Microstructures and mechanical properties of three-dimensional C_f/Si—O—C composites fabricated by polysiloxane pyrolysis

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The precursor-infiltration-pyrolysis (PIP) route to processing of continuous fiber reinforced ceramic matrix composites (CFRCMCs) has attracted increasing interest 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 development by Yajima *et al.* [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.

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 pores and microcracks in composites resulting 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 of 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 low. In their subsequent study [8], temperature and pressure were optimized, and the mechanical properties were increased because of desirable interfacial structure and high density.

In contrast to the study of Nakano *et al.* [7], hot-pressing was performed in the first cycle in this paper, and the effects of processing variables on mechanical properties and microstructures of three-dimensional braided carbon fiber reinforced Si—O—C composites (3D-B C_f/Si—O—C) were discussed.

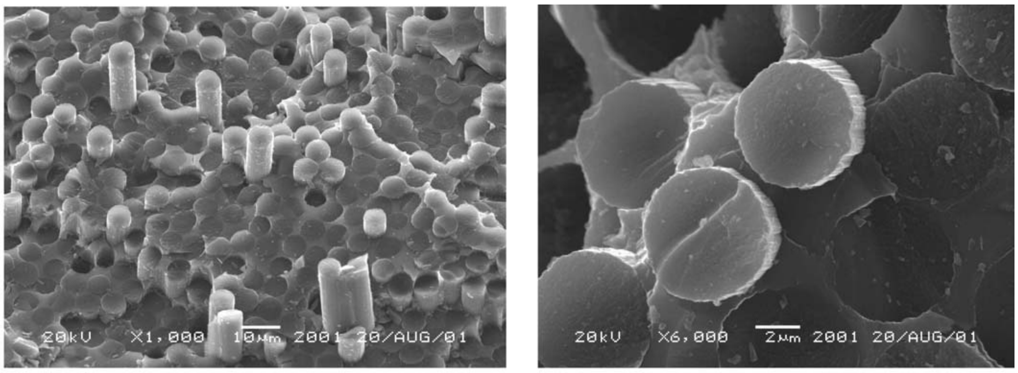
In this study, polysiloxane (PSO), a colorless transparent liquid containing 1.4 wt% hydrogen, was selected as precursor to Si—O—C ceramics. Divinylbenzene (DVB), a light yellow transparent liquid, was selected as cross-linking reagent for the PSO. Chloroplatinic acid (H_2PtCl_6), dissolved in anhydrous ethanol, was used as catalyst. The cure and pyrolysis of DVB/PSO were reported earlier [9, 10]. Carbon fibers with tensile strength of 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.

Carbon fiber preform was infiltrated with PSO/DVB solution under vacuum for 1 hr, then cured at 120 °C for 6 hr. The first pyrolysis was carried out under two processing conditions, e.g., (A) the cured sample was pyrolyzed under atmospheric pressure at 1000 °C for 60 min with a heating rate of 1 °C/min. (B) the cured sample was hot-pressed at 1600 °C for 5 min with a heating rate of 30 °C/min and a pressure of 10 MPa. Then, the two samples, denoted as sample A and sample B, were densified by repeating six cycles of vacuum infiltration and pyrolysis under the same condition as processing A. In all cases, high purity flowing N_2 was used as protective atmosphere.

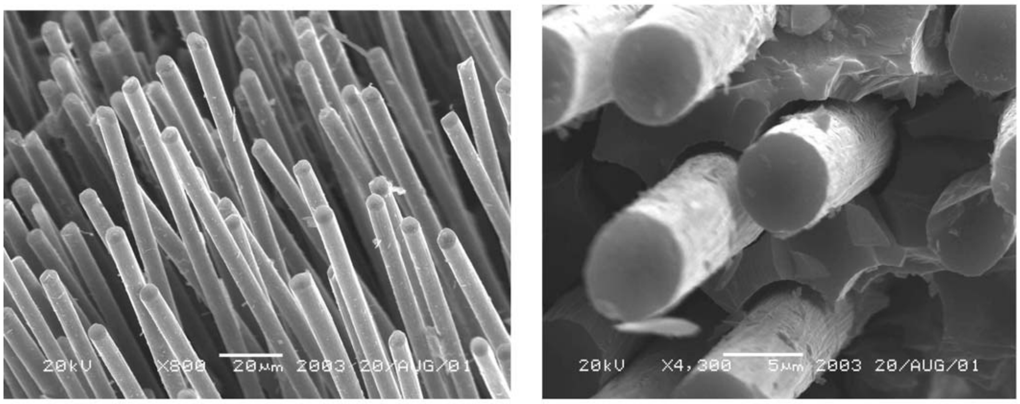
The bulk densities of sample A and B were measured according to Archimedes' principle with deionized water as immersion medium. Each data point was an average of eight values. The flexural strength was tested by a three-point bending method with the span/height ratio of 15 and a cross-head speed of 0.5 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 0.48. 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.

The mechanical properties and densities of sample A and B are summarized in Table I. As shown, the mechanical properties and density of sample B are superior to those of sample A, demonstrating that the mechanical properties and density of 3D-B C_f/Si—O—C composites is increased if the first pyrolysis was assisted by hot-pressing.

Figs 1 and 2 show the fracture surfaces and load-displacement curves of sample A and B, respectively. It is clear from Fig. 1 that sample A shows little fiber pull-

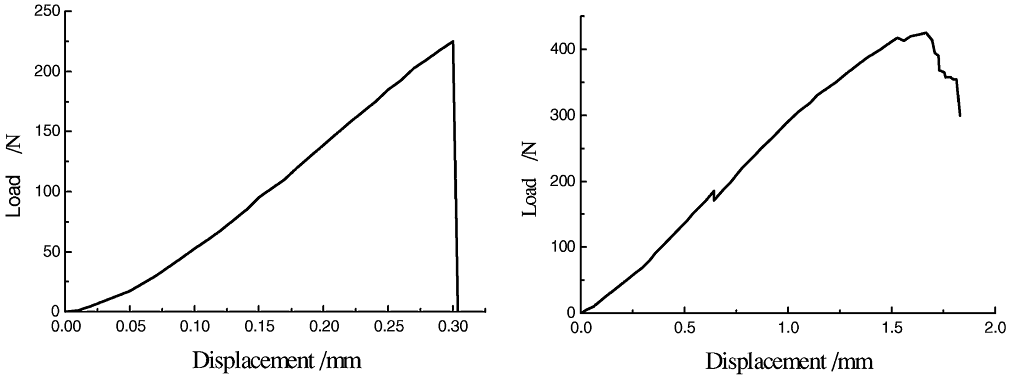


Sample A



Sample B

Figure 1 SEM photos of fracture surfaces of sample A and B.



sample A

sample B

Figure 2 Load-displacement curves of sample A and B.

out and the pull-out length is very short, indicating that fiber/matrix bonding is very strong. Consequently, sample A exhibited typical brittle fracture behavior (Fig. 2). In this sample, it was found that Si atoms diffused into the carbon fibers during fabrication, as shown in Fig. 3. The diffusion of Si atoms in matrix into carbon fibers is responsible for the low mechanical properties of sample A because it has been documented 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]. It is proposed that the interphase resulting from the 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.

TABLE I The mechanical properties and densities of sample A and B

Sample	Flexural strength (MPa)	Fracture toughness (MPa$\sqrt{m}$)	Density (g · cm^{-3})
A	246.2	9.4	1.728
B	502.0	23.7	1.780

In the SEM image of the fracture surface of sample B, many pulled-out fibers are observed, and the pull-out length is much longer than that of sample A. In addition, obvious interfacial debonding is also observed, indicating that fiber/matrix bonding is weak. Accordingly, sample B showed tough fracture behavior (Fig. 2).

TABLE II Processing parameters of each cycle and flexural strengths of sample HR and PT

Sample	HR	PT
Flexural strength /MPa	173.9	173.4

HR: RT (30 °C/min) → 1000 °C, hold 60 min (the 1st cycle) + RT (1 °C/min) → 1000 °C, hold 60 min (the 2nd–7th cycle).
PT: RT (30 °C/min) → 1600 °C, hold 5 min (the 1st cycle) + RT (1 °C/min) → 1000 °C, hold 60 min (the 2nd–7th cycle).

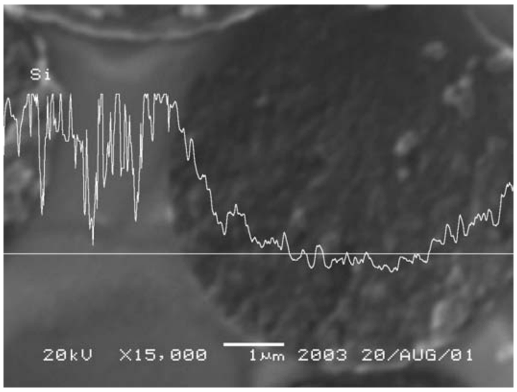


Figure 3 Characteristic X-ray line profile of Si atom.

In order to elucidate why the first pyrolysis carried out at 1600 °C for 5 min with a pressure of 10 MPa can improve the mechanical properties of 3D-B C_f/Si—O—C composites, sample HR and PT were fabricated by repeating seven cycles of vacuum infiltration-curing-pyrolysis under atmospheric pressure. Detailed processing parameters and flexural strength are shown in Table II.

As shown, when the first pyrolysis was carried out at 1000 °C for 60 min with a heating rate of 30 °C/min, the flexural strength of sample HR is inferior to that of sample A, indicating that increasing the heating rate of the first pyrolysis cannot enhance flexural strength. The decrease in flexural strength of sample HR compared with sample A is attributed to the still strong fiber/matrix bonding (Fig. 4) and the pores resulting from rapid pyrolysis. 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 [12] 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 fiber/matrix bonding.

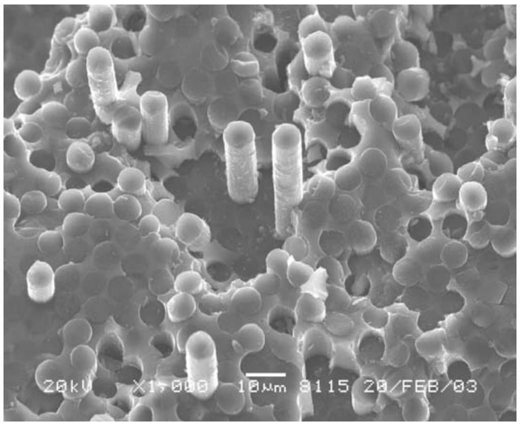


Figure 4 SEM photo of fracture surface of sample HR.

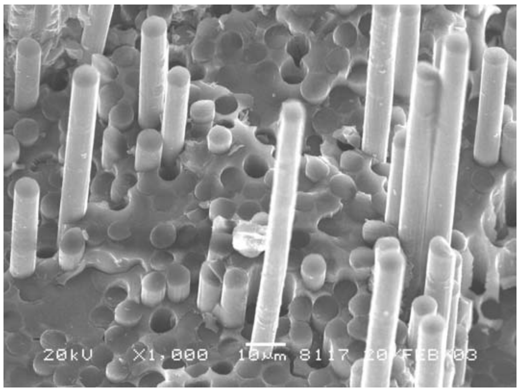


Figure 5 SEM photo of fracture surface of sample PT.

As shown in Table II, when the first pyrolysis was performed at 1600 °C for 5 min with a heating rate of 30 °C/min, the flexural strength of sample PT is also lower than that of sample A. Fig. 5 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. Decomposition of interphase consisting of Si—O—C at above 1400 °C is responsible for the weakened fiber/matrix bonding [9, 10]. However, the pulled-out fibers are almost as many as those of sample A, indicating that the fiber/matrix bonding is still strong. In this sample, large size lenticular-shaped pores were observed, as shown in Fig. 6. These pores resulted from the decomposition of Si—O—C matrix because no such pores were found in sample HR. As mentioned above, these large size lenticular-shaped pores and the large quantities of pores resulting from rapid pyrolysis are responsible for the still strong fiber/matrix bonding and the low flexural strength of sample PT.

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

Based on the above results, the high mechanical properties of sample B are attributed to: (1) The interphase resulting from the diffusion of Si atoms in matrix into the carbon fibers was decomposed at above 1400 °C. As the results, fiber/matrix bonding became weak and *in-situ* strength of carbon fibers increased. (2) The density of sample B was increased because the large quantities of pores derived form 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.

Figure 6 Large size lenticular-shaped pores in sample PT.

In summary, 3D-B C_f/Si—O—C composites were fabricated through the PIP route. The mechanical properties and density of 3D-B C_f/Si—O—C composites could be increased if the first pyrolysis was assisted by hot-pressing. The flexural strength and fracture toughness of the composite, which was hot-pressed at 1600 °C for 5 min with a pressure of 10 MPa in the first cycle and treated subsequently with six cycles of vacuum infiltration and pyrolysis under atmospheric pressure, are 502 MPa and 23.7 MPa$\sqrt{\text{m}}$, respectively. The high mechanical properties are attributed to desirable interfacial structure and high density.

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