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Effects of pyrolysis temperatures on the microstructure and mechanical properties of 2D-C_f/SiC composites using polycarbosilane

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Abstract

Two-dimensional carbon fiber cloth reinforced silicon carbide (2D-C_f/SiC) composites were fabricated with polycarbosilane (PCS) and divinylbenzene (DVB) as precursors and SiC as inert fillers. The effects of the pyrolysis temperatures in the first cycle on the microstructure and mechanical properties of C_f/SiC composites were investigated. The results showed that increasing the pyrolysis temperature of the first cycle could weaken the interfacial bonding between carbon fiber and SiC matrix. As a result, the composites fabricated with higher pyrolysis temperature exhibit better mechanical properties. When the pyrolysis temperature of the first cycle was raised from 1000 °C to 1600 °C, the flexural strength, shear strength and fracture toughness were elevated from 200.7 MPa, 16.8 MPa and 7.4 MPa $m^{1/2}$ to 319.2 MPa, 29.8 MPa and 15.0 MPa $m^{1/2}$, respectively.

Keywords: B. Interface; Pyrolysis temperatures; Precursor infiltration pyrolysis; 2D-C_f/SiC composites

1. Introduction

C_f/SiC materials benefit from the high temperature capability of carbon fibers and high modulus and oxidation resistance of the SiC matrix [1]. As a fiber-reinforced composite, the mechanical and thermal properties can be tailored by adjusting fiber volume and placement to meet the needs of many applications. Additional flexibility can be achieved with the wide variety of carbon fibers available for reinforcement. Silicon carbide has good high-temperature strength that is maintained to around 1700 °C, sufficient thermal shock resistance, a relatively low thermal expansion coefficient, and potentially a good thermal conductivity [2]. As a result, C_f/SiC composites are considered as desirable high-temperature structure materials and have wide application in many various fields.

There are several methods to fabricate C_f/SiC composites, such as chemical vapor infiltration (CVI), slurry infiltration combined with hot-pressing, polymer-infiltration-pyrolysis (PIP), etc. [3–5] Of these methods, the PIP route is being actively developed because it offers many potential advantages, such as low processing temperature, controllable ceramic compositions, and near-net-shape technologies [6].

The mechanical properties of C_f/SiC composites are determined by their microstructures. Fibre-matrix (FM) interfacial structure is one of the most important factors [7]. It is well demonstrated that weak interfacial is preferred in order to obtain high performance C_f/SiC composites. The microstructures of C_f/SiC composites are governed by fabrication process. The manufacturing of C_f/SiC composites via PIP includes three stages. In stage 1, the fiber preform is infiltrated with precursor solution. In stage 2, the precursor is cured into a solid. In stage 3, the cured solid is pyrolyzed in an inert or reactive atmosphere. Several infiltration-cure-pyrolysis cycles are required to densify composites because the evolution of gaseous products and volume shrinkage occur during pyrolysis, resulting in micro-cracks and pores in matrix. Of the three stages, the pyrolysis is the most important stage because the FM interfacial structure and the matrix are mainly formed in this stage. And early work showed that the first cycle had the most important influence on the microstructure and mechanical properties of the composites [8]. Consequently, the pyrolysis process of the first cycle plays a key role in determining the

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mechanical properties of PIP-derived C_f/SiC composites. But there are still relatively few reports about the effects of different pyrolysis temperatures on the mechanical properties and microstructures of the C_f/SiC prepared by PIP route.

In this paper, two-dimensional carbon fiber cloth reinforced silicon carbide (2D-C_f/SiC) composites were fabricated with polycarbosilane (PCS) and divinylbenzene (DVB) as precursors and SiC as inert fillers, and the effects of the pyrolysis temperatures in the first cycle on the microstructures and mechanical properties of C_f/SiC composites were investigated.

2. Experimental procedure

2.1. Raw materials

The reinforcement used to prepare 2D-C_f/SiC compsoites was plain carbon cloth of type HS of 3 K PAN based fibers made in Jilin Carbon Corporation, China. The tensile strength and elastic modulus of the fibers were about 3000 MPa and 210 GPa, respectively.

Polycarbosilane, the precursor of SiC matrix, with molecular weight ~1300 and softening point ~210 °C, was synthesized in our laboratory. Divinylbenzene was used as solvent and cross-linking reagent for PCS. In previous work, the PCS/DVB solution with a mass ratio of 1:0.4 was demonstrated to be proper to prepare C_f/SiC composites [9].

SiC particles used as inert fillers were produced in the Second Gear Plant of Zhengzhou, China. The density and size were about 3.2 g/cm^3 and 1.0 μm, respectively.

2.2. Preparation of 2D-C_f/SiC

Two-dimensional carbon fiber cloth reinforced silicon carbide composites were fabricated with PCS and DVB as precursors and SiC as inert fillers. To prepare the slurry, PCS was initially dissolved in DVB to which SiC particles were added. For the initial processing cycle, the carbon fiber cloth was cut into ~60 mm × ~90 mm pieces. Twelve cloths were painted with the slurry with an ordinary paintbrush, then put into a graphite mold and then pressed to about 15 MPa. Whereafter the mold was clamped and cured to 150 °C in the oven. The plate together with the mold was pyrolysed to high temperature under inert gas; afterwards it was removed from the mold. Cycles 2–8 consisted of vacuum infiltration with PCS/DVB only and pyrolysed to 1200 °C under an inert gas. The processing of 2D-C_f/SiC composites is shown in Fig. 1.

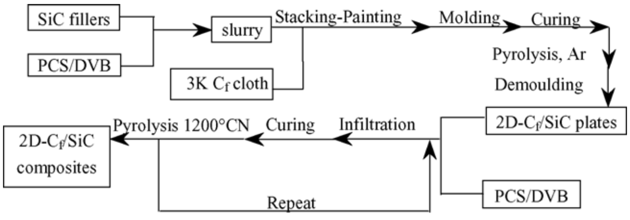

Fig. 1. Fabrication of the 2D-C_f/SiC.

2.3. Characterization of the composites

The apparent densities of the composites were computed from the weight-to-volume ratio.

The mechanical properties were tested at Central South University, China, using a universal testing machine (Instron-1342). Flexural strengths and inter-laminar shear strengths of the composites were determined using a three-point-bending test on specimens of 3.2 mm × 4.2 mm × 60 mm with a span of 40 mm and 16 mm, respectively, and the crosshead speed was 0.5 mm/min. The load–displacement curves were recorded simultaneously by using load-cell and laser extensometer.

For the fracture toughness, a single-edge-notched-beam (SENB) test was applied on notched specimen of 3.2 mm × 6.4 mm × 60 mm in size with a crosshead speed of 0.05 mm/min and a span of 22 mm. The notch, 0.3 mm in width and 3.2 mm in depth, was made in the plane normal to the carbon fiber cloth. The fracture toughness of the composites was obtained from

$$K_{IC} = \left(\frac{P_{\max}L}{wb^2}\right)^n a^{1/2}\left[\left(\frac{3}{2}\right)Y\left(\frac{b}{a}\right)\right] \tag{1}$$

where $P_{\max}$ is the maximum of applied load, b the specimen thickness, w the specimen width, a the notched depth, L the span of support pins, Y a geometrical factor that depends on the test method and the ratio of notched depth to specimen thickness. In this case, Y is given by

$$Y\left(\frac{b}{a}\right) = 1.93 - 3.07\left(\frac{b}{a}\right) + 13.66\left(\frac{b}{a}\right)^2 - 23.98\left(\frac{b}{a}\right)^3 + 25.22\left(\frac{b}{a}\right)^4 \tag{2}$$

The fracture surfaces of specimens after three-point bending tests were examined by scanning electron microscopy (SEM). The phases contained in the SiC matrix derived from PCS/DVB pyrolysis at different temperatures were identified by X-ray diffraction (XRD) with Cu Kα radiation.

The interfacial bonding force between the carbon fiber and SiC matrix was tested by push-in individual fiber from a polished cross-section of the composites at Harbin Institute of Technology, China, using a HIT-100 testing machine. For the test, the force was averaged from those of the 60 individual fibers in one sample. The detailed testing methods had been described in previous papers [10,11].

3. Results

Six composites, which were denoted as A-1000, A-1200, A-1300, A-1400, A-1500 and A-1600, were fabricated with different pyrolysis temperatures in the first cycle, and the densities and mechanical properties of them are shown in Table 1. It is clear that the mechanical properties increase remarkably when the pyrolysis temperature is raised from 1000 °C to 1600 °C, but the densities of the composites were nearly the same. When the pyrolysis temperature of the first cycle was raised from 1000 °C to 1200 °C, the flexural strength,

Table 1
Influence of pyrolysis temperature of the first cycle on the density and mechanical properties of 2D-C_f/SiC composites

Samples	The pyrolysis temperature of the 1st cycle (°C)	The pyrolysis temperature of the 2nd–8th cycle (°C)	Density (g/cm^3)	Flexural strength (MPa)	Shear strength (MPa)	Fracture toughness (MPa m$^{1/2}$)
A-1000	1000	1200	1.922	200.7	16.8	7.4
A-1200	1200	1200	1.914	240.2	19.6	11.4
A-1300	1300	1200	1.901	242.6	19.4	10.7
A-1400	1400	1200	1.878	250.6	22.1	13.5
A-1500	1500	1200	1.898	288.7	26.3	14.7
A-1600	1600	1200	1.887	319.7	29.8	15.0

shear strength and fracture toughness were increased from 200.7 MPa, 16.8 MPa and 7.4 MPa m$^{1/2}$ to 240.2 MPa, 19.6 MPa and 11.4 MPa m$^{1/2}$, respectively. The mechanical properties remained at the same level when the pyrolysis temperature changed from 1200 °C to 1400 °C. But when the pyrolysis temperature was raised to 1500 °C and 1600 °C, the mechanical properties increased farther. A-1600 exhibited the best mechanical properties and the flexural strength, shear strength and fracture toughness of A-1600 reached 319.2 MPa, 29.8 MPa and 15.0 MPa m$^{1/2}$, respectively.

4. Discussion

The mechanical properties of C_f/SiC composites are determined by their microstructures. The interfacial structure and density are two most important factors [7,12]. Weak interfacial bonding and high density could result in high mechanical properties. As noted in Table 1, there is a slight difference in densities of the samples. The increase of the mechanical properties did not seem to result from the change of the densities. Another important factor, which affects the mechanical properties of the composites, is the FM interfacial structure. The fracture surfaces of A1000, A1200 and A1600 are given in Fig. 2. In Fig. 2, A1600 shows extensive fiber debonding and pullout, whereas A1000 exhibits little fiber pullout and the length of the pullout fibers is very short. It is well known that interfacial bonding strength could be evaluated by the morphology of fracture surfaces. Extensive fiber pullout of composites usually indicates a relatively weak FM interfacial bonding, while little fiber pullout and short pullout length indicats a strong FM interfacial bonding. Therefore, the SEM micrographs (Fig. 2) show that the FM interfacial bonding of A1600 is more desirable than those in A1200 and A1000. The pullout mechanism is further supported by a typical load–displacement curve that is shown in Fig. 3. It shows typical delayed fracture behavior of A1600 and brittle fracture behavior of A1000 that is in accord with the results derived from SEM micrographs.

The interfacial bonding force between the carbon fiber and SiC matrix was tested directly and Fig. 4 shows the interface bonding force of C_f/SiC composites pyrolysed at different temperatures. It can be seen that with increasing pyrolysis temperature, the interface bonding force is lowered. Weak interfaces are preferred in order to obtain high-performance C_f/SiC composites that have high toughness and strengths. Because A1000 has a strong FM interfacial bonding, cracking in the matrix can easily propogate across the interface between the fiber and matrix, resulting in failure at low strain as shown in Fig. 3. On the other hand, the weak interfacial bonding in A1600 impedes propogation of matrix cracks into the carbon fibers by debonding of the FM interface, although the cracks propogated throughout the matrix. After that, carbon fibers still support the load through friction between the fibers and matrix. As a result, it can be concluded that the better mechanical properties of the composites can be attributed to the weaker interfacial bonding between the carbon fibers and SiC matrix.

The different interfacial structures of the composites are governed by the various fabrication processes. It has been demonstrated that the interfacial structure between fiber and matrix was formed basically in the first cycle. The interface structures in composites are considered to be relative to the surface characterization of fibres, microstructure of matrix and processing conditions of the composites. Because the HS carbon fibers are fabricated at low temperature (about 1300–1400 °C), it would be expected that the composition and microstructure of the fibers changed greatly when the pyrolysis temperature exceeded 1400 °C, which might modify the bonding between the fibers and matrix. At the same time, it is reasonable to consider that the difference of the interfacial bonding force was also caused by the matrix microstructure,

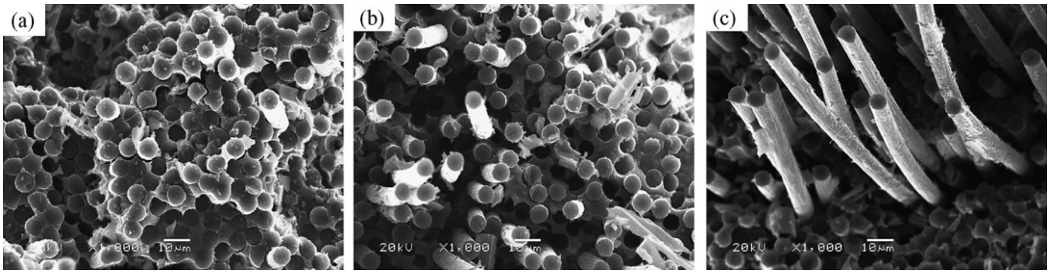

Fig. 2. SEM photos of the fracture surfaces of the C_f/SiC composites (a) A-1000; (b) A-1200; and (c) A-1600.

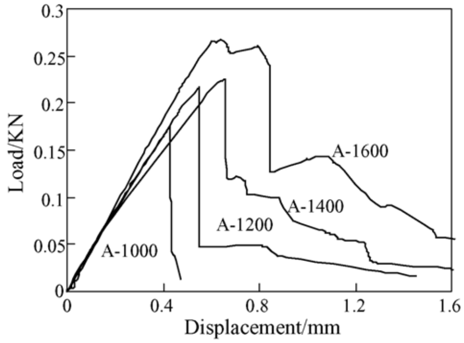

Fig. 3. Load/displacement curves of 2D-C_f/SiC composites with different pyrolysis temperature.

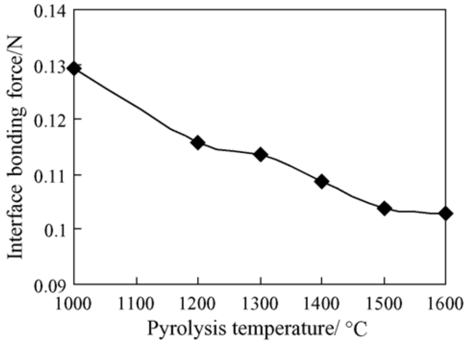

Fig. 4. Interface bonding force of the 2D-C_f/SiC composites with different pyrolysis temperature.

which depends strongly on the pyrolysis temperature. Fig. 4 shows an XRD pattern of the pyrolytic residue of PCS/DVB treated at 1000 °C, 1200 °C and 1600 °C in an inert atmosphere. The three broad peaks are considered to be (1 1 1), (2 2 0) and (3 1 1) peaks of β-SiC. It is expected that their crystallinities and microstructures differ remarkably between the three groups. The peaks of the samples pyrolysed at 1000 °C are broad, whereas those of samples pyrolysed at 1200 °C and 1600 °C are much narrower. It could be concluded that the crystallinity of β-SiC was not well developed when the pyrolysis temperature was 1000 °C. Significant amount of amorphous Si–C phase exists in the pyrolytic residue which could result in the strong interface bonding. With increasing pyrolysis temperature, the amorphous Si–C phase could yield SiC and C. As the result of decomposition of amorphous Si–C phase, fiber-matrix bonding will be weaker. When the pyrolysis temperature is raised to 1600 °C, the PCS/DVB will be pyrolysed more completely and most of the amorphous Si–C phase could yield SiC crystallite (Fig. 5).

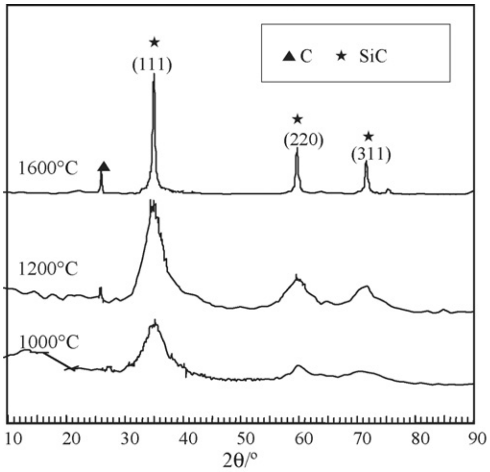

Fig. 5. XRD patterns of paralysis products of PCS/DVB at different temperatures.

5. Conclusions

2D-C_f/SiC composites were fabricated with polycarbosilane and divinylbenzene as precursors and SiC as inert fillers. Effects of pyrolysis temperature on the microstructure and properties of the composites were investigated. Six kinds of composites were fabricated and their mechanical properties and microstructures were evaluated. The following conclusions could be drawn from the present investigations:

(1) Raising the pyrolysis temperature of the first cycle, 2D-C_f/SiC composites results in better mechanical properties. The flexural strength, shear strength and fracture toughness of A-1000 were only 200.7 MPa, 16.8 MPa and 7.4 MPa $m^{1/2}$, respectively, while those of A-1000 are 319.2 MPa, 29.8 MPa and 15.0 MPa $m^{1/2}$, respectively.
(2) The better mechanical properties are attributed to the appropriate FM interfacial structure. With raising the pyrolysis temperature, the precursor decomposes more completely and the interfacial bonding becomes weaker. As a result, the mechanical properties of C_f/SiC composites are increased.

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