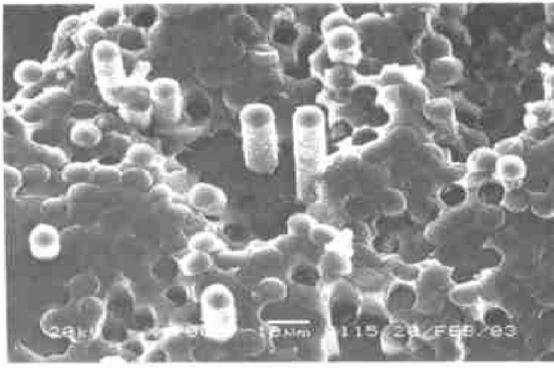
Fig. 5   SEM image of fracture surface
of sample HR

It is found that the cured DVB/ PSO "blasts" when being pyrolyzed with a heating rate of 30 ℃/ min, resulting in large quantities of pores in composites. On one hand, these pores have many fibers uncoated by matrix and the uncoated fibers react with DVB/ PSO solution in subsequent cycles to create strong fiber/ matrix bonding. On the other hand, these pores are detrimental to bendng strength[11]. Consequently, the bending strength of sample HR is lower than that of sample A.

When the first pyrolysis cycle is performed at 1 600 ℃ for 5 min with a heating rate of 30 ℃/ min, the bending strength of the resultant sample PT is also lower than that of sample A. Fig. 6 shows the fracture surface of sample PT. It can be seen that the pull-out length is longer than that of sample A, demonstrating that the fiber/ matrix bonding of sample PT is weaker than that of sample A. The weakened fiber/ matrix bonding of sample PT is ascribed to the decomposition of interphase at above 1 200 ℃[12, 13]. However, the quantities of pulled-out fibers of sample PT are almost as same as those of sample A, indicating that the fiber/ matrix bonding is still strong. In this sample, large size lenticular-shaped pores are observed, as shown in Fig. 7. These pores result from the decomposition of Si-O-C matrix at above 1 200 ℃ because no such pore is found in sample HR. As mentioned above, these large size lenticular-shaped pores as well as the large quantities of pores due to rapid pyrolysis are responsible for the still strong fiber/ matrix bonding and the lower bending strength of sample PT compared with those of sample A.

However, there is no large size lenticular-shaped pore in sample C. The only difference between fabrication processes of sample PT and sample C is that sample C is fabricated with a pressure of 10 MPa while sample PT without pressure, so the pores are eliminated by the pressure.

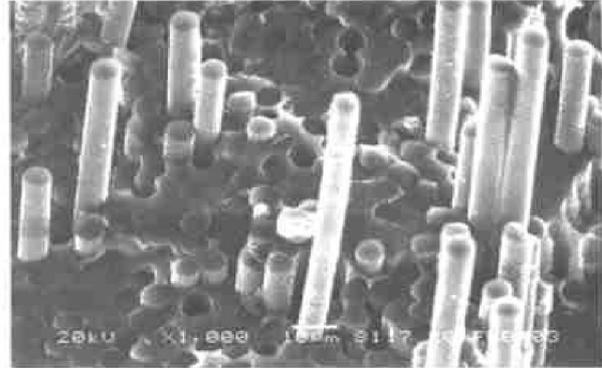Based on the results above, it can be deduced

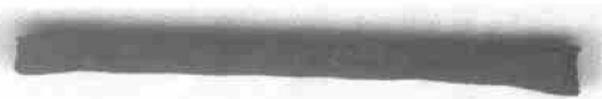**Fig. 6**   SEM image of fracture surface
of sample PT

Fig. 7   Morphology of large size lenticular-shaped
pores in sample PT

that the reasons why hot-pressing assisted pyrolysis can enhance the mechanical properties of 3D-B C$_f$/ Si-O-C composites are as follows: 1) The interphase resulted from the diffusion of Si atoms in matrix into carbon fibers decomposes at above 1 200 ℃. As a result, fiber/ matrix bonding become weak. At the same time, in-situ strength of carbon fibers in composites increases. In CFRCMCs, fibers bear the major part of the applied load. The ultimate tensile strength of CFRCMCs was deduced theoretically by Curtin[14], as shown by the equation as

$$\sigma_s = \varphi_f \sigma_c \left(\frac{2}{m+1}\right)^{1/(m+1)} \left(\frac{m+1}{m+2}\right) \qquad (1)$$

where φ_f represents the fiber volume fraction in tensile direction (i. e. x direction), σ_c is the characteristic strength of fibers, m is the Weibull modulus of fiber strength distribution. The m volue of carbon fibers used in this study is measured to be 4.02 by testing the monofilament strength of as-received fibers. Here we estimate approximately the ultimate tensile strength of 3D-B C$_f$/ Si-O-C composites by assuming that σ_c is equal to the average strength of carbon fibers(3 GPa). The fiber volume fractions in tensile directions of samples A, B and C are 32%, 34.4% and 38.4%, respectively, and the ultimate tensile strengths of sample A, B and C are then calculated to be 666.4, 716.4, and 799.7 MPa, respectively. It was reported that bending strength are approximately 1.4 times of the tensile strength in CFRCMCs[15]. Therefore the predicted bending strengths of samples A, B and C are obtained as 933, 1 003, and 1 119.6 MPa, respectively. Compared with the mea-

sured values in Table 2, it can be noted that the measured bending strengths of samples A, B and C are about 26.4%, 38.8%, and 44.8% of the predicted values. Therefore, it may be suggested that the insitu strengths of carbon fibers in samples A, B and C are 26.4%, 38.8% and 44.8% of characteristic strength of carbon fibers, respectively. 2) The densities of samples B and C are increased because the large quantities of pores due to rapid pyrolysis and the large size lenticular-shaped pores resulted from the decomposition of Si-O-C matrix are eliminated by the 10 MPa pressure. 3) Carbon fibers are protected by compacted matrix from reacting with DVB/PSO solution in subsequent cycles to create strong interfacial bonding and reduction in fiber strength.

In addition, the increase of fiber volume fraction resulted from pressure is partially responsible for the higher mechanical properties of samples B and C than those of sample A. Taking samples A and C for example, fiber volume fraction in tensile direction of sample A is 32% and sample C 38.4%. As mentioned above, the extra 6.4% in fiber volume fraction in tensile direction of sample C can increase theoretically the bending strength by 186.6 MPa. The actual increase in bending strength of sample C is 83.6 MPa since the in-situ strength of carbon fibers in sample C is 44.8% of characteristic strength of carbon fibers, which is only 32.7% of the span between the bending strengths of samples A and C. The rest 67.3% is thankful to the weakened interfacial bonding and increased in-situ strength of carbon fibers.

The results of previous study[13] show that the decomposition of Si-O-C begins to occur at approximately 1 200 ℃ and becomes obvious at above 1 400 ℃. The decomposition extent of Si-O-C interphase at 1 300 ℃ is low and the decomposition is completed at 1 600 ℃. Consequently, the interfacial bonding of sample B is stronger than that of sample C and the in-situ strength of carbon fibers in sample B is lower than that in sample C. At the same time, the decomposition extent of Si-O-C matrix at 1 600 ℃ is much higher than that at 1 300 ℃. As a result, matrix in sample C is much looser than that in sample B. The increases in fiber volume fraction and density of sample C due to the 10 MPa pressure are greater than those of sample B. In short, the higher mechanical properties of sample C compared with sample B are attributed to weaker interfacial bonding, higher density and in-situ strength of carbon fibers, and higher

fiber volume fraction.

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