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Microstructure and properties of 2D-C_f/SiC composite fabricated by combination of CVI and PIP process with SiC particle as inert fillers

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ABSTRACT

2D-C_f/SiC composite was manufactured by chemical vapor inflation (CVI) combined with polymer impregnation and pyrolysis (PIP) with SiC particle as inert fillers. The effects of CVI processes on SiC morphologies and the properties of composite were investigated. The composites were characterized by XRD, flexural strength test and SEM. The results revealed that uniform SiC coatings and nanowires were prepared when MTS/H_2 ratio of 1:8 was employed, while gradient thick coatings were fabricated as MTS/H_2 ratio of 1:1 was employed. The flexural strength of composites varied from 156 MPa at MTS/H_2 ratio of 1:1 to 233 MPa at MTS/H_2 ratio of 1:8. All of composites exhibited toughness due to significant debonding and pullout of fibers. The laminated structure of coatings on the fibers and nanowires were manufactured by combination of above different CVI process, and the obtained composites showed flexural strength of as high as 248 MPa and impressive toughness.

1. Introduction

SiC ceramic matrix composite reinforced by carbon fiber is of many unique properties such as relative low density, high specific modulus, excellent oxidation [1,2]. Therefore it is projected to be endured severe environment (e.g., elevated temperature up to 1600 °C at oxidizing atmosphere), and it has a bright prospect to be applied in the aerospace field [3,4].

Previous researchers had successfully fabricated C_f/SiC composites via chemical vapor infiltration (CVI) [2,5–8], polymer-infiltration-pyrolysis (PIP) [9–11] or liquid silicon infiltration (LSI) [12,13]. Taken into account the essence of carbon fiber which is sensitive to environment effects (e.g. to high temperature with oxygen), the CVI route, as one of the prior processing routes [14], has been testified effective for the formation of dense and high purity SiC matrix at relative low temperature (1000–1100 °C) and the density of obtained composites are as high as 2.1–2.2 g/cm^3 [1]. However, the CVI route usually takes several hundred hours and lots of raw material to densify carbon fiber preforms, which restricts its development and application in industry. To enhance the efficiency of CVI process, Oh et al. [15] changed dilute gas in ICVI process and successfully spent less time on fabricating C_f/SiC composite with SiC whiskers and SiC matrix. The PIP route is also employed to fabricate SiC matrix as its several merits such as steerable ceramic compositions and near-net-shape technologies [10]. Whereas, due to large shrinkage resulted from the conversion of the preceramic polymer into inorganic materials, it is hard to fabricate compact SiC matrix that coats fibers tightly [16]. To overcome the disadvantage of PIP route, Jian et al. [17] and Zhu et al. [18] added SiC particle into PCS solution in the first infiltration-pyrolysis circle and prepared more dense and higher strength composites. Therefore, CVI route can prepare compact and pure matrix which can allow for tight packing of fabrics, while PIP route is more industrially effective than CVI route. Ortona et al. [19] combined CVI and PIP processes to fabricate SiC$_f$/SiC in order to maximize advantage and reduce costs of process. Little attention has been devoted to combined CVI with PIP process to fabricate C_f/SiC composite. The aim of the paper is to research the influence of SiC morphologies by different CVI process on microstructure and properties of composites, and analyze the impacts of SiC nanowires and interfaces on the obtained composites.

2. Experimental procedure

2.1. Raw materials

2D plain carbon preform of type high strength (HS) of 3K PAN was chosen as the reinforcement and made in Tianniao High Technology Corporation, China. Phenol formaldehyde resin was used as the precursor of pyrolytic carbon, and the ethanol was chosen as solvent for phenol formaldehyde resin.

Methyltrichlorosilane (MTS, CH_3SiCl_3) was employed as a precursor for depositing SiC. Hydrogen (H_2) as bubbling agent was designed to carry MTS into reaction chamber, and Argon (Ar) as dilution gas was

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Table 1
Process parameters of CVI.

Sample (ID)	Process	The flow of MTS (L/min)	The flow of H_2 (L/min)	The flow of Ar (L/min)	The MTS/H_2 ratio
C-1	CVI-1	0.8	0.8	1.6	1:1
C-2	CVI-2	0.2	1.6	3	1:8
C-1-2	CVI-1 first, then CVI-2	/	/	/	/

used for adjusting the concentration of MTS.

The Polycarbosilane (PCS, provided by National University of Defense Technology, NUDT, China) with the molecular weight of ~1300 and the soften point of ~226 °C was adopted as the precursor of SiC matrix and Xylene(Analytical Reagent) was used as a solvent for PCS. Besides, the micron SiC powder (~1.3 μm) obtained from Saint-Gobain Industrial Ceramics, Inc. was employed as inert fillers.

2.2. Experimental procedure

C fiber preforms were cut into required shape, then soaked with acetone in order to remove impurity such as dust and glue from the surface of C fiber. The preforms were impregnated with phenol formaldehyde resin solution with 25 wt% phenol formaldehyde resin by a negative pressure infiltration process (−0.1 MPa). The samples were centrifuged subsequently for 20 min with 1000 r/min to remove excess phenol formaldehyde resin solution and were cured at 80 °C.

The SiC interface was deposited on C fibers by CVI at 1100 °C with 1000 Pa, and other process parameters were listed on the Table 1. The key point of CVI process is to keep the perform porosity open throughout the whole process, and this is related to the mean free path of the gas molecules [20] as Eq.(1) [21].

$$l = \frac{k_B T}{\sqrt{2}\,\pi d^2 P} \quad (1)$$

where l is the mean free path, k_B is the Boltzmann constant, T is absolute temperature, d is mean molecular diameter, and P is the pressure.

The mean free path must be large enough to avoid sealing the pore entrance. In this experiment, we chose the temperature as 1100 °C to accelerate the reaction rate, the pressure as 1 kPa to increase the mean free path, the ratio of H_2/MTS as 1 and 8 inasmuch as the morphologies of SiC were researched and comparative trials were designed.

The phenol formaldehyde resin was pyrolysed, followed by the process of CVI. Thus, a very thin pyrolytic carbon layer on fibers was obtained.

After the treatment of CVI process, the specimens were impregnated with PCS slurry by vacuum process. The PCS slurry was composed of 30:20:50 wt% SiC particle: PCS:xylene. Samples were dried in 80 °C and the curing of samples was done at 180 °C in air for dwelling time of 6 h. The cured samples were pyrolysed at 1050 °C with the heating rate of 2 °C/min under argon environment in the quartz tube furnace. In order to decrease the residual porosity of the obtained composites, the same infiltration-cure-pyrolysis process was repeated for 6 cycles. The constitution of PCS solution was changed without SiC particle, and the constitution of PCS solution was shown in Table 2. After 6 circles, the samples were annealed at 1400 °C for 2 h in order to fabricate crystalline SiC matrix. After the samples were treated by PIP process, the names of samples were added P as a suffix such as C-1-P, C-2-P and C-1-2-P.

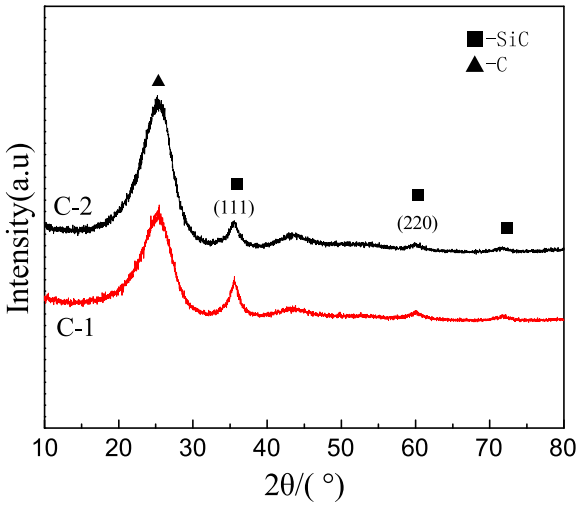

Fig. 1. XRD patterns of specimens fabricated by CVI route.

2.3. Evaluation of the properties and microstructure of composites

The bulk densities of the samples were measured by means of the water displacement technique (Archimede's method).

The preforms with SiC coating under different CVI process parameters were grinded into powder and detected by X-ray diffraction (XRD, Rigaku D/max 2500) with Cu K_α radiation of 0.15405 nm.

The three-point bending test was performed on samples of 2.0 mm×5.5 mm×40 mm with a span of 28 mm and the cross-head speed of 0.5 mm/min at room temperature by using Instron 3382 machine.

The polished cross-section and fracture cross-section of samples after three-point bending test were observed by scanning electron microscope (FEI QuANTA 200) attached with an energy dispersive spectrometer (EDS, EDAX).

3. Result and discussion

3.1. The XRD patterns and SEM of SiC coating morphologies on C fibers by CVI

The XRD patterns (Fig. 1) of samples after CVI treatment reveals that reaction products of different CVI process are beta silicon carbon. The two broad peaks are considered to be (111) and (220) peaks. The peaks of C-1 and C-2 are both broad, but the peaks of C-1 are a little narrower than the C-2's, indicating that the β-SiC crystalline degree of C-1 is better than that of C-2. It is deduced that increase of MTS/H_2 ratio could contribute to SiC crystallization in CVI process.

The microstructure of specimens after CVI process is shown in Fig. 2. It can be seen that there was a coating with ~0.8 μm in thickness around C fiber (Fig. 2(a)), while a ~0.1 μm thick coating was formed around the fiber and a sphere-like with many ~400 nm thick randomly oriented nanowires with straight or curved morphologies was embedded in fiber bundle (Fig. 2(b)). The nanowires were also testified to be SiC by EDX. Some paper [22,23] has been reported that the SiC nanowires fabricated by similar process were verified to be with

Table 2
The constitution of PCS solution after the first time of PIP.

Time of PIP	The second	The third	The forth	The fifth	The sixth	The seventh
The weight fraction of PCS (wt%)	50	50	40	30	20	15