RAPID FABRICATION OF CARBON FIBERS REINFORCED SILICON CARBIDE COMPOSITES

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Introduction

Carbon fibers reinforced silicon carbide composites have been designed and developed for high-temperature structural applications, such as engines and reentry thermal protection for spacecraft [1,2], due to the combination of both high-strength carbon fibers and high-modulus, oxidation resistance silicon carbide matrix. The common fabrication processes for 3D C/SiC composites are isothermal/isobaric chemical vapor infiltration (ICVI)[3] and polymer precursor conversion (PPC)[4], whereas the both processes have long produce cycles (beyond three months). Moreover, the composites fabricated by the later have poor mechanical and oxidation resistance properties. Here, a newly combined process is introduced to fabricate 3D C/SiC composites, with short produce cycle and improved composite properties. The influences of the process parameters of both ICVI and PPC process on the combined process and composite properties were also investigated. The composites were characterized by microstructure analysis and mechanical test.

Experimental

The T-300 carbon fibers were used in this work. The carbon fibers were braided into 3D fibrous preforms through four-step braiding technique with the fiber volume content of about 45%. Before the densification, the fibrous preforms were firstly coated with pyrolytic carbon as interphase from cracking of C_3H_6 at 900℃ and whose mean thickness is about 0.3 μ m. The matrix densification by a newly combined process includes two steps. In the first step, the coated fibrous preforms were infiltrated with CVI-SiC matrix formed from a CH_3SiCl_3 (MTS)/H_2, with a H_2/MTS molar ratio of 3 and a MTS usage of 35～40g/h, and a reduced pressure of 3kPa. In the second step, the C/SiC(CVI) porous composites were densified with pyrolytic SiC (pyr-SiC) matrix from impregnating and pyrolysising of polycarbosilane (PCS), with a pyrolysising temperature of 800℃ in nitrogen. After 3 impregnation- pyrolysis cycles, the composites were heat treated (1200℃ × 1h) to make the pyr-SiC matrix crystallized. Three-point bend test was performed using a 16mm span for testing shear strength and a 50mm span for testing flexural strength with a crosshead speed of 0.5mm/min at room temperature. The span to depth ratio was about 5 for shear specimens and about 17 for flexural specimens. The fracture toughness (K_{IC}) of composites was examined through single edge notch beam (SENB) method using a 40mm span and a 0.2mm notch width and a 3mm notch depth with a crosshead speed of 0.2mm/min. The microstructures of deposition and cross-section of fracture specimens were analyzed by scanning electron microscopy (SEM), the matrix distribution in the porous preform have also been characterized through metallograph analysis.

Results and Discussion

The results of the deposition microstructure by SEM show that the CVI-SiC matrix deposited at 900℃～1000℃ is uniform and deep, whereas that deposited above 1100℃ is uneven and overcoating on the surface of the preforms. The composite deposited at 1000℃ for 72 hours have a density of 1.75g/cm^3 with large quantities of open porosity in the composites to be further densificated by PPC process, and the density could reach 2.05g/cm^3 by 3 impregnation- pyrolysis cycles, with the flexural strength and shear strength and fracture toughness were 643MPa and 63.7MP and 17.9MPa • m$^{1/2}$ respectively. To lengthen the deposition time or to increase the deposition temperature would lead to a deposition on the fibrous preforms surface, which sealed the passage of the impregnant and made the further PPC process impossible. To deposit below 900℃ would lead to a very long ICVI produce cycle(Table 1). All these were disadvantageous to the later process(PPC) and the final composite properties.

Table 1. Influences of ICVI processing parameters on the C/SiC(CVI) composite densities

Sample	Process	density (g/cm^3)	Deposition
A	950℃×72h	1.50	Uniform, Deep
B	1000℃×72h	1.75	Uniform, Deep
C	1000℃×120h	1.84	Uneven, surficial
D	1100℃×72h	1.86	Uneven, surficial

As illustrated in Table 2, the impregnant influences the final composite density heavily. The C/SiC(CVI) composite with a density of 1.75g/cm^3 impregnated by different precursor (PCS/divinylbenzene and PCS/xylene),

have different densities. The density reaches to 2.05g/cm^3 by three impregnation-pyrolysis cycles from PCS/ divinylbenzene and to 1.94g/cm^3 by five cycles from PCS/divinylbenzene. The composite flexural strength and fracture toughness improve significantly with little increase in density when the composite density was above 1.90 g/cm^3, so there is a strong relation between the precursor system and the composite properties. This is because of the PCS/ divinylbenzene offering low viscosity, low bubble, and high SiC yield contrasting to PCS/xylene. The weight ratio of PCS to divinylbenzene or xylene is used 10/6 because it has highest SiC yield (from TGA). The pyrolysis Pressure has also influenced the densification efficiency. The thermogravimetric analysis (heating rate 5℃/min) showed that the SiC yield of pure PCS in nitrogen increases from 52wt% to 65wt% with the pressure from 0.1MPa to 6.0MPa (Table3). In this work we used a 3.0MPa pressure due to the furnace capability.

Table 2. Composite density after every impregnation-pyrolysis cycle (g/cm^3)

Impregnant	impregnation-pyrolysis cycle				
1	2	3	4	5	
PCS/xylene	1.84	1.89	1.92	1.93	1.94
PCS/DVB	1.91	2.00	2.05		

Table 3. Weight loss of PCS in nitrogen (wt%)

Pressure	0℃	200℃	400℃	600℃	900℃
0.1MPa	0	0.5	5	27	35
1.5MPa	0	0.5	4	30	40
3.0MPa	0	0.4	9	38	43
6.0MPa	0	0.6	12	38	48

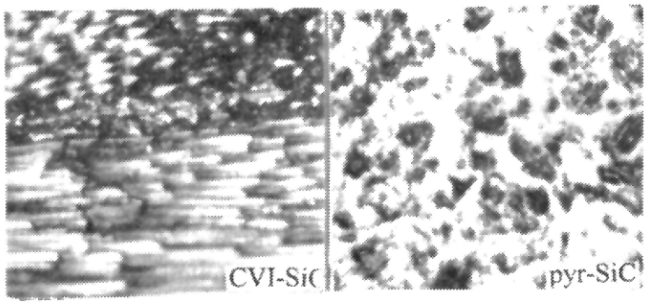

Figure 1. Microstructure of CVI-SiC and pyr-SiC matrix composites by metallograph analyses

The metallograph analysis showed that CVI-SiC matrix tends to occur preferentially in the small porosity between the fibers in the bundle and left the large pores between the bundle which can easily be impregnated by PCS, whereas pyr-SiC matrix tends to occur preferentially in large pores between the fiber bundles (Fig.1). Hence the combined process must be ICVI+ PPC rather than. The density of the composite fabricated by PPC+ICVI combined process is merely up to 1.85 g/cm^3 at the same ICVI and PPC processing parameters and produce cycle (150 hours) as that in the ICVI+PPC combined process.

The cross-section microstructure analysis (SEM) of fracture specimens showed that the failure module of the composites fabricated the newly process was toughness with fibers pulled out (fig. 2).

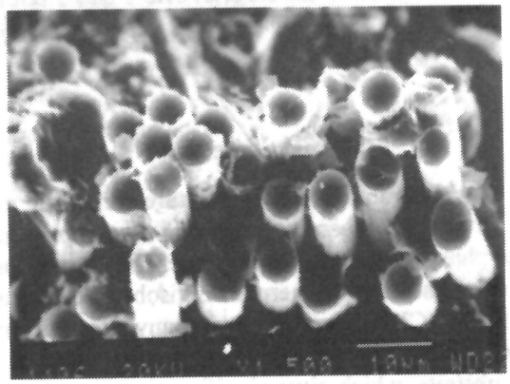

Figure 2. Cross-section microstructure (SEM) of the fracture composites specimens

Conclusions

3D C/SiC fibrous composites were successfully fabricated by a newly combined process with short produce cycle about 150 hours and improved composite properties, the flexural strength and fracture toughness were 643MPa and 17.9MPa • m$^{1/2}$ respectively. In the combined process, the first step must be ICVI rather PPC for the different densification mechanism fo two SiC-matrix. The CVI-SiC matrix deposited at 1000 ℃ is uniform and deep and a quick deposition rate, whereas that deposited above 1100℃ is uneven and limited on the surface of the preforms. To lengthen the deposition time or to increase the deposition temperature would lead to a deposition on the fibrous preforms surface The precursor system and pyrolysis pressure influence the final composite density and properties heavily.

References

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