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Mechanical properties and oxidation resistance of SiC_f/CVI-SiC composites with PIP-SiC interphase

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Abstract

SiC coatings were successfully synthesized on SiC fibers by precursor infiltration and pyrolysis (PIP) method using polycarbosilane (PCS) as precursor. The morphology of as-fabricated coatings was observed by SEM, and its structure was characterized by XRD and Raman spectrum. The SiC fiber reinforced chemical vapor infiltration SiC (SiC_f/CVI-SiC) composites with PIP-SiC coatings as interphase were fabricated. And, the effects of PIP-SiC interphase on mechanical properties of composites were investigated. The experimental results point out that the coating is smooth and there is little bridging between fibers. The coating is amorphous with SiC and carbon micro crystals. The flexural strength of composites with and without PIP-SiC interphase is 220 and 100 MPa, respectively. And the composites with PIP-SiC interphase obviously exhibit a toughened fracture behavior. The oxidation resistance of composites with PIP-SiC interphase is much better than that of composites with pyrolytic carbon (PyC) interphase.

Keywords: C. Mechanical properties; SiC_f/SiC composites; PIP-SiC interphase; Oxidation resistance

1. Introduction

SiC_f/SiC composites are excellent thermal structural materials due to their outstanding high-temperature strength, fracture toughness, chemical inertness and low activation characteristics [1,2]. The interphase between fiber and matrix, which can deflect matrix cracks, is essential for tough fracture behavior of SiC_f/SiC composites [3]. Pyrolytic carbon (PyC) and h-BN with a layered structure were thought to be the best interphase materials for SiC_f/SiC composites, and can effectively improve mechanical properties of SiC_f/SiC composites. Unfortunately, they are oxidation prone at high temperature with results that PyC or BN interphase can be consumed and the mechanical properties of SiC_f/SiC composites degrade [4–10]. Therefore, for SiC_f/SiC composites, interphase with oxidation resistance is needed imperatively. On the other hand, for fusion reactor components, PyC and BN interphases are not favorable because of their micro structural radioactivity under neutron irradiation [5]. Recently, SiC materials as interphase of composites have been generating attention due to its high oxidation resistance and microstructural stability under neutron irradiation. Applications of CVD SiC interphase acting as constituent layers in multilayer interphase [5,11,12] and single layer interphase [13,14] have been reported by some researchers. However, the single layer CVD SiC may not be suitable for interphase in CVI SiC matrix composites due to its strong bonding with matrix, and the preparation process of multilayer interphase is relative sophisticated.

In the other hand, besides as matrix in composites, SiC fabricated by the method of PIP was widely used for oxidation resistance coatings on carbon materials [15,16]. As interphase of composites, Taguchi et al. studied the influence of PIP-SiC interphase on properties of the 2D SiC_f/SiC composites prepared by reaction bonding (RB) process. Unfortunately, PIP-RB composites show catastrophic failure behavior. The reason may be that the SiC fibers are not fully coated by PIP-SiC with uniform thickness and the contact of fiber with molten Si severely damages it during the RB process. Although the PIP-SiC may be suitable for interphase in SiC_f/CVI-SiC composites, the reports on the effects of PIP-SiC interphases for SiC_f/CVI-SiC composites are rare.

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In the present investigation, the PIP-SiC was proposed as interphase in CVI-SiC matrix composites. Then, its effects on mechanical properties of SiC_f/CVI-SiC composites were researched. Finally, the oxidation resistance capability of composites with PIP-SiC interphase was evaluated.

2. Experimental

The KD-1 SiC fibers were provided by National University of Defense Technology (China). Table 1 shows the parameters of KD-1 fibers [10]. The fabrics were braided by Nanjing Glass Fiber Institute (China). The fabrics structure is 2.5D shallow straight-joint shown by Fig. 1. The fiber volume fraction of the fabrics is 40%. PCS powders with molecular weight ~1800 and softening point ~180 °C were provided by National University of Defense Technology (China).

Before coating, the SiC fiber fabrics were desized in vacuum at 700 °C for 30 min and ultrasonically cleaned in acetone solution for 10 min. For PIP-SiC coatings preparation, PCS solutions were firstly obtained by dissolving PCS powder into xylene. The PCS concentration is 10 wt%. Then, SiC fiber fabrics were dipped into PCS solution in vacuum for 5 min. After infiltration, the samples were dried at 90 °C for 12 h. The dried samples were heated at a rate of 5 °C/min in a vacuum sintering furnace (ZRS-150, Sante, Jinzhou, China) up to 1100 °C, and then hold for 2 h. The cooling rate was about 2 °C/min. During the heating, holding and cooling process, the chamber pressure was below 0.1 Pa.

After preparation of PIP-SiC coatings, the SiC matrix was fabricated by CVI. The methyltrichlorosilane (MTS) is the gas precursor, and hydrogen is the carrier and diluent gas. The temperature and pressure of CVI are 1100 °C and 5 KPa, respectively. And the flow ratio of H_2 as carrier gas and diluent gas are 300 and 30 ml/min, respectively. The infiltration time is 15 h. The fabrication route of the SiC_f/CVI-SiC composites is shown in Fig. 2. For comparison, composites without interphase were also fabricated. The structure of as prepared coatings was characterized by XRD (X′Pert PRO MPD, PANalytical, Almelo, the Netherlands) and Raman spectroscopy (LabRAM HR800). SEM was used to investigate the fiber coating surface morphology, and to determine if there is bridging between coated fibers.

In order to evaluate the oxidation resistance of composites with PIP-SiC interphase, the SiC_f/CVI-SiC composites with PyC interphase were fabricated. The PyC interphase was fabricated according to the process of Yu et al. [17]. The composites with PIP-SiC interphase and PyC interphase were oxidized in air at 900 °C in a closed box-type furnace with a heating rate of 20 °C/min for 6 h and 12 h.

The open porosity of samples was tested by the Archimedes method. Three-point bending tests on composites were carried out at room temperature, with a crosshead rate of 0.5 mm/min and outer support span of 30 mm. The test was conducted following the general guidelines of ASTM standard C 1341, using five specimens. The σ was calculated by the following Eq. (1):

$$\sigma = \frac{3PL}{2wt^2} \quad (1)$$

where P is load at a point of deflection of a load–displacement curve in test, L is outer support span, w is specimen width, t is specimen thickness. The samples were cut and polished to 40 mm in length, 4 mm in width and 3 mm in thickness. The length and width directions were parallel to warp and weft directions, respectively. Finally, the as-received cross sections of composites after three-point bending tests were characterized by SEM.

Table 1
Parameters of KD-1 fibers.

Fiber type	Diameter (μm)	Density (g cm^{-3})	Tension strength (MPa)
KD-1	14–16	2.54	1800–2200

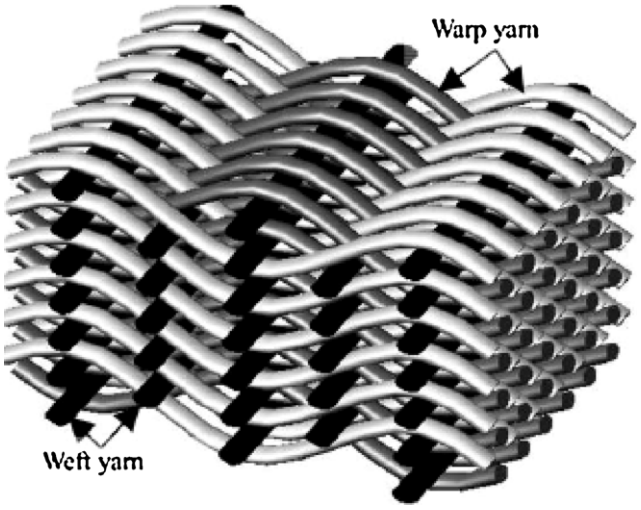

Fig. 1. Schematic showing of the fabrics structure.

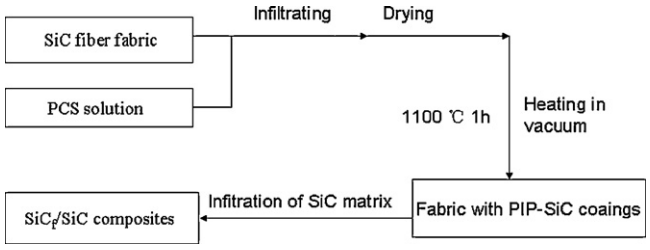

Fig. 2. Preparation route of composites with PIP-SiC interphase.

3. Results and discussion

3.1. Characterization of PIP-SiC coatings

The morphology of the original and coated fibers were investigated by SEM. From Fig. 3a, it can be seen that the SiC fiber surface is rough, and there are some pimples and defects. Fig. 3b–d shows the surface topography of fibers with coatings. After PIP, shown in Fig. 3b, the fibers are covered by coatings and its surface is relatively smooth and uniform. And, few bridging between fibers can be observed from Fig. 3c. And, the

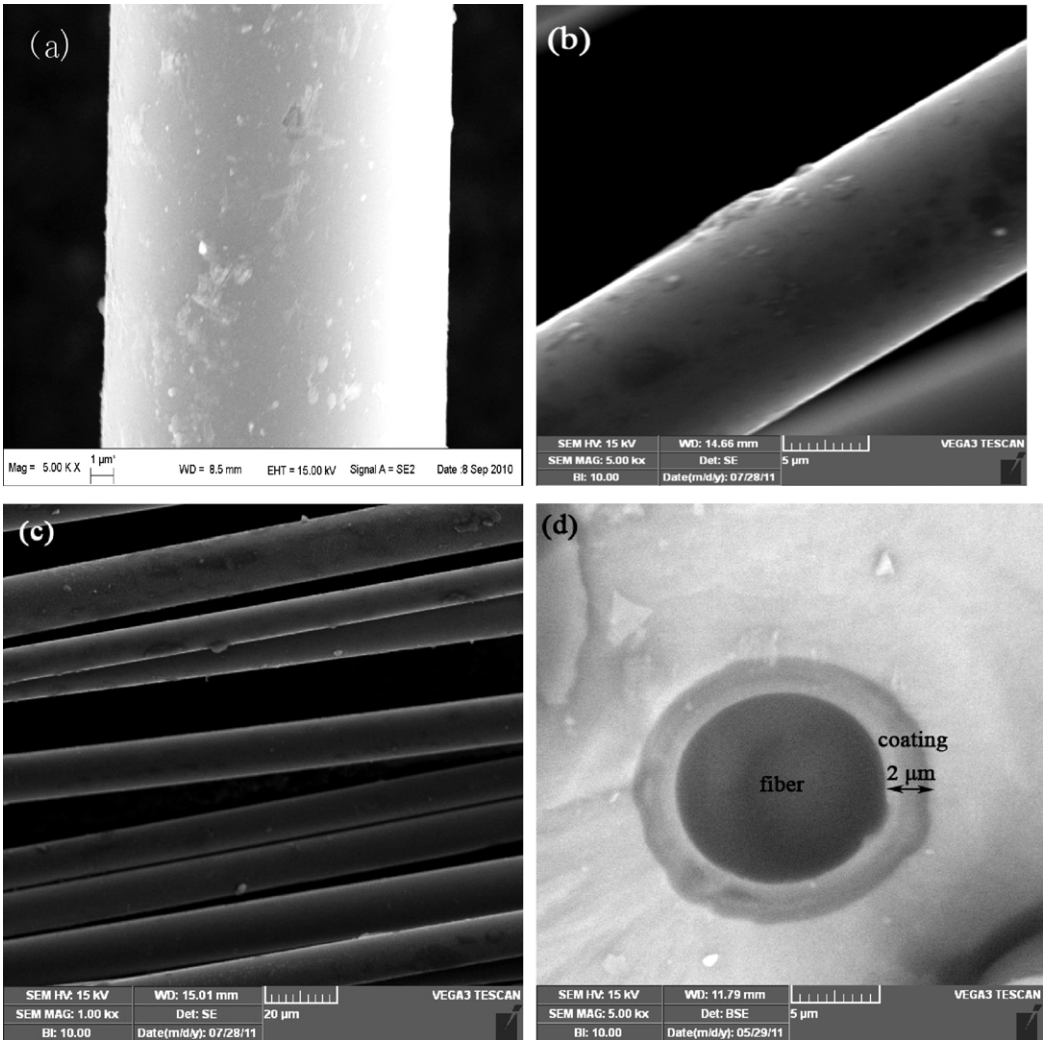

Fig. 3. SEM photographs of as received SiC fiber (a) and fiber with coatings (b–d).

thickness of PIP-SiC interphase is about 3 μm shown by Fig. 3d.

The XRD method is employed to study the micro-structure of the coatings. In the XRD spectrum shown by Fig. 4, the broad peaks at 26.6°, 60.0° and 71.8° associate with (1 1 1), (2 2 0) and (3 1 1) planes of β-SiC crystals. Fig. 5 shows the Raman spectrum of the coatings. The bands at about 1380 and 1580 cm^{-1}, which were called D and G bands of carbon,

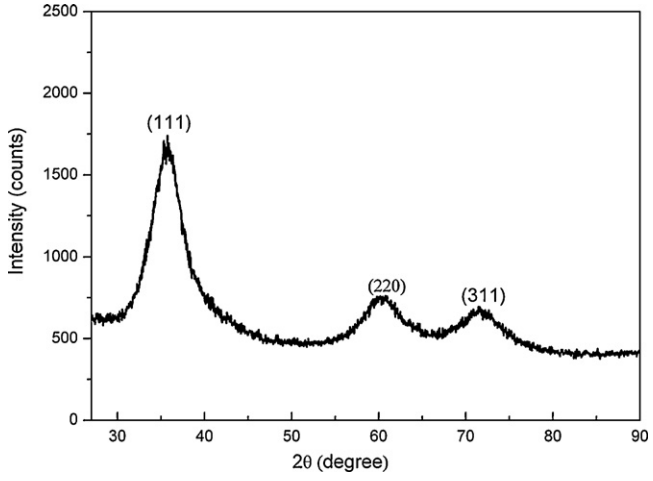

Fig. 4. XRD pattern of as prepared coatings.

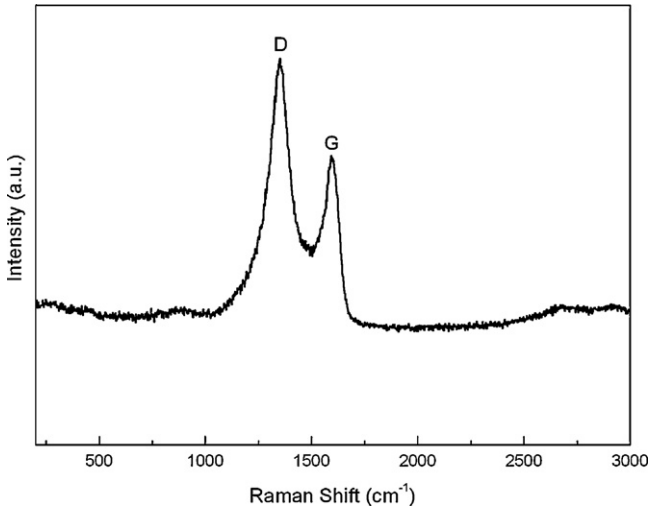

Fig. 5. Raman spectrum of as prepared coatings.

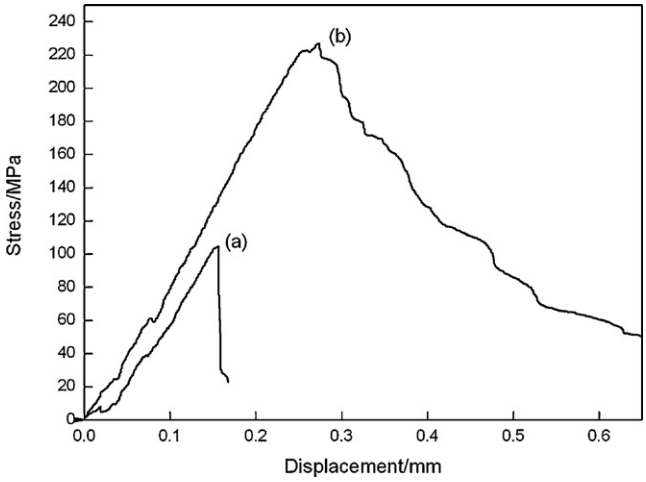

Fig. 6. Stress-displacement curved of the composites without interphase (a) and the composites with PIP-SiC interphase (b).

indicate the existence of free carbon [18]. The peaks of SiC cannot be observed because the Raman scattering efficiency of carbon species can be assumed to be at lest ten times higher than that of pure SiC materials due to their optical absorption [19,20]. The results above exhibit clearly that the coatings is amorphous state embedded with SiC and carbon micro crystals.

3.2. Mechanical properties of the composites

Characteristics of the composites with and without PIP-SiC interphase are listed in Table 2. It can be seen that the flexural strength is significantly improved by PIP-SiC interphase between fibers and matrix. The flexural strength of the composites without PIP-SiC interphase is only 100 MPa. However, for the composite with PIP-SiC interphase, the flexural strength reaches 220 MPa even though no obvious differences in the bulk density and porosity are observed.

Typical flexural stress/displacement curves of these two composites are shown in Fig. 6. As shown in Fig. 6a, the

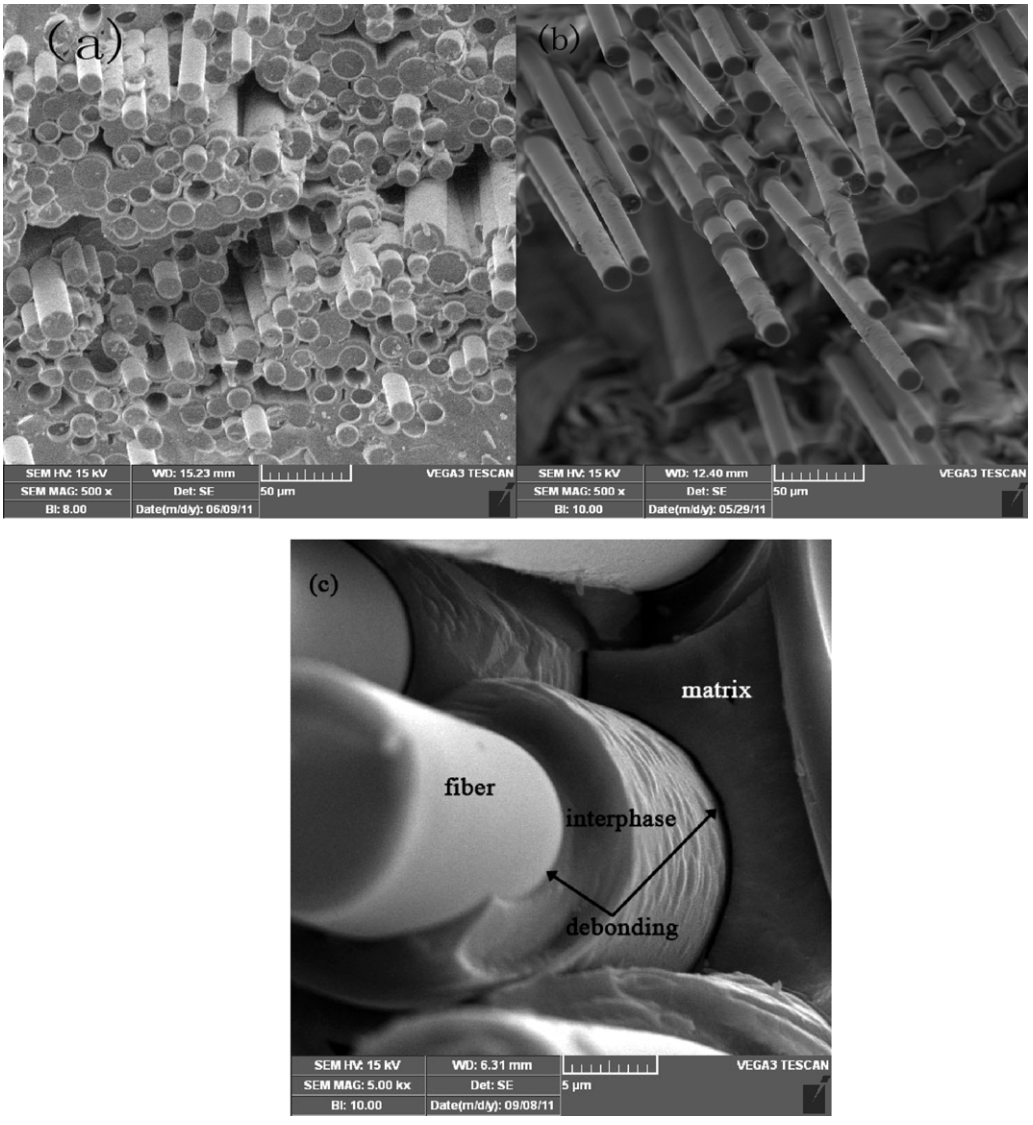

Fig. 7. SEM graphs of fracture surface morphologies of composites without interphase (a) and composites with PIP-SiC interphase (b and c).

Table 2
Characteristics of the as-fabricated composites with and without PIP-SiC interphase.

Sample	Density (g cm^{-1})	Porosity (%)	Flextural strength (MPa)	Failure displacement (mm)
Without interphase	2.10	12	100 (5*)	0.1 (0.02)
With PIP-SiC interphase	2.07	14	220 (10)	0.28 (0.02)

* Numbers in parentheses show standard deviations.

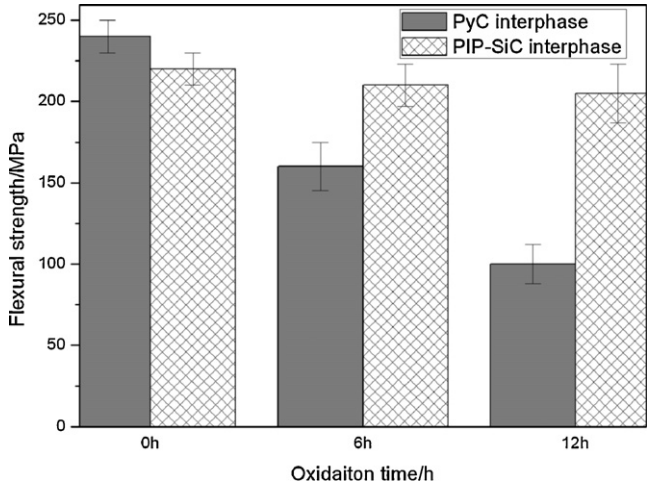

Fig. 8. Room temperature flexural strength retentions of composites with PyC interphase and PIP-SiC interphase after heat treating in air at 800 °C for 6 and 12 h.

composites without PIP-SiC interphase exhibit an obvious brittle fracture behavior, and its failure displacement is only 0.05 mm. In contrast, for composites with PIP-SiC interphase, the curve indicates a standard toughened fracture behavior (Fig. 6b). When the load reaches maximum it will but drop off gradually. The failure displacement of composites with interphase reaches 0.25 mm.

Fig. 7 shows the fracture surface morphology of composites after bending test. It can be observed from Fig. 7a that the fracture surface of the composite without interphase is very plane and no pullout fibers can be seen. For the composites with PIP-SiC interphase shown in Fig. 7b, long pullout fibers dominate the fracture surface indicating weak interfacial bonding between fibers and matrix. Furthermore, the residual interphase on fibers shows that its strength is lower than that of fibers and matrix. Observed from Fig. 7c, debonding occurs not only between fibers and interphase, but also between interphase and matrix.

Generally, for continuous fibers reinforced ceramic matrix composites, the interfacial bond strength of fibers and matrix play a key role in its fracture behavior [3,5]. For SiC fibers without coatings shown by Fig. 3a, the rough surface characteristics of as-received KD-1 SiC fibers would lead to strong physical interfacial bonding with CVI-SiC matrix. The strong interfacial bonding can make the fiber reinforced mechanisms be out of service [13,21]. Thus, the composites without interphase exhibit an obvious brittle fracture behavior, and its strength is relative low.

When the fibers are coated by PIP-SiC, it weakens the interfacial bonding and improves the accommodation of the fiber/matrix due to its weak bonding both with fibers and with CVI-SiC matrix. Most matrix cracks deflect, round and even disappear when they meet the interface layer during fracture process of the composites. As a result, the weak interfacial bonding makes the composites exhibit higher flexural strength and an evident toughened fracture behavior.

3.3. Effects of thermal oxidation on mechanical properties of composites

Fig. 8 shows the room temperature flexural strength retentions of composites with PyC interphase and PIP-SiC interphase after thermal oxidation at 900 °C for 6 and 12 h. It

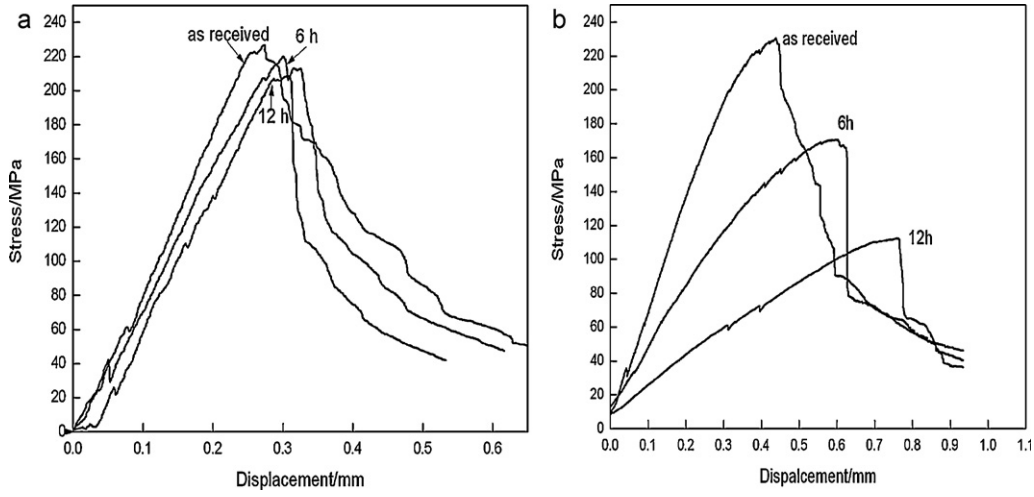

Fig. 9. Flexural stress/displacement curves of composites with PIP-SiC (a) and PyC (b) interphases after heat treating in air.

was observed that the flexural strength retention of composites with PIP-SiC interphase is obviously higher than that of composites with PyC interphase even though no obvious differences in original strength and porosity of the two composites. Fig. 9 shows the typical flexural stress/displacement curves of two composites after thermal oxidation. It cans be seen that the composites with PIP-SiC interphase exhibit standard toughened fracture behavior even though after thermal oxidation, while the fracture behavior of composites with PyC interphase composites gradually change to brittle fracture.

In the process of thermal oxidation, for composites with PyC interphase, the consumption of PyC interphase and formation of silica should degrade the composites due to strong bonding with fibers and matrix, which has been recognized [4–8]; for composites with PIP-SiC interphase, the PIP-SiC interphase can effectively protect SiC fibers against oxidation. Therefore, the oxidation resistance of composites with PIP-SiC interphase is much better than that of composites with PyC interphase.

4. Conclusions

SiC coatings with smooth surface were successfully synthesized on KD-1 SiC fibers by PIP method using PCS as precursors. The results of XRD and Raman spectrum show that the coatings are amorphous with SiC and carbon micro crystals.

The PIP-SiC interphase improves the mechanical properties of SiC_f/CVI-SiC composites. The composites with PIP-SiC interphase exhibit an obvious toughened fracture behavior and its flexural strength is more than twice as high as that of composites without PIP-SiC interphase.

The oxidation resistance of composites with PIP-SiC interphase is much better than that of composites with PyC interphase.

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