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Effects of 1600 °C annealing atmosphere on the microstructures and mechanical properties of C/SiC composites fabricated by precursor infiltration and pyrolysis

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Abstract

Effects of 1600 °C annealing atmosphere on microstructures and mechanical properties of the C/SiC composites fabricated by PIP route were remarkable. Due to carbothermic reductions, the ratios of weight loss of the C/SiC composites were all above 7 wt% in 1 h. Consequently, the mechanical properties all had a significant drop during the first hour of annealing because of the bonding between the fibers and matrix remarkably weaken by cracks and pores. And then the flexural strengths gradually decreased with the annealing time increasing, when the flexural moduli slightly changed within the range of 44.2–49.7 GPa. However, the fracture behaviors of the C/SiC composites annealed under Ar faster became brittle than the C/SiC composites annealed under vacuum. The C/SiC composites annealed under Ar for 5 h and under vacuum for 10 h both became brittle mainly due to the sensitive to annealing of the weak carbon interphase, while the C/SiC composites annealed under Ar for 7 h became brittle mainly due to the chemical bonding between the fibers and matrix. And these phenomena were confirmed by the post densification and the stress-releasing annealing.

Keywords: B. Interface; C. Mechanical properties; C/SiC composites; PIP route; Annealing

1. Introduction

Continuous carbon fiber reinforced silicon carbide composites (C/SiC) are a promising way to improve the fracture toughness of the bulk ceramics [1]. And compared with carbon/carbon composites, C/SiC composites exhibit good mechanical properties and excellent oxidation resistance properties [2]. Therefore, several processes have been developed to fabricate the composites, including slurry infiltration and hot pressing [3,4], precursor infiltration and pyrolysis (PIP) [5–8], chemical vapor infiltration [9,10] and liquid silicon infiltration [11]. The PIP route has advantages as follow: great composition homogeneity, forming unique multiphase matrix and ease of infiltration of forming. Additionally, near-net-shaped composite components can be fabricated by this method at relatively lower temperatures (900–1200 °C). So as one kind of the most popular methods to fabricate C/SiC composites, the PIP route is highly focused.

It is expected that C/SiC composites can withstand exposure to a service environment up to 1650 °C for applications in space and aero-engine turbines [12]. However, the SiC matrix derived from precursors always contains the excess carbon and heteroatoms (O, N), so the physical and chemical behavior of the matrix, even including the interface between the fibers and matrix, can be changed in a high-temperature environment at 1600 °C [13,14]. Consequently, the mechanical properties of C/SiC composites will be affected [14].

In this paper, three-dimensional braided carbon fiber reinforced silicon carbide composites were fabricated by PIP route using polycarbosilane (PCS), and effects of 1600 °C annealing atmosphere on microstructures and mechanical properties of the C/SiC composites were investigated.

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2. Experimental procedure

2.1. Substrate materials

Three-dimensional braided carbon fiber preforms (T-300, ex-PAN carbon fiber, Toray) with a fiber volume fraction about 45% were used as reinforcements [8]. PCS with molecular weight ~1742 and soften point ~175 °C was used as the matrix precursor.

The C/SiC composites denoted as raw sample were prepared using 9–12 cycles of infiltration of PCS–xylene solution and subsequently pyrolysis at 1200 °C under an inert atmosphere [7]. Then some specimens were further annealed at 1600 °C under vacuum or Ar for various times.

2.2. Analytical methods

Bulk densities of the composites were measured according to the Archimede's principle. Three-point bending tests were used to evaluate the flexural strength and modulus of C/SiC composites with the span/height ratio of 15 and a crosshead speed of 0.5 mm/min. And three specimens were measured for each annealing condition with the size of 3 mm × 4 mm × 70 mm. And the error ranges for all mechanical test data are less than ±16 MPa (or GPa). Fracture surfaces of the specimens after three-point bending tests were examined on the scanning electron microscopy (SEM). The microstructures of the fiber/matrix interface before and after annealing were investigated by the transmission electron microscopy (TEM).

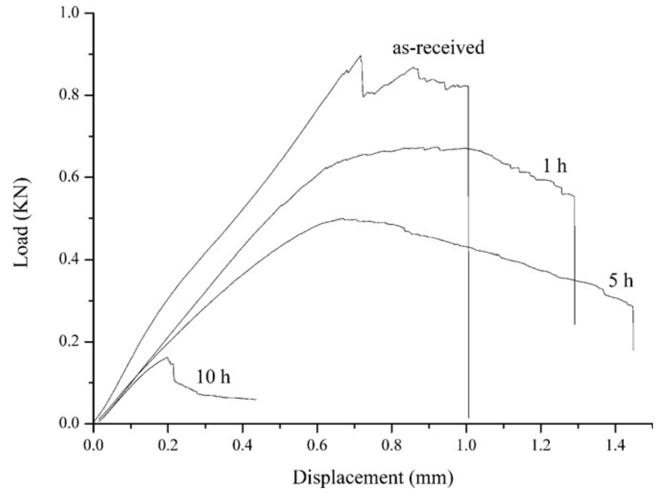

Fig. 1. Load–displacement curves of the C/SiC composites annealed under vacuum for various times.

3. Results and discussions

3.1. Under vacuum, the influence of 1600 °C annealing on microstructures and mechanical properties of the composites

Mechanical properties of the C/SiC composites annealed under vacuum for various times are listed in Table 1. From the data, the ratios of weight loss were all above 8 wt% due to carbothermic reductions [6], and hardly increased with the annealing time increasing. Obviously, the heteroatoms had

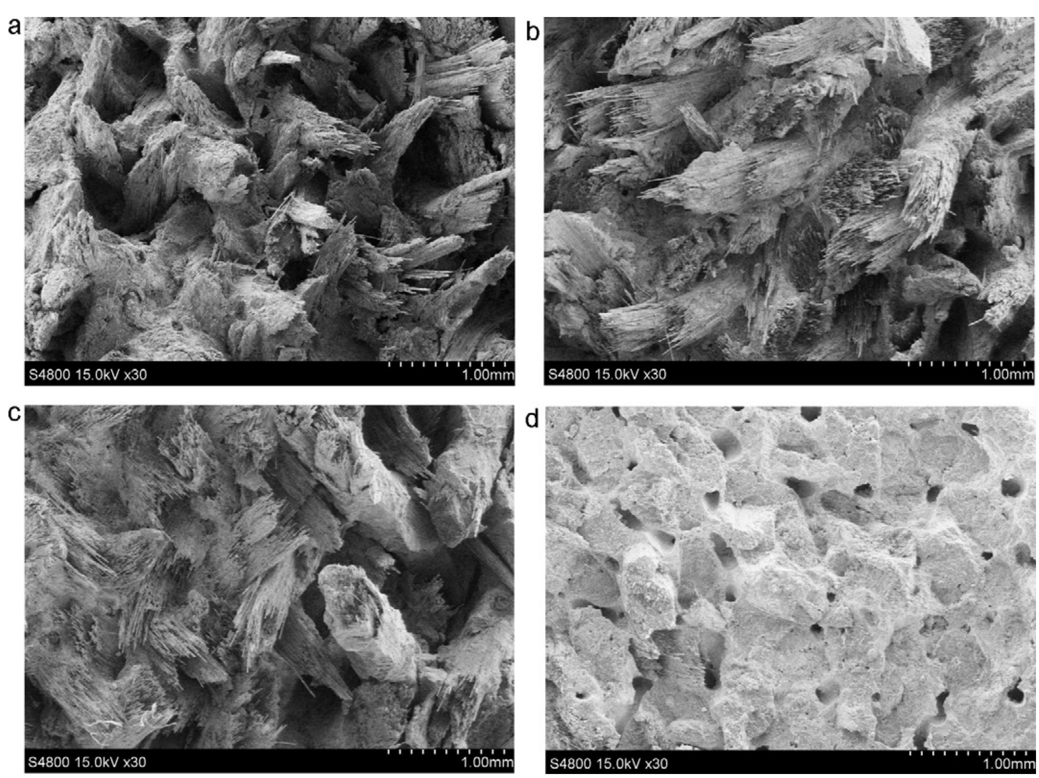

Fig. 2. SEM images of fracture surfaces of the C/SiC composites annealed under vacuum for various times: (a) 0 h, (b) 1 h, (c) 5 h, (d) 10 h.

Table 1
Mechanical properties of the C/SiC composites annealed under vacuum for various times.

Annealing time (h)	Ratio of weight loss (wt%)	Density (g/cm^3)	Flexural strength (MPa)	Flexural modulus (GPa)
–[a]	Null	1.96	473	73.6
1	8.21	1.83	324	44.2
5	8.25	1.85	247	44.4
10	8.37	1.82	92.4	49.7

[a] The raw sample.

been almost released in 1 h, and as a result, many cracks and pores appeared in the matrix. So the mechanical properties of the C/SiC composites had a significant drop during the first hour of annealing because of the bonding between the fibers and matrix remarkably weaken by the cracks and pores. With the annealing time further increasing, the flexural strength of the C/SiC composites slowly decreased, and the flexural modulus slightly changed within the range of 44.2–49.7 GPa. However, the flexural strength of the C/SiC composites annealed for 10 h was very low (only 19.5% of the raw sample) and the fracture mode became brittle from tough, as seen in Fig. 1.

Fig. 1 is load–displacement curves of the C/SiC composites annealed under vacuum for various times. Although the load peaks became lower with the longer annealing time, the fracture mode kept tough until 5 h in Fig. 1. However, when the annealing time was 10 h, the brittle fracture behavior appeared. It was confirmed in Fig. 2, there were no fibers pulled out in the fracture surface of the C/SiC composites annealed for 10 h.

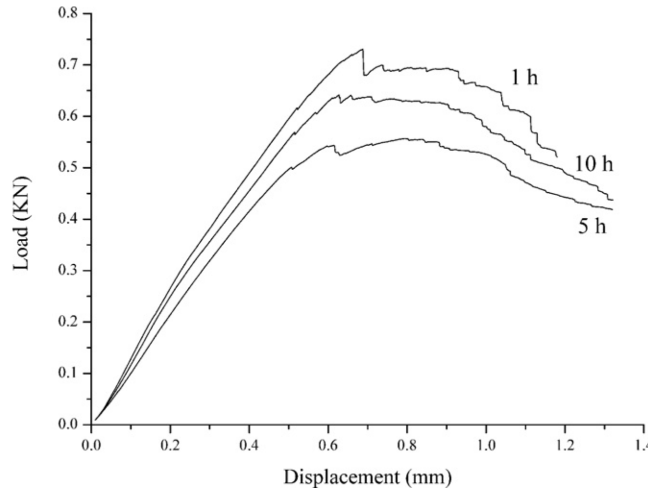

Fig. 3. Load–displacement curves of the C/SiC composites with the post densification after annealed under vacuum.

Due to the matrix shrinkage caused by weight loss and density increase during crystallization, the resistance of the matrix to the reinforcing fiber bundles decreased [14]. So in Fig. 1, the plateau zone of the curves extended when the annealing time increased from 0 to 5 h. In order to eliminate effects of the matrix shrinkage, the annealed C/SiC composites were redensified by 4 cycles of the infiltration and pyrolysis of the PCS–xylene solution (called as the post densification).

Table 2 is the mechanical properties of the annealed C/SiC composites with the post densification. From the data, the mechanical properties of the C/SiC composites all increased

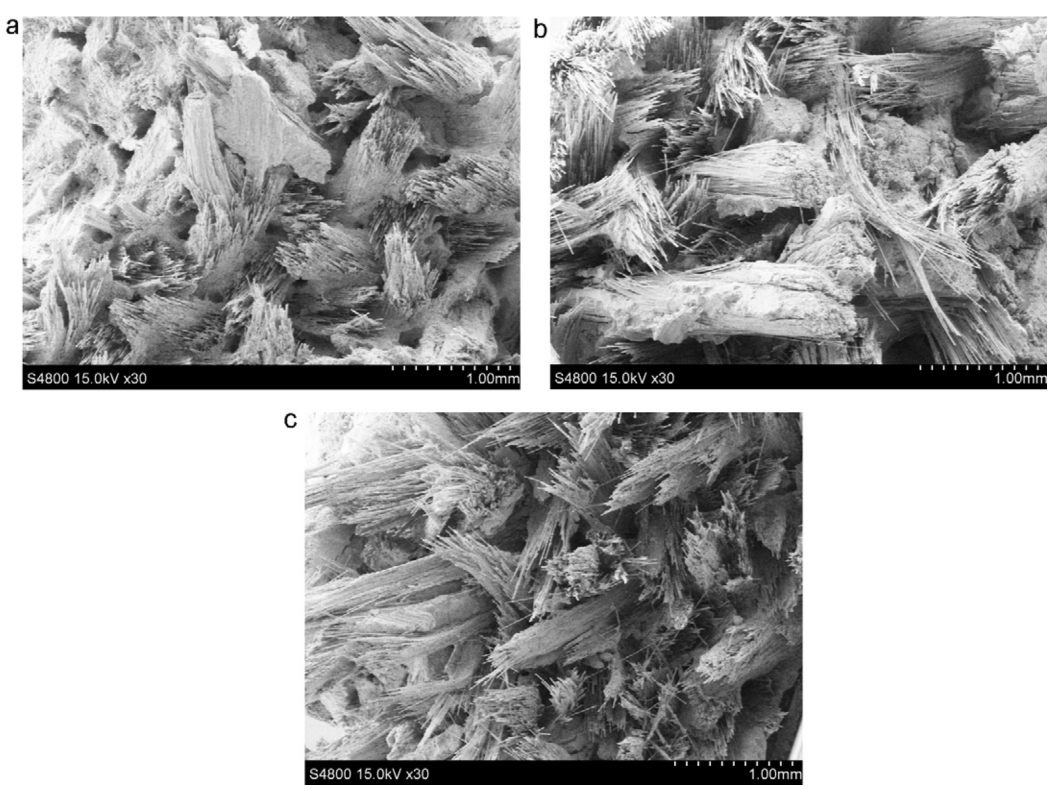

Fig. 4. SEM images of fracture surfaces of the C/SiC composites with the post densification after annealed under vacuum: (a) 1 h, (b) 5 h, (c) 10 h.

Table 2
Mechanical properties of the C/SiC composites with the post densification after annealed under vacuum.

Annealing time (h)	Density (g/cm^3)	Flexural strength (MPa)	Flexural modulus (GPa)
1	1.93	339	67.5
5	1.90	310	68.6
10	1.97	319	65.6

after the post densification. The flexural strengths were all above 310 MPa, while the flexural moduli were all higher than 65 GPa. So the C/SiC composites all had the delayed fracture behavior as shown in Fig. 3. And there were many long fibers pulled out in Fig. 4. Especially after annealed for 10 h, the C/SiC composites with the post densification became tough again.

3.2. Under Ar, the influence of 1600 °C annealing on microstructures and mechanical properties of the composites

Mechanical properties of the C/SiC composites annealed under Ar for various times are listed in Table 3. From the data, the ratios of weight loss of the C/SiC composites remarkably increased in the first hour, and then slowly increased with the annealing time increasing. So the mechanical properties had a significant drop during the first hour of annealing due to the bonding between the fibers and matrix remarkably weaken by cracks and pores. Then the flexural strengths gradually became lower with the longer annealing time, while the flexural moduli kept around 46 GPa. And compared with the C/SiC composites annealed under vacuum, the C/SiC composites annealed under Ar fast became brittle from tough, as seen in Fig. 5.

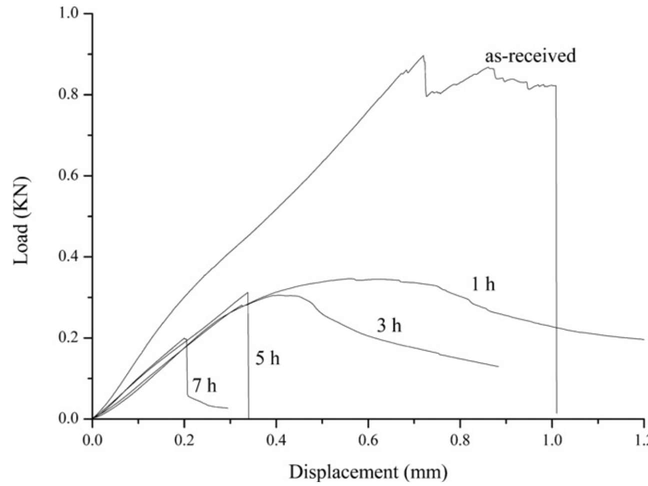

Fig. 5. Load–displacement curves of the C/SiC composites annealed under Ar for various times.

Fig. 5 is load–displacement curves of the C/SiC composites annealed under Ar for various times. In Fig. 5, when the annealing time reached 5 h, the C/SiC composites became brittle from tough. And it was further supported by SEM images in Fig. 6. It showed that there were scarcely fibers pulled out when the annealing time was 5 or 7 h.

The C/SiC composites annealed under Ar also went through the post densification, and the mechanical properties are listed

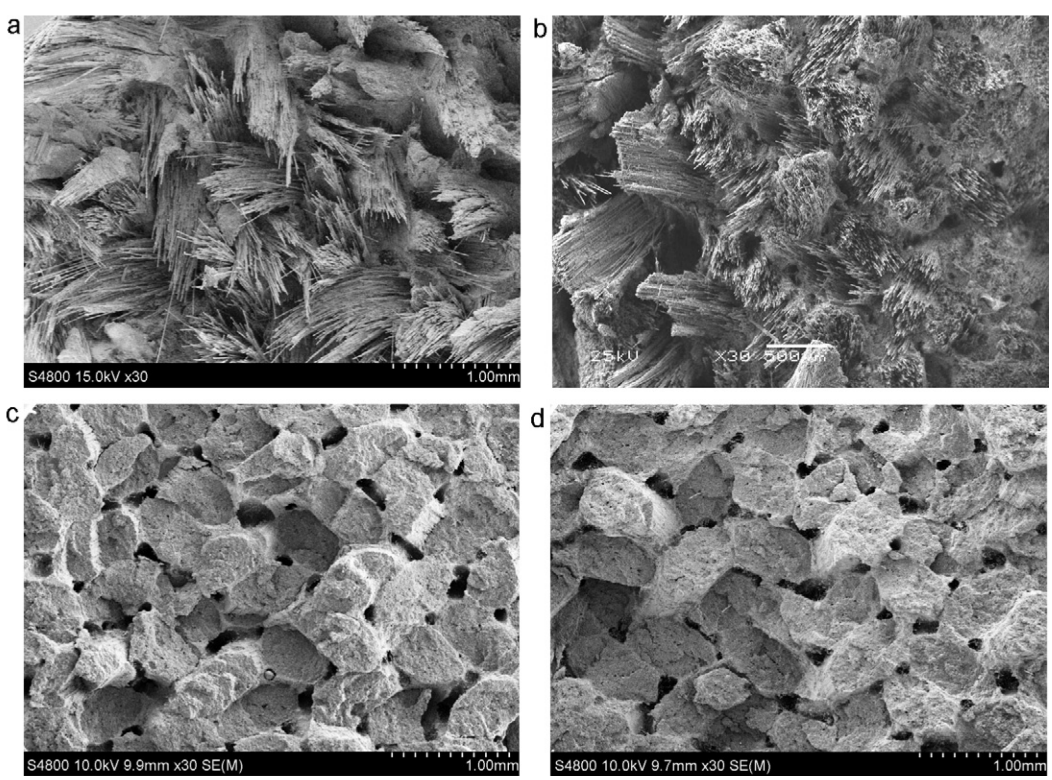

Fig. 6. SEM images of fracture surfaces of the C/SiC composites annealed under Ar for various times: (a) 1 h, (b) 3 h, (c) 5 h, (d) 7 h.

Table 3
Mechanical properties of the C/SiC composites annealed under Ar for various times.

Annealing time (h)	Ratio of weight loss (wt%)	Density (g/cm^3)	Flexural strength (MPa)	Flexural modulus (GPa)
–[a]	Null	1.96	473	73.6
1	7.61	1.91	194	44.9
3	7.75	1.90	175	45.8
5	8.20	1.85	168	45.5
7	8.48	1.81	112	46.4

[a] The raw sample.

Table 4
Mechanical properties of the C/SiC composites with the post densification after annealed under Ar.

Annealing time (h)	Density (g/cm^3)	Flexural strength (MPa)	Flexural modulus (GPa)
1	1.98	423	71.4
3	1.95	403	74.8
5	1.97	329	70.8
7	1.99	153	65.3

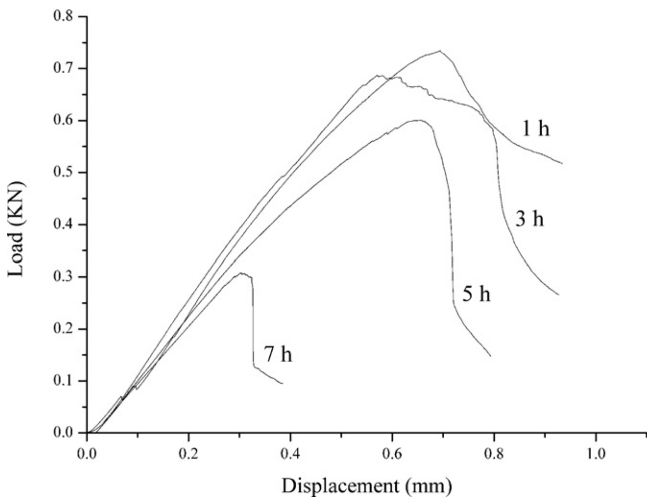

Fig. 7. Load–displacement curves of the C/SiC composites with the post densification after annealed under Ar.

in Table 4. When the annealing time was in 5 h, the flexural strengths of the annealed C/SiC composites recovered above 69% with the post densification and the flexural moduli were all higher than 70 MPa. However, when the annealing time was 7 h, the flexural strengths of the annealed C/SiC composites increased little with the post densification.

Fig. 7 is load–displacement curves of the annealed C/SiC composites with the post densification. In Fig. 7, the C/SiC composites with the post densification still kept brittle after annealing for 7 h, while the others all showed the tough fracture behaviors. It was confirmed in Fig. 8.

Fig. 8 is SEM images of the fracture surfaces of the annealed C/SiC composites with the post densification. After annealed for 1, 3 and 5 h, the C/SiC composites with the post densification had many fibers pulled out in the fracture surfaces. But the annealing time was 7 h, there were no fibers pulled out in the fracture surfaces of the annealed C/SiC composites with the post densification.

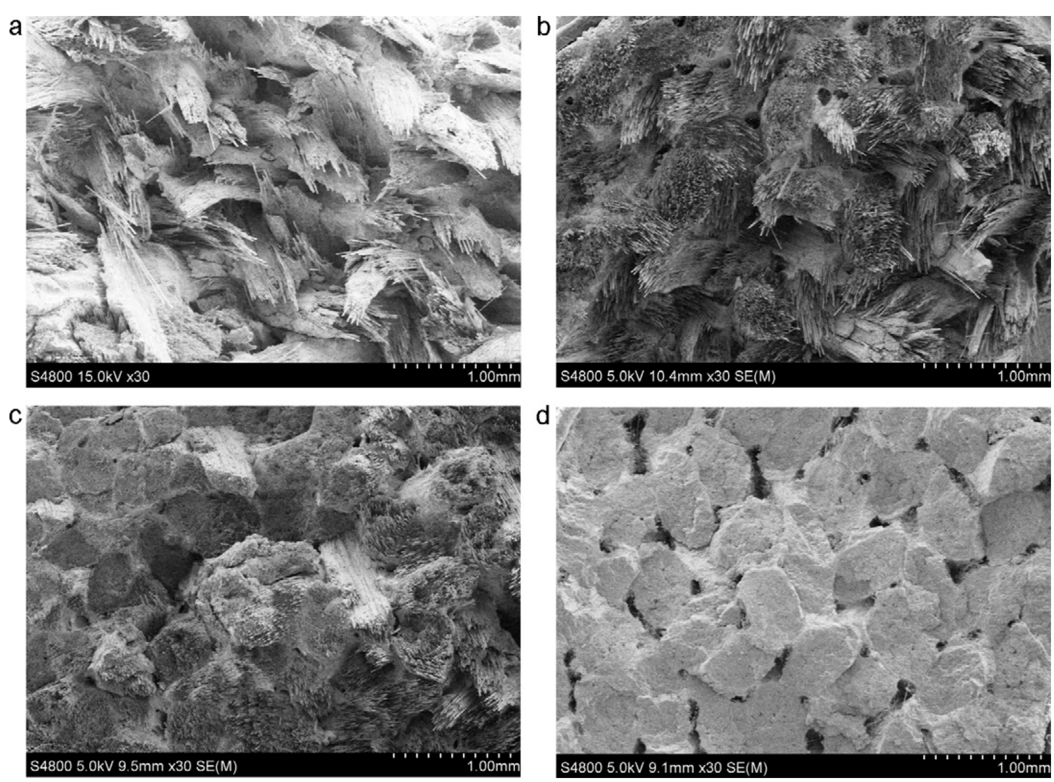

Fig. 8. SEM images of fracture surfaces of the C/SiC composites with the post densification after annealed under Ar: (a) 1 h, (b) 3 h, (c) 5 h, (d) 7 h.

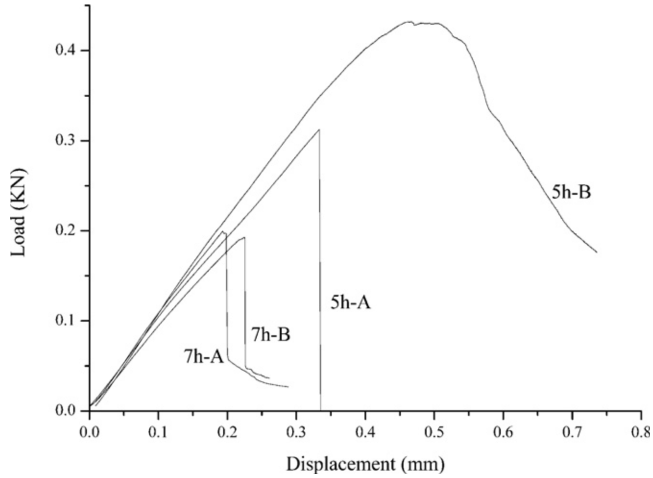

Fig. 9. Load–displacement curves of the Ar atmosphere annealing C/SiC composites with or without the stress-releasing annealing (A was the 1600 °C annealing sample, B was the stress-releasing sample).

3.3. The influence of stress-releasing annealing on microstructures and mechanical properties of the annealed composites

From the former discussions, the effects of the post densification were obviously different on the annealed C/SiC composites, when they became brittle after the 1600 °C annealing. In order to discover their differences, the C/SiC composites annealed at 1600 °C under Ar for 5 and 7 h were sequentially annealed at 1200 °C under Ar for 0.5 h (denoted as the stress-releasing annealing). Mechanical properties of the annealed C/SiC composites with or without the stress-releasing annealing are listed in Table 5.

Table 5
Mechanical properties of the Ar atmosphere annealing C/SiC composites with or without the stress-releasing annealing.[a]

Annealing time (h)	Flexural strength (MPa)		Flexural modulus (GPa)	
	A	B	A	B
5	168	258	45.5	57.0
7	112	120	46.4	53.2

[a] A was the 1600 °C annealing sample; B was the stress-releasing sample.

With the stress-releasing annealing, the mechanical properties of the C/SiC composites annealed for 5 h greatly increased in Table 5, while the mechanical properties of the C/SiC composites annealed for 7 h recovered little. And the changes of fracture behaviors of the C/SiC composites annealed for 5 and 7 h were also different in Fig. 9.

Fig. 9 is load–displacement curves of the 1600 °C annealing C/SiC composites with or without the stress-releasing annealing. With the stress-releasing annealing, only the C/SiC composites annealed for 5 h showed the delayed fracture behavior, because there were many fibers pulled out in Fig. 10(b).

TEM pictures of the fiber/matrix interface before and after annealing are shown in Fig. 11. In Fig. 11(a), there was a weak carbon interphase at the fiber/matrix interface [15], which would be extremely sensitive to annealing. So the C/SiC composites annealed under vacuum for 10 h and under Ar for 5 h both became tough again after the post densification and the

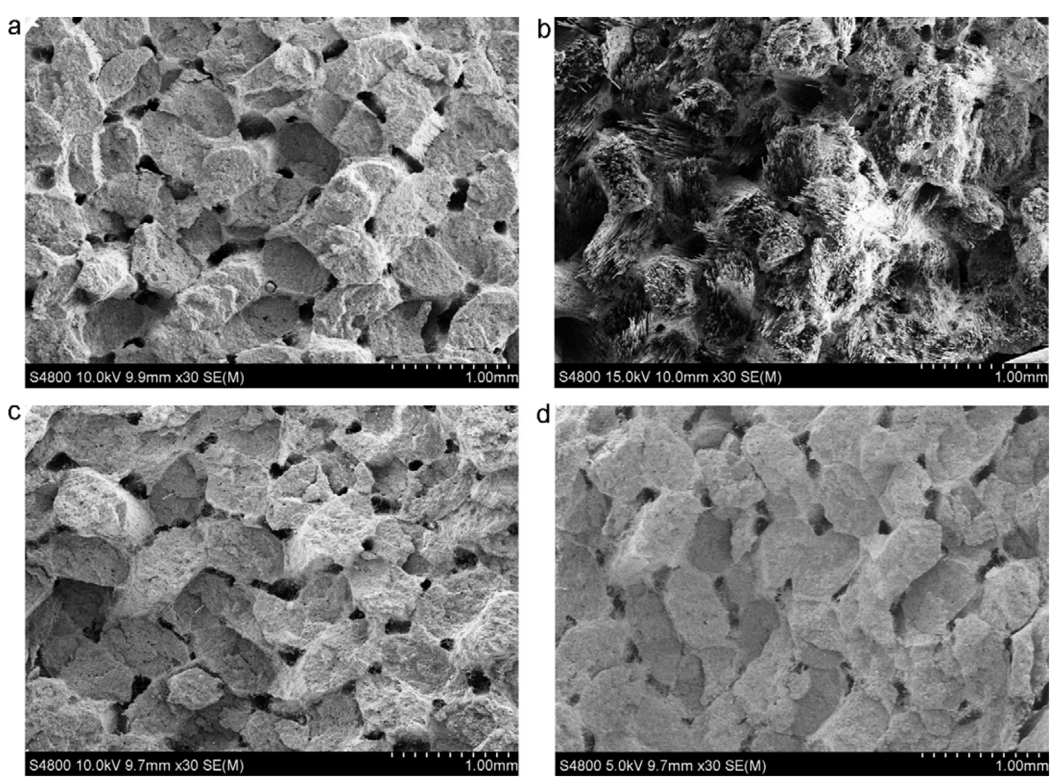

Fig. 10. SEM images of fracture surfaces of the Ar atmosphere annealing C/SiC composites with or without the stress-releasing annealing (A was the 1600 °C annealing sample, B was the stress-releasing sample): (a) 5 h-A, (b) 5 h-B, (c) 7 h-A, (d) 7 h-B.

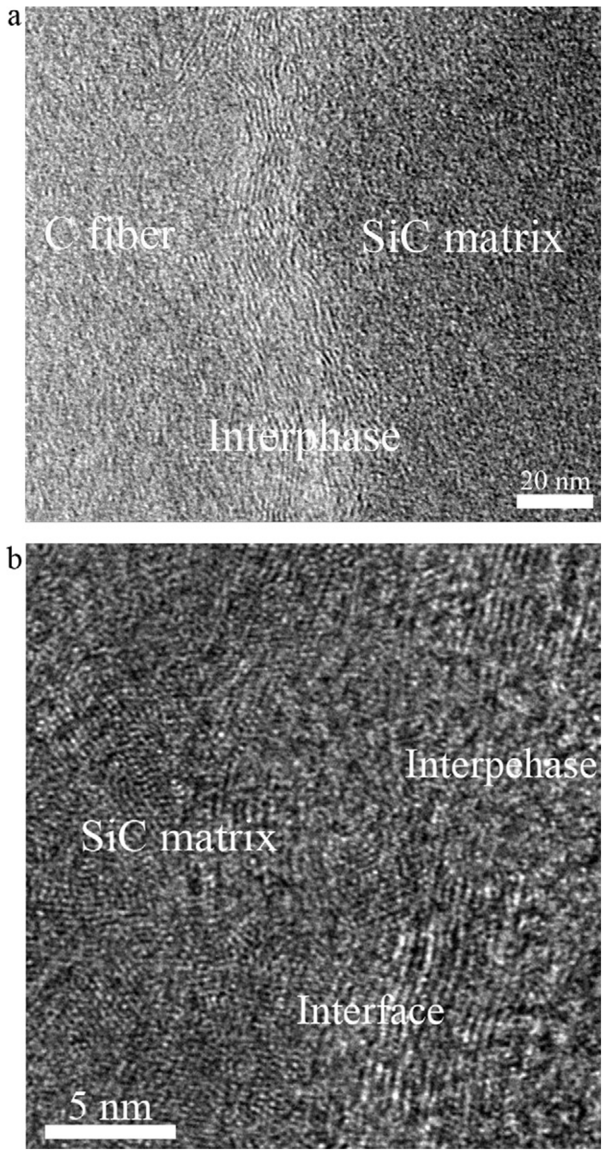

Fig. 11. TEM pictures of the fiber/matrix interface before and after annealing: (a) the raw sample, (b) the sample annealed under Ar for 7 h.

stress-releasing annealing. However, when the C/SiC composites were annealed under Ar for 7 h, the interphases were badly destroyed and the chemical bonding were formed between fibers and matrix in Fig. 11(b). As a result, the C/SiC composites annealed under Ar for 7 h kept brittle after the post densification and the stress-releasing annealing.

4. Conclusions

Effects of 1600 °C annealing atmosphere on microstructures and mechanical properties of the C/SiC composites fabricated by PIP route were remarkable. Due to carbothermic reductions, the ratios of weight loss of the C/SiC composites were all above 7 wt% in 1 h. Consequently, the mechanical properties all had a significant drop during the first hour of annealing because of the bonding between the fibers and matrix remarkably weaken by cracks and pores. And then the flexural strengths gradually decreased with the annealing time increasing, when the flexural moduli slightly changed within the range of 44.2–49.7 GPa. However, the fracture behaviors of the C/SiC composites annealed under Ar faster became brittle than the C/SiC composites annealed under vacuum. The C/SiC composites annealed under Ar for 5 h and under vacuum for 10 h both became brittle mainly due to the sensitive to annealing of the weak carbon interphase, while the C/SiC composites annealed under Ar for 7 h became brittle mainly due to the chemical bonding between the fibers and matrix. Therefore, after annealed under Ar for 5 h or under vacuum for 10 h, the C/SiC composites with the post densification showed tough fracture behaviors again. And after annealed under Ar for 7 h, the C/SiC composites with the post densification kept brittle. Obviously, these phenomena were also confirmed by the stress-releasing annealing.

Acknowledgments

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