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Effects of pyrolysis processes on microstructure and mechanical properties of C_f/Si–O–C composites fabricated by preceramic polymer pyrolysis

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Abstract

Three-dimensional braided carbon fiber reinforced silicon oxycarbide (3D-B C_f/Si–O–C) composites were fabricated by multiple polysiloxane impregnation and pyrolysis cycles, and the effects of pyrolysis processes on microstructures and mechanical properties were investigated. Increasing heating rate of each cycle could not weaken interfacial bonding and would lower flexural strength due to the pores resulting from rapid pyrolysis. Increasing the pyrolysis temperature of the first cycle from 1000 °C to 1600 °C could weaken interfacial bonding to a certain extent. At the same time, many pores derived from high temperature and rapid pyrolysis were created, decreasing flexural strength. The mechanical properties of 3D-B C_f/Si–O–C composites could be improved when the pyrolysis temperature of the seventh cycle was increased from 1000 °C to 1400 °C because of the weakened interfacial bonding.

The mechanical properties and densities of 3D-B C_f/Si–O–C composites could be remarkably increased if the first pyrolysis was assisted by hot-pressing. When the first pyrolysis was conducted at 1600 °C for 5 min with a pressure of 10 MPa, the resultant composites showed 502 MPa in flexural strength and 23.7 MPa $m^{1/2}$ in fracture toughness while the composites fabricated without the assistance of hot-pressing showed only 246.2 MPa in flexural strength and 9.4 MPa $m^{1/2}$ in fracture toughness. The high mechanical properties were mainly attributed to desirable interfacial structure and high density.

Keywords: A. Precursors; B. Interfaces; C. Mechanical properties; Silicon oxycarbide; Carbon fiber; Ceramic-matrix composites

1. Introduction

Continuous fiber reinforced ceramic-matrix composites (CFRCMCs) show promise for overcoming the brittleness of monolithic ceramics and are attractive materials for applications requiring low specific weight and 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), etc.

The PIP route is gaining 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 and coworkers [1]. Of all the precursors for PIP, polysiloxane (PSO) has attracted increasing interest 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 as a desirable precursor for low-cost CFRCMCs with high performance.

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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. Weak interfacial bonding and high density can result in high mechanical properties. The microstructures of CFRCMCs are governed by fabrication process. The manufacturing of CFRCMCs via PIP includes three stages. In stage 1, fiber preform is infiltrated with precursor solution. In stage 2, the precursor is cured into a solid. In stage 3, the cured solid is pyrolyzed in inert or reactive environment. Several infiltration-cure-pyrolysis cycles are required to densify composites because evolution of gaseous products and volume shrinkage occur during pyrolysis, resulting in microcracks and pores in matrix. Of the three stages, pyrolysis is the most important stage because interfacial structures and the content and morphology of pores are mainly determined in this stage. Consequently, pyrolysis process plays a key role in determining the mechanical properties of PIP-derived CFRCMCs.

However, there is little work concerning the effects of pyrolysis process on the microstructures and mechanical properties of CFRCMCs. In this paper, three-dimensional braided carbon fiber reinforced silicon oxycaribde (3D-B C_f/Si–O–C) composites were fabricated via PIP route, and the effects of different pyrolysis processes on the microstructures and mechanical properties of 3D-B C_f/Si–O–C composites were investigated.

2. Experimental

Polysiloxane (PSO), a colorless transparent liquid containing 1.4 wt.% hydrogen, was selected as the precursor to Si–O–C ceramics. Divinylbenzene (DVB), a light yellow transparent liquid, was used as the cross-linking reagent for PSO. Chloroplatinic acid (H_2PtCl_6), dissolved in anhydrous ethanol, was used as the catalyst. The cure and pyrolysis behaviors of DVB/PSO were reported earlier [5-7].

Carbon fibers with tensile strength of 3000 MPa and elastic modulus of 210 GPa were selected for this study. Fiber volume fraction in x, y, z directions of three-dimensional braided carbon fiber preform was 8:1:1.

Four batches of 3D-B C_f/Si–O–C composites were fabricated by different pyrolysis processes. The first batch of 3D-B C_f/Si–O–C composites included sample C7, sample C8, and sample C9, which were fabricated by repeating seven, eight, and nine cycles of vacuum infiltration-curing-pyrolysis, respectively. The pyrolysis of each cycle of the three samples was conducted at 1000 °C for 60 min with a heating rate of 1 °C/min. Detailed pyrolysis parameters of the second, the third and the fourth batch of 3D-B C_f/Si–O–C composites are shown in Tables 1–3, respectively.

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

Table 1
Pyrolysis parameters of each cycle of the second batch of 3D-B C_f/Si–O–C composites

Sample	Pyrolysis parameters of each cycle					
	First cycle			Second–eighth cycle		
	Heating rate (°C/min)	Pyrolysis temperature (°C)	Holding time (min)	Heating rate (°C/min)	Pyrolysis temperature (°C)	Holding time (min)
HR-1 (i.e. C8)	1	1000	60	1	1000	60
HR-2	5	1000	60	1	1000	60
HR-3	10	1000	60	1	1000	60
HR-4	30	1000	60	1	1000	60
HR-5	10	1000	60	10	1000	60
HR-6	30	1000	60	30	1000	60

Table 2
Pyrolysis parameters of each cycle of the third batch of 3D-B C_f/Si–O–C composites

Sample	Pyrolysis parameters of each cycle					
	First–sixth and the eighth cycles			Seventh cycle		
	Heating rate (°C/min)	Pyrolysis temperature (°C)	Holding time (min)	Heating rate (°C/min)	Pyrolysis temperature (°C)	Holding time (min)
HT-0 (i.e. C8)	1	1000	60	1	1000	60
HT-1	1	1000	60	30	1400	10
HT-2	1	1000	60	30	1400	30

Table 3
Pyrolysis parameters of each cycle of the fourth batch of 3D-B C_f/Si–O–C composites

Sample	Pyrolysis parameters of each cycle						
	First cycle				Second–seventh cycle		
	Heating rate (°C/min)	Pyrolysis temperature (°C)	Holding time (min)	Pressure (MPa)	Heating rate (°C/min)	Pyrolysis temperature (°C)	Holding time (min)
HP-0 (i.e. C7)	1	1000	60	0	1	1000	60
HP-1	30	1300	30	10	1	1000	60
HP-2	30	1600	5	10	1	1000	60

3. Results and discussion

3.1. Influence of the number of pyrolysis cycle on mechanical properties of 3D-B C_f/Si–O–C

For a long period of time, the typical pyrolysis of PIP has been conducted under atmospheric pressure with a heating rate of less than 5 °C/min in order to reduce the shrinkage and a temperature between 900 °C and 1200 °C because the pyrolytic conversion of preceramic polymer to ceramics is completed at approximately 800 °C and 1000 °C.

The mechanical properties of sample C7, C8 and C9, which were fabricated by the typical pyrolysis processes, are presented in Table 4. As shown, the flexural strength and fracture toughness of the three samples were about 250 MPa and 10.0 MPa $m^{1/2}$, respectively. It can be noted that the increase of pyrolysis cycle number (i.e. from 7 to 9) did not change mechanical properties much when the number of pyrolysis cycle was over seven. Fig. 1 shows the fracture surface of sample C8, which is representative of the three samples. It is clear that sample C8 showed little fiber pull-out and the pull-out length was very short, indicating that interfacial bonding was very strong.

Table 4
Flexural strength and fracture toughness of sample C7, C8 and C9

	Sample		
	C7	C8	C9
Pyrolysis cycle	7	8	9
Flexural strength (MPa)	246.2	265.1	266.5
Fracture toughness (MPa $m^{1/2}$)	9.4	10.1	—

For CFRCMCs, in situ strength of fibers dominates the flexural strength and interfacial bonding determines the fracture toughness. In the three samples, the diffusion of Si atoms into carbon fibers was observed, as shown in Fig. 2. 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 interfacial bonding and a great reduction in fiber strength [8–10]. Accordingly, the three samples exhibited low flexural strength and fracture toughness.

According to the results of the study of Hähnel et al. [11], the O atoms in glass matrix could diffuse into fibers. So, it is rationally proposed that the interphase resulting from the

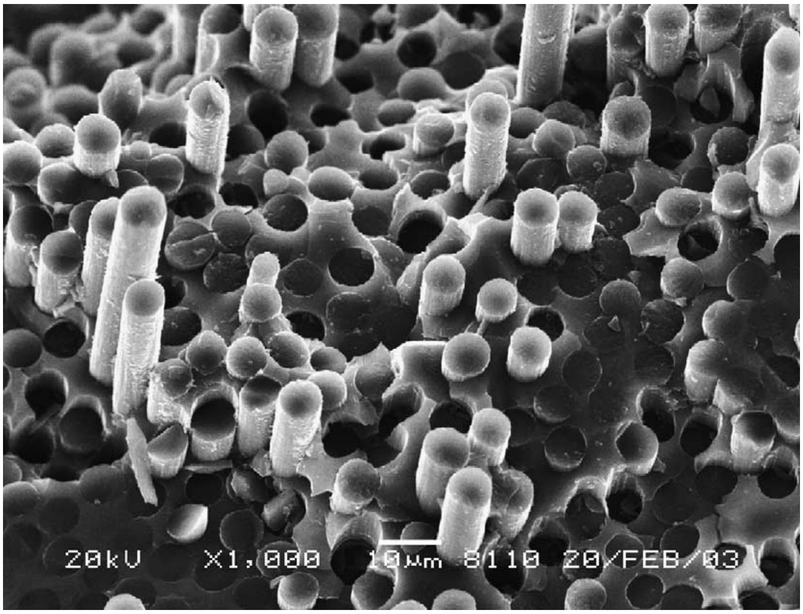

Fig. 1. A representative SEM photo of fracture surface of sample C8 (i.e. sample HT-0), HR series, and HP-0.

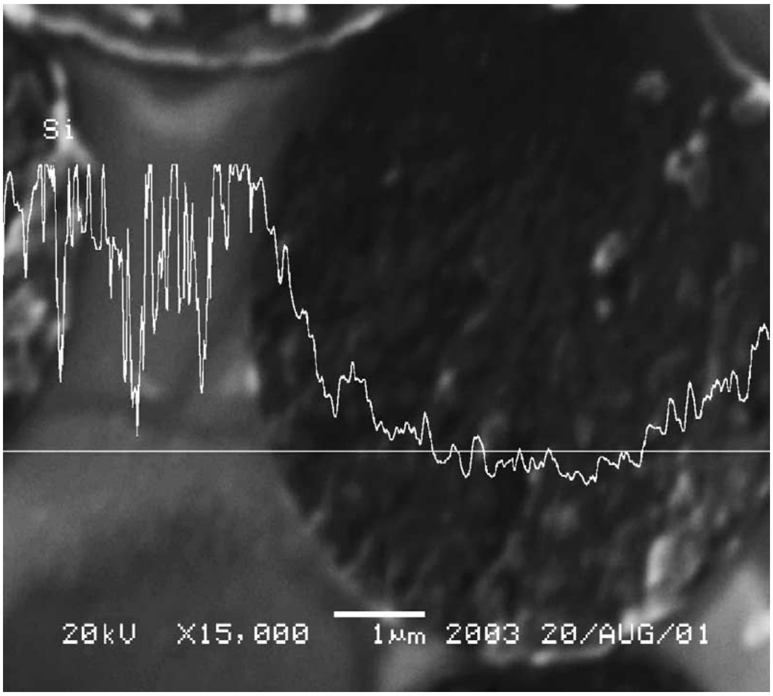

Fig. 2. Characteristic X-ray line profile of Si atom in sample C8.

diffusion of Si atoms into carbon fibers consisted of Si, C, and O in which oxygen atoms were derived from surface sizing of carbon fibers and Si–O–C matrix.

3.2. *Influence of heating rate on microstructures and mechanical properties of 3D-B C_f/Si–O–C*

Based on the results above, weak interfacial bonding and increased in situ strength of carbon fibers, and also high mechanical properties will be obtained if the degree of diffusion of Si atoms into fibers is reduced. Increasing heating rate is expected to be able to shorten the time of reaction or diffusion between matrix and carbon fibers, and then reduce the degree of diffusion of Si atoms into fibers.

The effects of the heating rate of the first pyrolysis on the microstructures and mechanical properties were investigated firstly since the first pyrolysis had significant influence on interfacial structure [12,13]. Table 5 shows the flexural strengths of sample HR series. It can be found that the flexural strengths of sample HR-1, HR-2, and HR-3 were almost the same when the heating rate of the first pyrolysis was increased from 1 °C/min to 10 °C/min. Fig. 1 shows the fracture surface of sample HR-1, which is representative of the three samples.

When the heating rate of the first pyrolyis reached 30 °C/min, the resultant sample HR-4 exhibited lower flexural strength compared with sample HR-1. The fracture surface of sample HR-4 is almost the same as sample HR-1 (Fig. 1). Sample HR-4 illustrated flat fracture surface with very short fiber pull-out, demonstrating strong interfacial bonding. In this study, it was found that the cured DVB/PSO "blasted" when pyrolyzed with a heating rate of 30 °C/min, resulting in large quantities of pores in composites. These pores were detrimental to flexural strength [14] on the one hand and resulted in many fibers being uncoated by matrix on the other hand. The uncoated fibers reacted with DVB/PSO solution in subsequent cycles to create strong interfacial bonding. As a result, the flexural strength of sample HR-4 was inferior to that of sample HR-1.

As shown in Table 5, the flexural strength of the resultant sample HR-5 was only about 50% of that of sample HR-3 when each pyrolysis was performed with a heating rate of 10 °C/min. The fracture surface of sample HR-5 is almost the same as sample HR-1, as shown in Fig. 1 in which flat fracture surface with very short fiber pull-out was also observed, demonstrating that the interfacial bonding of sample HR-5 was very strong. In this sample, large size lenticular-shaped pores were observed, as shown in Fig. 3.

Table 5
Influence of heating rate on flexural strength of 3D-B C_f/Si–O–C

	Sample					
	HR-1	HR-2	HR-3	HR-4	HR-5	HR-6
Heating rate of the first PIP cycle (°C/min)	1	5	10	30	10	30
Flexural strength (MPa)	265.1	233.2	265.7	173.9	118.5	167.6

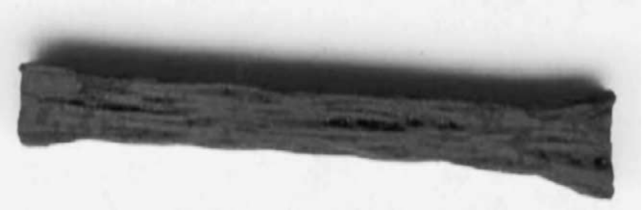

Fig. 3. Large size lenticular-shaped pores in sample HR-5 and PT.

How the pores were created was not clear, but it was reported that the pores could result in much decrease in flexural strength even at low porosity levels [14]. Consequently, the flexural strength of sample HR-5 was much lower than that of sample HR-3. When each pyrolysis was carried out with a heating rate of 30 °C/min, the flexural strength of the resultant sample HR-6 was also much lower than that of sample HR-1. Fig. 1 shows the fracture surface of sample HR-6, indicating strong interfacial bonding. As mentioned above, the strong interfacial bonding and the lower flexural strength of sample HR-6 were ascribed to pores derived from rapid pyrolysis, respectively.

It can be inferred from the above results that increasing heating rate could not weaken interfacial bonding and enhance flexural strength, and resulted in decrease in flexural strength because of the pores derived from rapid pyrolysis on the contrary.

3.3. Influence of pyrolysis temperature on microstructures and mechanical properties of 3D-B C_f/Si–O–C

Our previous studies [5–7] showed that the Si–O–C phase was metastable and would decompose at above 1200 °C. It is expected that increasing pyrolysis temperature could weaken interfacial bonding and enhance mechanical properties.

Sample PT was fabricated to investigate the effects of the pyrolysis temperature of the first cycle on microstructure and flexural strength. The first pyrolysis of sample PT was carried out at 1600 °C for 5 min with a heating rate of 30°C/min and the second–eighth pyrolysis were performed under the same conditions as sample HR-4.

The fracture surface of sample PT is presented in Fig. 4. It can be found that the length of some pulled-out carbon fibers was much longer than that of sample HR-4, demonstrating that the interfacial bonding of sample PT was weaker than that of sample HR-4. The decomposition of interphase consisting of Si–O–C at 1600 °C was suggested being responsible for the weakened interfacial bonding. However, the flexural strength of sample PT was 173.4 MPa that was almost equal to that of sample HR-4. It can be seen from Fig. 4 that sample PT showed as many pulled-out fibers as sample HR-4, suggesting that the interfacial bonding was still strong. In this sample, large size lenticular-shaped pores (as shown in Fig. 3) were also observed. These pores were attributed to the decomposition of Si–O–C matrix at above 1200 °C since such pores were not observed in sample HR-4. As stated in previous paragraph, the large size lenticular-shaped pores and the pores resulting from rapid pyrolysis were responsible for the still strong interfacial bonding and low flexural strength of sample PT.

Table 6 shows the mechanical properties of sample HT series whose fabrication processes are presented in Table 2. As shown, sample HT-0 (i.e. C8), which was fabricated through eight cycles of pyrolysis at 1000 °C, exhibited the lowest flexural strength and fracture toughness.

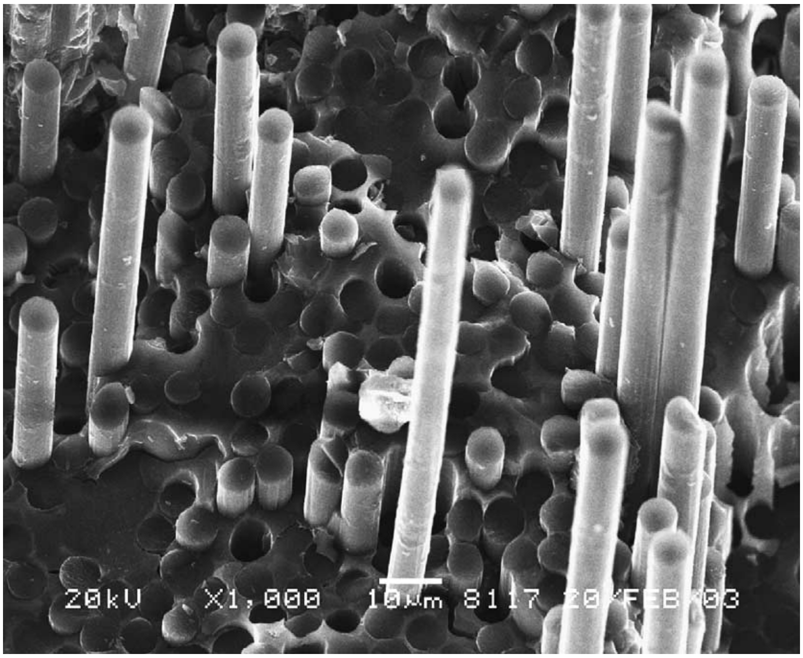

Fig. 4. SEM photo of fracture surface of sample PT.

Table 6
Mechanical properties of sample HT series

	Sample		
	HT-0	HT-1	HT-2
Flexural strength (MPa)	265.1	388.7	455.1
Fracture toughness (MPa $m^{1/2}$)	10.1	13.0	14.8

When the seventh pyrolysis was performed at 1400 °C for different time, the resultant sample HT-1 and HT-2 showed much higher flexural strength and fracture toughness compared with those of sample HT-0. In addition, no large size lenticular-shaped pores that existed in sample PT were observed in the three samples. Figs. 5 and 6 show the fracture surfaces of sample HT-1 and HT-2, respectively. In Fig. 5, it can be seen that the number of pulled-out fibers and the pull-out length of sample HT-1 were almost the same as those of sample HT-0 (Fig. 1). However, sample HT-1 illustrated obvious interfacial debonding that was not observed in sample HT-0, indicating that the interfacial bonding of sample HT-1 was weaker than that of sample HT-0. In Fig. 6, obvious interfacial debonding was also observed in sample HT-2. At the same time, sample HT-2 showed more pulled-out fibers compared with sample HT-1, and the pull-out length was longer than that of sample HT-1, demonstrating that the interfacial bonding of sample HT-2 was weaker than that of sample HT-1.

The decomposition of interphase consisting of Si–O–C was responsible for the weakened interfacial bonding and the increased mechanical properties of sample HT-1 and HT-2 compared with sample HT-0. The extent of decomposition increased gradually with the increase of pyrolysis

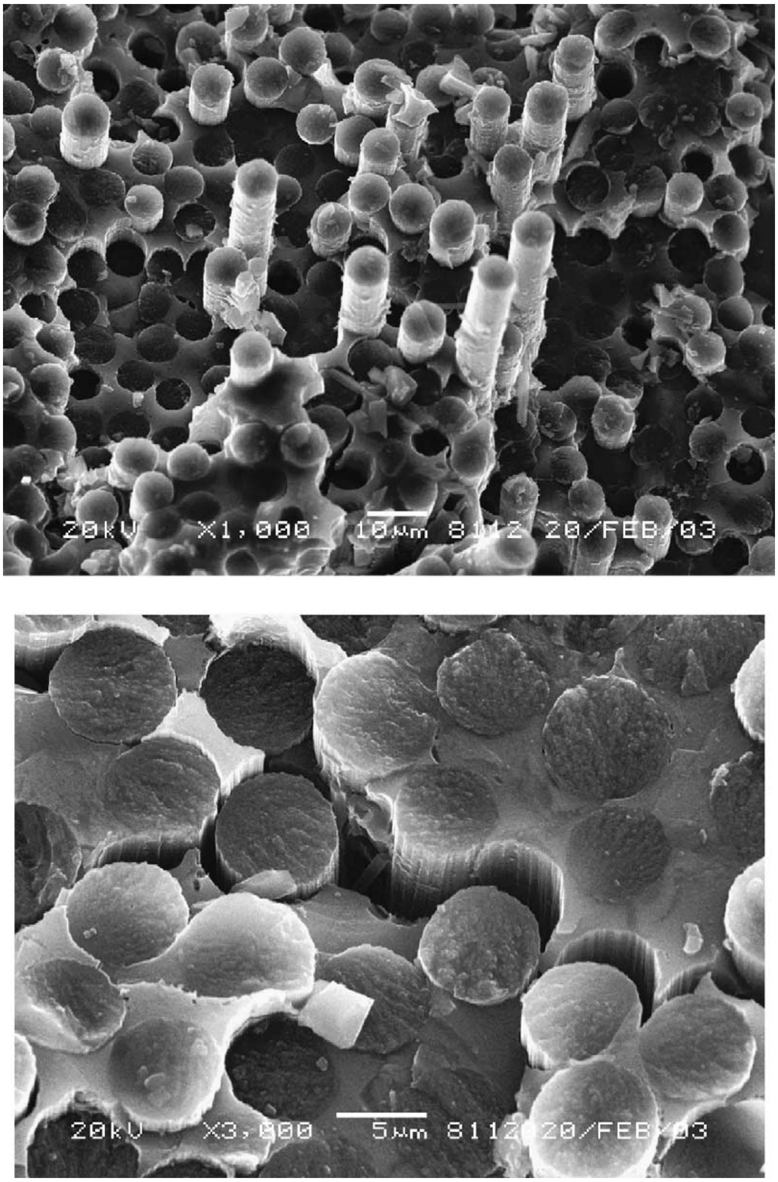

Fig. 5. SEM photos of fracture surface of sample HT-1.

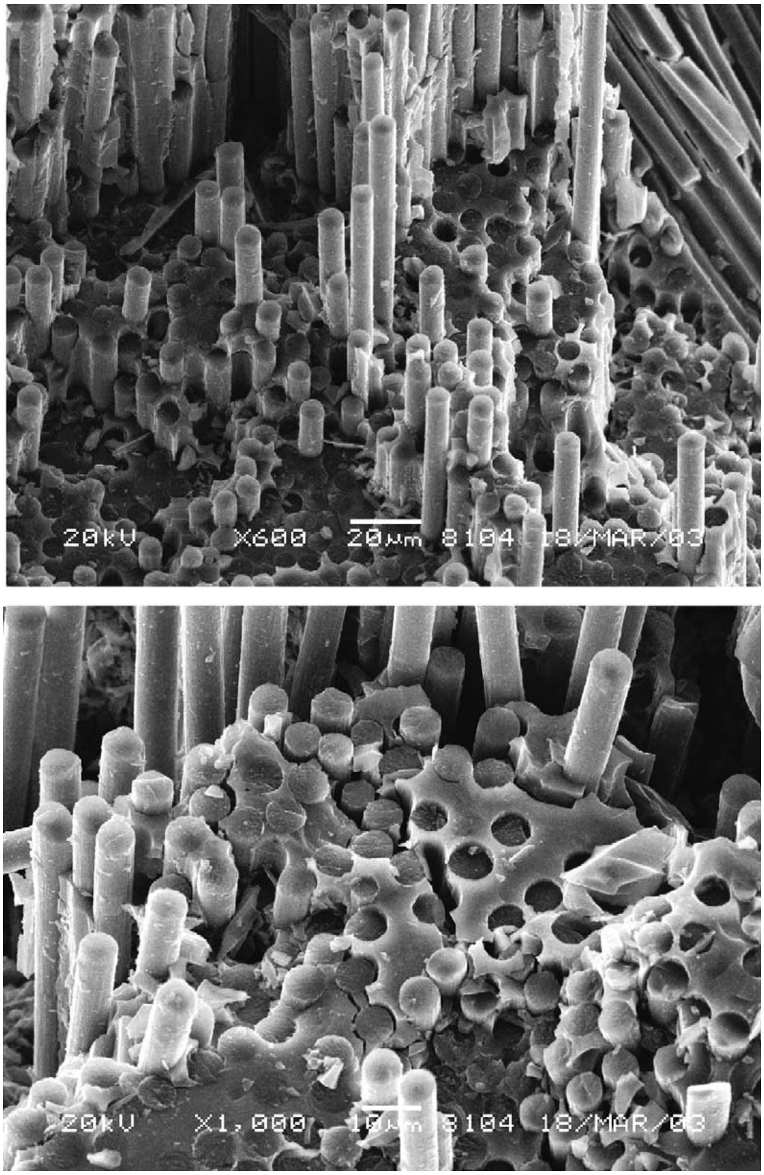

Fig. 6. SEM photos of fracture surface of sample HT-2.

time at 1400 °C. As a result, the interfacial bonding became weaker and weaker and in situ strength of carbon fibers also increased gradually.

3.4. Microstructures and mechanical properties of 3D-B C_f/Si–O–C composites fabricated by hot-pressing-assisted pyrolysis of polysiloxane

In Section 3.3, it was found that the interfacial bonding of 3D-B C_f/Si–O–C composites could be weakened to a certain extent when the first pyrolysis was performed at 1600 °C with a heating rate of 30 °C/min. At the same time, many pores were created due to high temperature and rapid pyrolysis, leading to the decrease in mechanical properties. So, high density is a key factor to obtain 3D-B C_f/Si–O–C composites with high mechanical properties.

Hot-pressing is an effective method to increase the density of composites. In the study of Nakano et al. [10], 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 interfacial bonding were observed. As a result, the mechanical properties were low. In their subsequent study [15], temperature and pressure were optimized, and the mechanical properties were increased because of desirable interfacial structure and high density.

Contrary to the studies of Nakano and coworkers [10,15], hot-pressing was performed in the first cycle in this paper. Table 3 shows the fabrication processes of sample HP series whose mechanical properties and densities are presented in

Table 7
Mechanical properties and densities of sample HP series

Sample	Flexural strength (MPa)	Fracture toughness (MPa m$^{1/2}$)	Density (g cm^{-3})	Theoretical density (g cm^{-3})
HP-0	246.2	9.4	1.728	1.844
HP-1	388.9	16.7	1.742	1.840
HP-2	502.0	23.7	1.780	1.833

Note. Theoretical density was defined as $\nu_f\rho_f + (1 - \nu_f)\rho_m$, where ν_f was fiber volume fraction, and ρ_f and ρ_m were the densities of fiber and matrix, respectively. ρ_m was measured to be 1.90 g cm^{-3}. ρ_f was 1.76 g cm^{-3}. Fiber volume fractions of sample HP-0, HP-1 and HP-2 were 40%, 43% and 48%, respectively.

Table 7. As shown, the mechanical properties and densities of sample HP-1 and HP-2 were superior to those of sample HP-0, demonstrating that the mechanical properties and densities could be increased if the first pyrolysis was assisted by hot-pressing.

Figs. 1, 7 and 8 show the fracture surfaces of sample HP-0, HP-1, and HP-2. In Fig. 1, sample HP-0 showed little fiber pull-out and the pull-out length was very short, indicating that the interfacial bonding was very strong. In the SEM photo of sample HP-1 (Fig. 7), many pulled-out fibers were observed, and the pull-out length was much longer than that of sample HP-0, indicating that the interfacial bonding of sample HP-1 was weaker than that of sample HP-0. However, it can be found that there was some matrix debris adhering to pulled-out fibers, indicating that the interfacial bonding was still locally strong. Of the three samples, sample HP-2 (Fig. 8) illustrated the most extensive fiber pull-out and the longest pull-out length. In addition, obvious interfacial debonding and smooth fiber surface were observed in Fig. 8, indicating that the interfacial bonding was the weakest.

In sample HP-1 and HP-2, no large size lenticular-shaped pores that existed in sample PT were observed. The only difference between fabrication processes of sample PT and HP-2 was that sample HP-2 was fabricated with a pressure of 10 MPa while sample PT without pressure, so the pores were eliminated by the pressure.

Based on the results above, the reasons why hot-pressing-assisted pyrolysis can enhance the mechanical properties of 3D-B C_f/Si–O–C composites were as follows: (1) The interphase resulting from the diffusion of Si atoms in matrix into carbon fibers decomposed above 1200 °C. As a result, interfacial bonding became weak and in situ strength of carbon fibers increased [16]. (2) The densities of sample HP-1 and HP-2 were increased because the large quantities of pores due to rapid pyrolysis and the large size lenticular-shaped pores resulting from the decomposition of Si–O–C matrix were eliminated by the 10 MPa pressure. (3) Carbon fibers were protected by compacted matrix from reacting with DVB/PSO solution in subsequent cycles, thus preventing the formation of strong interfacial bonding. In addition, the increase of fiber volume fraction resulting from pressure was also responsible for the higher mechanical properties of sample HP-1 and HP-2 than those of sample HP-0, but only in a small part [16].

The differences of interfacial bonding and mechanical properties between sample HP-1 and HP-2 were ascribed to the different pyrolysis temperatures, which has been analyzed in detail in our previous study [16].

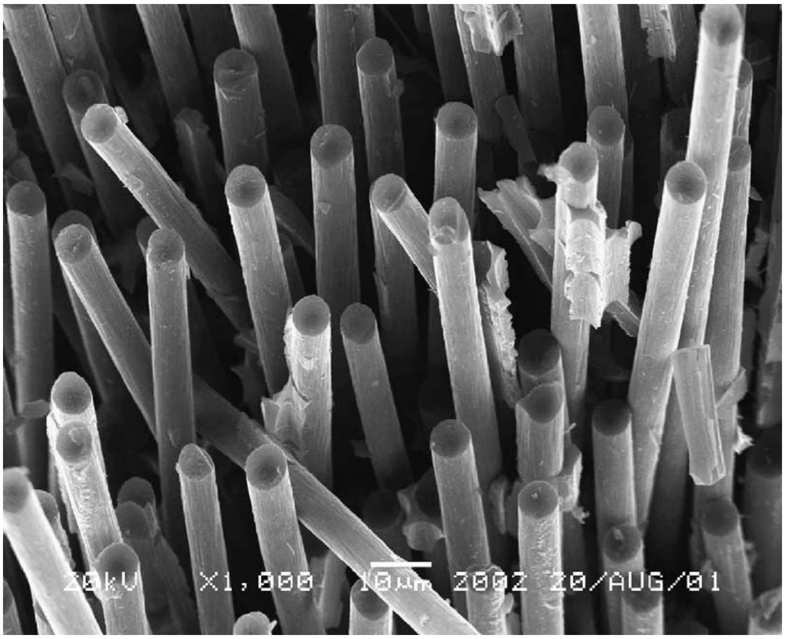

Fig. 7. SEM photo of fracture surface of sample HP-1.

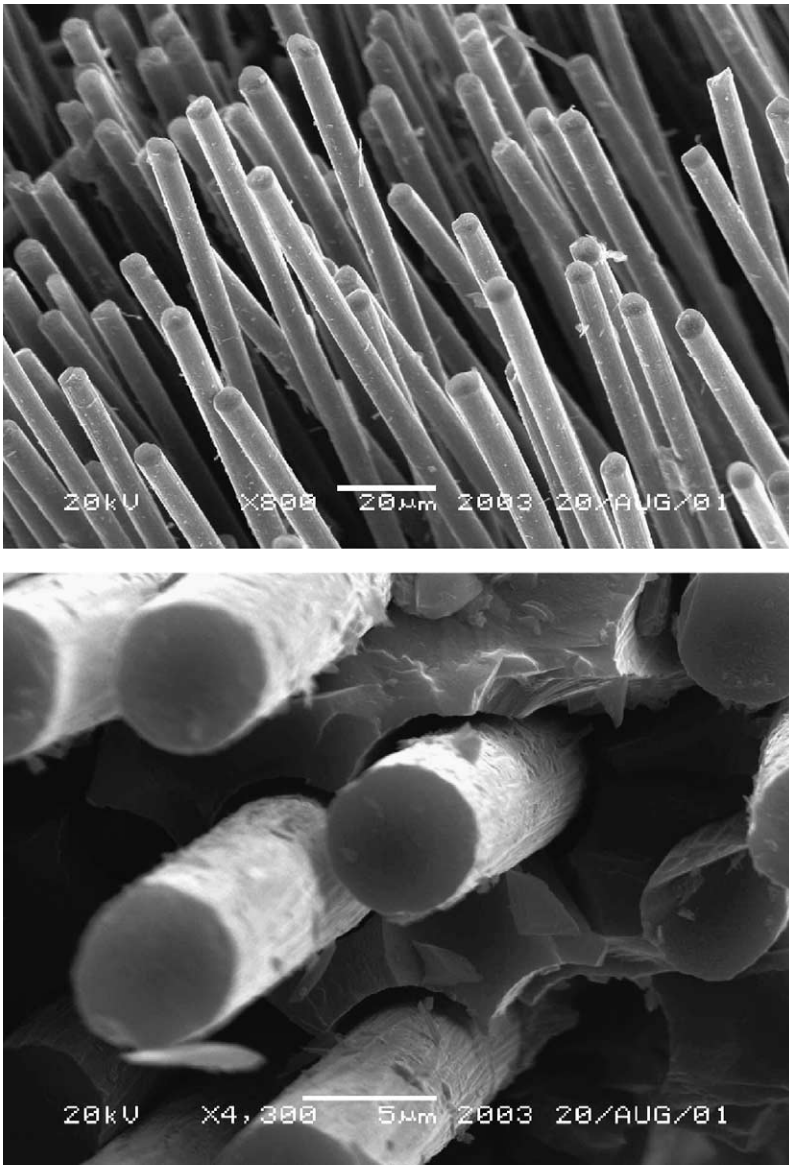

Fig. 8. SEM photos of fracture surface of sample HP-2.

4. Conclusions

3D-B C_f/Si–O–C composites were fabricated by polysiloxane impregnation and pyrolysis, and the effects of pyrolysis processes on microstructures and mechanical properties were investigated. The following generalized conclusions can be drawn:

(1) The atoms in Si–O–C matrix could diffuse into carbon fibers during fabrication, creating strong interfacial bonding and low mechanical properties.
(2) Increasing heating rate of each pyrolysis cycle could not weaken interfacial bonding and enhance mechanical properties. On the contrary, it caused decrease in flexural strength due to the pores resulting from rapid pyrolysis.
(3) Increasing the pyrolysis temperature of the first cycle from 1000 °C to 1600 °C could weaken interfacial bonding to a certain extent. However, many pores derived from high temperature and rapid pyrolysis were created, resulting in decrease in flexural strength. The mechanical properties of 3D-B C_f/Si–O–C composites could be improved when the pyrolysis temperature of the seventh cycle was increased from 1000 °C to 1400 °C because of the weakened interfacial bonding. When the seventh pyrolysis was performed at 1400 °C for 30 min, the flexural strength and fracture toughness of 3D-B C_f/Si–O–C were increased from 265.1 MPa and 10.1 MPa $m^{1/2}$ to 455.1 MPa and 14.8 MPa $m^{1/2}$, respectively.
(4) The mechanical properties and densities of 3D-B C_f/Si–O–C composites could be remarkably increased if the

first pyrolysis was assisted by hot-pressing. When the first pyrolysis was conducted at 1600 °C for 5 min with a pressure of 10 MPa, the resultant composites showed 502 MPa in flexural strength and 23.7 MPa $m^{1/2}$ in fracture toughness while the composites that was fabricated without assistance of hot-pressing showed only 246.2 MPa in flexural strength and 9.4 MPa $m^{1/2}$ in fracture toughness. The high mechanical properties were mainly attributed to desirable interfacial structure and high density.

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