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ARTICLE

Microstructure and Properties of C/SiC Composites Prepared by Reactive Melt Infiltration

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Abstract: C/SiC composites were prepared by reactive melt infiltration (RMI) of molten Si into the C/C porous preform. Influences of C/C porous preform embedded in silicon powder at different positions on the capillary absorption behaviors were investigated. Lots of free Si can be found inside of C/SiC composites prepared by RMI. The free Si decreases significantly in amount after desilication treatment of C/SiC composite, the densification degree and flexural strength decrease as well.

Key words: reactive melt infiltration (RMI); C/SiC composites; free Si

C/SiC composite has excellent properties such as low density, high specific strength, high specific modulus, oxidation resistance below 1600 °C and ablation resistance at 2000 °C. It has very strong application prospects in aerospace and other high-tech fields[1-4]. Common methods for preparing C/SiC composites include chemical vapor infiltration[5-7], hot pressing, precursor pyrolysis[8,9] and reactive melt infiltration (RMI), etc[10-12]. Among them, RMI is a kind of competitive production process, which uses liquid silicon to infiltrate C/C porous body to obtain C/SiC material. It has the characteristics of low cost, short production cycle and good performance. A lot of research work has been done on RMI technology, such as the principle of liquid silicon infiltration, the reaction mechanism of silicon and carbon, and the influence of infiltration parameters on material properties[13-17].

At present, the embedding method was widely used to prepare C/SiC materials by RMI. There is no report about the effect of the relative position of C/C porous body and silicon powder on infiltration. In addition, there was a large amount of free silicon in the C/SiC material prepared by RMI method, but little research has been done on the effect of free silicon on the microstructure and properties of the material. In this paper, the microstructure, phase composition and bending properties of C/SiC material prepared by RMI method were compared by removing silicon.

1 Experiment

The preform was made of T700 carbon fibers, which were arranged in sequence by 0° weft-free cloth, tire net layer and 90° weft-free cloth, and needled. The preform was prepared by CVI method, in which CVI-C was mainly wrapped around the fiber periphery. After the interface layer was prepared, porous carbon matrix was prepared by impregnation and pyrolysis of phenolic resin. The C/C porous body consists of the small holes in the bundle, the fetal reticulum layer and the larger holes near the needle bundle. With the increase of the density of C/C porous body, the porosity of C/C porous body decreased, and the thickness of CVI-C layer wrapped by fibers was about 800 nm. In addition, with the increase of the density of C/C porous body, the small holes in the fiber bundle decreased gradually. When the density was 1.35~1.45 g/cm^3, the holes in the C/C porous body were mainly distributed in the fetal reticulum layer and the large holes near the needle bundle, while the inner of the fiber bundle was denser.

C/C porous body (100 mm×100 mm×12 mm) was placed in a graphite crucible with SiC coating. The crucible was embedded with Si powder (the mass was 1.6~1.8 times of C/C porous body). The vacuum degree of crucible was −0.1 MPa and the reaction temperature was 1700 °C.

The density of C/SiC material was measured by Archimedes

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drainage method. The phase composition of C/SiC materials was analyzed by X-ray diffraction (XRD). The surface morphology of C/SiC materials was characterized by field emission scanning electron microscopy (ZEISS Supra55/3187). Three-point bending strength and modulus of C/SiC material was tested by electronic universal testing machine.

2 Results and Discussion

The conditions for the chemical reaction to be carried out are Gibbs free energy $\Delta G=\Delta H-T\Delta S<0$, and the reaction equation for molten Si and C at high temperature is as follows:

$Si(l)+C(s)\rightarrow SiC(s)$ $\Delta G=-47$ kJ/mol (1430 °C)

So judging from the thermodynamic conditions, the infiltration reaction of liquid Si and C can be carried out.

2.1 Effect of silicon location on density of C/SiC material prepared by reactive melting infiltration

As shown in Fig.1, the density of C/C porous body is 1.40 g/cm^3, the size of specimen is 106 mm×13 mm×12 mm (12 mm is *Z* direction), the total height of silicon powder is about 45 mm, and part of the specimen is embedded vertically in silicon powder for siliconizing treatment. After infiltration, 9 samples of 10 mm×10 mm×10 mm are processed from top to bottom (sawing seam is about 2 mm), and the samples are labeled 1~9 in turn. The positions of samples 1~5 are above the surface of silicon cloth and 6~9 are below the surface of silicon cloth. The density distribution of sample after infiltration is shown in Fig.2.

As shown in Fig.2, the density of sample 5 near the upper surface of silicon cloth is the highest. The density of the sample embedded in silicon powder and exposed in the surface decreases with the increase of the distance from the upper surface of silicon cloth.

It is harder to adsorb liquid silicon by capillary action when the samples 1~5 are exposed to the outside surface, so the densities of samples 1~5 decrease gradually with the increase of the distance from the surface of the silicon cloth. The deeper the sample was embedded in the silicon powder, the greater the influence on the vacuum (the whole process of vacuum extraction by RMI), which results in the gas in the sample pore difficult to release completely, thus affecting the capillary adsorption of the sample on liquid silicon. In addition, the embedded silicon powder will inevitably lead to the enrichment of liquid silicon in the surface layer of the sample, which is prone to pore sealing, and the infiltration reaction is hindered. Therefore, the deeper the sample is embedded in silicon powder, the smaller the sample density is.

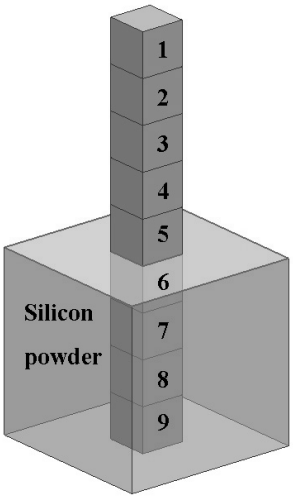

Fig.1 Schematic diagram of the relative position between silicon powder and C/C preform

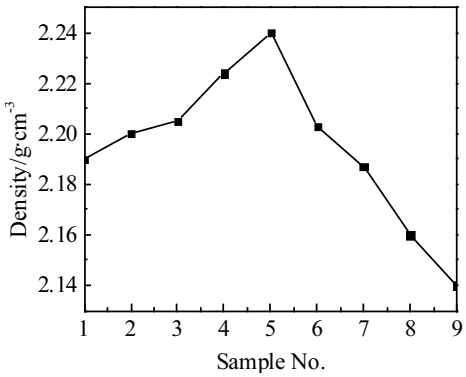

Fig.2 Density change of C/SiC composite along the embedding position in silicon powder

Table 1 shows the porosity of sample 1~9 and the calculated theoretical percentage of free silicon based on the porosity.

2.2 Microstructure and phase composition of C/SiC material prepared by RMI

Fig.3 shows the distribution of elements in C/SiC prepared by RMI. In the figure, A, B and C are 0° weft-free layers, 90° weft-free layers and net tire layers of needle-punched structure, respectively. From Fig.3, it can be seen that Si is

Table 1 Porosity of sample 1~9 and percentage of free silicon

Sample No.	Porosity/%	Percentage of free silicon/%
1	4.8	6.8
2	4.6	6.4
3	4.5	6.3
4	4.0	5.7
5	3.7	4.9
6	4.7	5.8
7	5.0	6.5
8	6.4	6.8
9	6.4	6.9

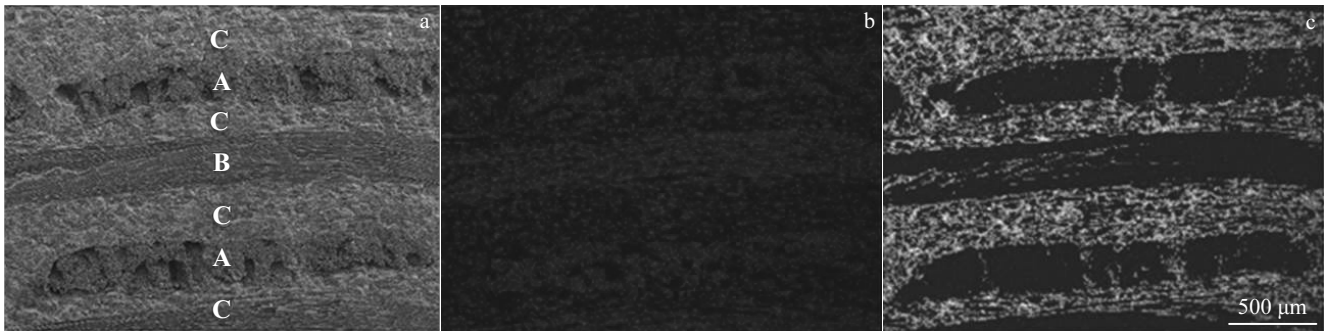

Fig.3 SEM image of C/SiC composite (a) and its element mapping of C (b) and Si (c)

mainly distributed in the reticulated tire layer, due to the fact that the weft-free layer of C/C porous body before infiltration (density of 1.35~1.45 g/cm^3) is relatively dense, and the capillary effect is weak, so it is difficult to overcome the surface tension between molten Si and C matrix. There are a lot of pores in the reticulated tire layer, and the molten Si is adsorbed to the material by capillary action. SiC forms inside the material and reacts with matrix C at high temperature.

Fig.4 is the SEM images of surface morphology of C/SiC material prepared by RMI. The enlarged maps of 0° weft-free cloth layer, 90° weft-free cloth layer and net tire layer in Fig.4a are shown in Fig. 4b, 4c, and 4d, respectively. It can be seen from Fig.4b that the interfacial layer on the surface of fibers is about 800 nm thick, and from Fig.4b and 4c, it can be seen that the interfacial layer on the surface of fibers is not damaged obviously during infiltration.

There will inevitably be unreacted free silicon in the C/SiC composites prepared by infiltration. In this paper, the C/SiC composites prepared by RMI are embedded in graphite powder and then treated at high temperature to remove free silicon. Fig. 5 shows the mass loss rate of C/SiC composites after silicon removal, which is 4.5%~6.5%. Fig.6 is the backscatter electron image of C/SiC prepared by RMI. Fig.6a and 6c are the morphologies before silicon removal and Fig.6b and 6d are the morphologies after silicon removal. According to the EDS analysis results in Table 2, it can be

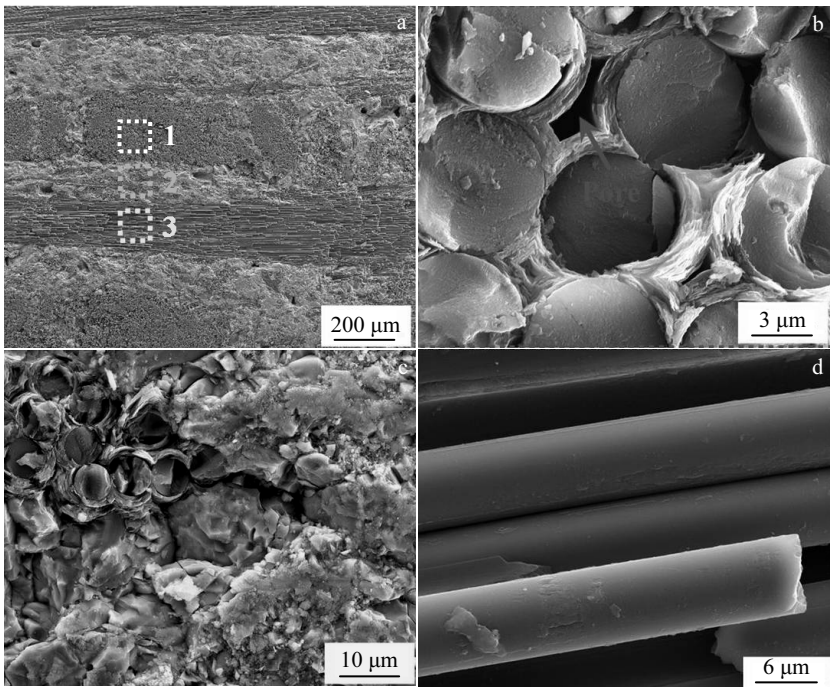

Fig.4 SEM images of surface morphologies of C/SiC composite (a) and enlarged view of the dashed box 1 (b), 2 (c), and 3 (d) in Fig.4a

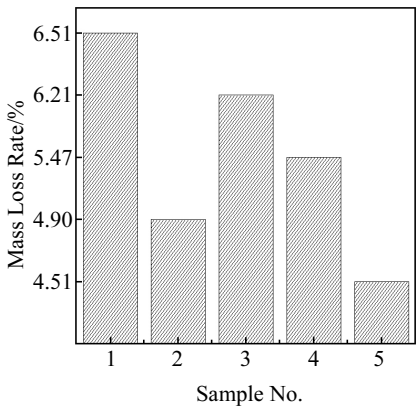

Fig.5 Mass loss rate of the sample after desilication

seen that the white and bright area 1 in Fig.6c is mainly Si element, and the gray area 2 is mainly Si and C elements, and the Si/C ratio is close to 1:1. It is difficult to find white and bright areas in Fig.6d, which are basically gray. According to the EDS results, the gray areas in Fig.6d are also similar to the Si/C ratio of 1:1. While the black part is mainly composed of C element.

Fig.7 is the XRD patterns of C/SiC composites before and after silicon removal. It can be seen that there are some characteristic peaks of elemental Si before silicon removal. And there is no obvious characteristic peak of elemental Si after silicon removal.

2.3 Bending properties of C/SiC composites prepared by RMI

In Table 3, the bending strength and modulus of C/SiC composites are given, and the single point values and average values are also present. The average bending strength before silicon removal is 338.6 MPa, while the bending strength after silicon removal is only 217.9 MPa. The main reason is that after silicon removal, a large number of voids appear in the C/SiC composites, resulting in a significant decline in the mechanical properties of the material. Fig.8 is stress-strain curves for bending test (taking sample 1 as an example). It can be seen from the figure that both curves show a stepped decline after passing through the highest point. This is due to the toughening effect of carbon fibers, showing pseudoplastic fracture.

Fig.9 is the fracture morphologies of the sample after bending test. Fig.9a is not desilicated, and Fig.9b is desilicated. The fiber pullout can be found in the fracture morphologies of both graphs. Therefore, the pseudoplastic fracture in Fig.8 will occur. From Fig.9b, it can be seen that the matrix phase around the fibers is looser and the fibers are easier to pull out after silicon removal. Therefore, in Fig.8, the red curve (silicon removal) is more moderate, and the toughening effect of the fibers is more obvious. However, the strength decreases obviously due to the decrease of densification degree.

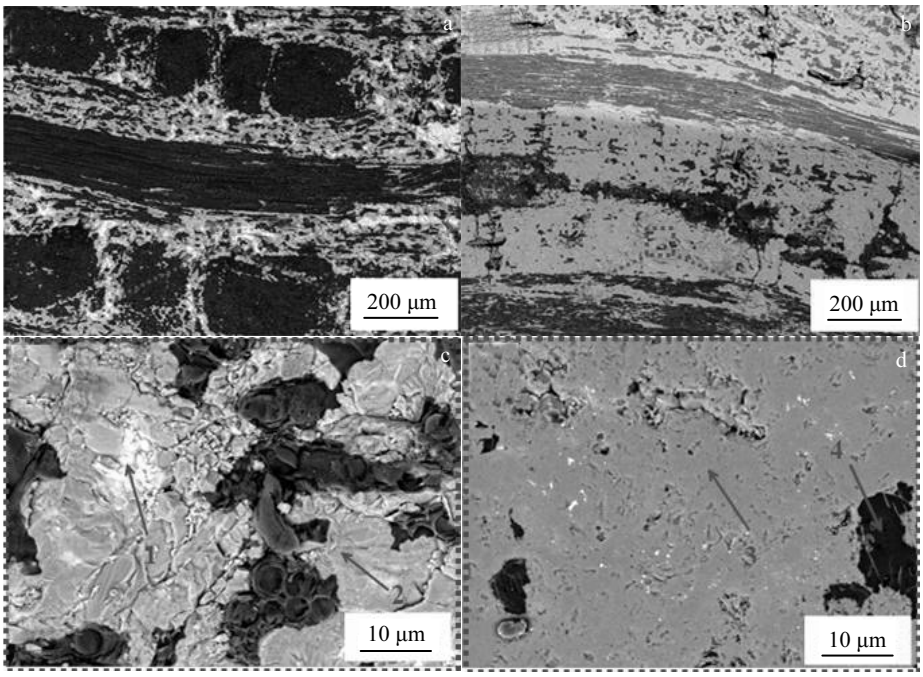

Fig.6 BEM of C/SiC composite material before (a, c) and after (b, d) desilication

Table 2 Results of EDS analysis of four areas in Fig.6 (at%)

Area	C	Si
1	9.58	90.42
2	46.47	53.53
3	50.97	49.03
4	99.78	0.22

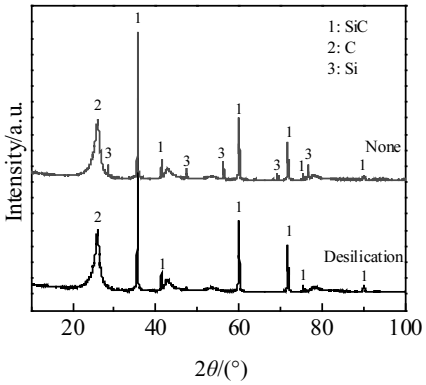

Fig.7 XRD patterns of C/SiC composites before and after desilication

Table 3 Single point value and mean value of the bending strength and modulus

State	Sample No.	Bending strength/MPa		Bending modulus/GPa	
Before silicon removal	1	330.7	338.6	29.7	32.0
	2	292.4		32.0	
	3	255.5		25.1	
	4	421.8		40.1	
	5	392.4		33.0	
After silicon removal	1	175.7	217.9	27.4	25.9
	2	152.2		30.2	
	3	151.2		18.9	
	4	333.3		33.3	
	5	276.9		19.7	

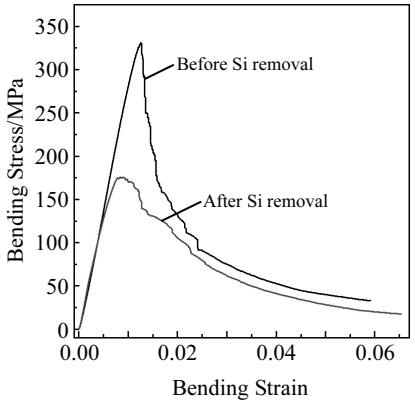

Fig.8 Bending stress-bending strain curves of sample 1

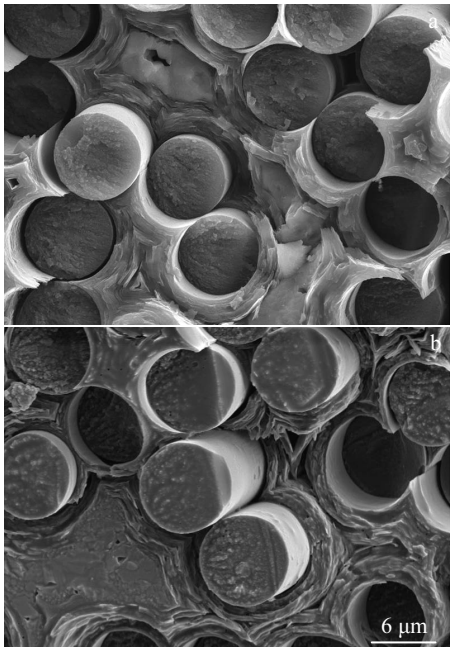

Fig.9 Fracture morphologies of sample after bending test: (a) before desilication and (b) after desilication

3 Conclusions

1) The density of C/SiC composites prepared by reactive melt infiltration decreases with the increase of the relative distance from the surface of the fabricated silicon.

2) There is residual free silicon in C/SiC composites prepared by RMI. The free silicon decreases significantly after silicon removal, but the degree of densification decreases (the mass loss rate is 4.5%~6.5%) which leads to a significant decrease in the flexural properties of C/SiC composites.

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反应熔渗制备 C/SiC 复合材料的微观组织与性能

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摘　要：采用反应熔渗法将熔融 Si 渗入 C/C 多孔体中制备了 C/SiC 复合材料。研究了包埋式布硅对 C/C 多孔体不同位置毛细吸附行为的影响以及对制备 C/SiC 复合材料密度的影响。反应熔渗制备的 C/SiC 复合材料内部存在残余的游离硅，经过除硅处理后游离硅显著减少，但其致密化程度有所降低，同时其抗弯曲强度明显下降。

关键词：反应熔渗；C/SiC 复合材料；游离硅

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