Carbon-fiber-reinforced silicon carbide composites prepared by precursor pyrolysis-hot pressing①

He Xinbo(何新波)[1], Zhang Xinming(张新明)[1]

1. Department of Materials Science and Engineering,

Central South University of Technology, Changsha 410083, P. R. China

Zhang Changrui(张长瑞)[2], Zhou Xingui(周新贵)[2] and Zhou Anchen(周安郴)[2]

2. Department of Materials Engineering and Applied Chemistry,

National University of Defense Technology, Changsha 410073, P. R. China

Abstract: The C_f/SiC composites were prepared by precursor conversion-hot pressing sintering with AlN and Y_2O_3 as additives. The effects of sintering temperature and additives on the microstructures and properties of the composites were investigated. The composite sintered at as low as 1 750 ℃ already showed higher density and better mechanical properties, which was mainly attributed to the liquid-phase-sintering and the formation of the AlN-SiC solid solution. With increasing the sintering temperature to 1 800 ℃, the flexural strength and fracture toughness of the composite were substantially improved up to 691.6 MPa and 20.7 MPa·m$^{1/2}$ respectively in spite of the slightly elevated density, and the composite exhibited "tough" failure. Despite the improved density, the composite sintered at 1 850 ℃ displayed brittle failure, which mainly attributed to the strongly bonded fiber/matrix interface and the degradation of the properties of the fibers.

Key words: precursor pyrolysis-hot pressing; C_f/SiC composites; sintering temperature

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1 INTRODUCTION

Silicon Carbide (SiC) is one of the promising candidate's ceramics for high-temperature structural components because of its many excellent properties, including strength retention, oxidation resistance at high temperature, low density and high hardness etc. However, like all ceramic materials, they are generally notch - sensitive and low in toughness, resulting in relatively low reliability as structural components and limited applications. Therefore, a number of investigations have been focused on the improvement in the reliability, and continuous fiber reinforced SiC composites have been demonstrated to be the most effective approach to improving toughness[1~3].

It is well demonstrated that the fiber/matrix interface plays a key role in determining the mechanical properties of the composites[3~5]. In general, a weakly bonded fiber/matrix interface leads to a toughened composite-like behavior, whereas a strongly bonded interface results in a brittle composite. So, it is of critical importance, in fiber reinforced ceramic composites, to control the fiber/matrix interface perfectly.

There are several methods to fabricate fiber/SiC composites, such as chemical vapor infiltration (CVI)[6,7], slurry infiltration combined with hot-pressing[2, 8, 9], polymer-impregnation[10~12] and reaction sintering etc. In this study, the C_f/SiC composites were fabricated by precursor pyrolysis-hot pressing with Y_2O_3-AlN as additives. The effects of the additives on the microstructures and the mechanical properties of the composites were studied. In addtion, the effect of the fiber coating of pyrolytic carbon (P_yC) on the fiber/matrix and the mechanical

properties of the composites was investigated.

2 EXPERIMENTAL

2.1 Fabrication of the composites

The commercially available α-SiC with average size about $0.8\,\mu m$, used as starting powder for the matrix, was mixed with AlN-Y_2O_3 (average grain size about $1.0\,\mu m$) as sintering additives, and a certain amount of polycarbosilane (average molecular weight about 1 400) was added to as precursor and binder. The mixture was milled in a jar made of agate with xylene as a dispersive medium using SiC grinding ball for 24 h. After milling, the resultant mixture was the slurry for the fabrication of the composites.

The composites were fabricated via slurry impregnation-hot pressing sintering. Unidirectional fiber aligned preform tapes were prepared by infiltrating the uncoated or coated carbon fiber (Model M40JB) with the slurry above-prepared and winding slurry-infiltrated strands onto a mandrel (150 mm in diameter). Afte drying, the prepared tapes were cut, stacked and prepressed in metal dies with size of 30 mm × 35 mm at about 180 ℃ into compacts, then, the compacts were hot pressed in graphite dies for 1h with the pressure of 25 MPa in a flowing argon atmosphere (100 kPa). The sintering temperatures were 1750 ℃, 1 800 ℃ and 1 850 ℃.

2.2 Characterization of the composites

The bulk densities of the samples were measured by the Archimedes principle using deionized water as the immersion medium. The flexural strength was measured using three-point-bending test with a cross-head speed of 0.5 mm/min and a span of 30 mm. The samples were 3 mm × 4 mm × 35 mm in size. For fracture toughness, single-edge-notched-beam (SENB) test was used with a cross-head speed of 0.05 mm/min and a span of 20 mm. The samples were 2.5 mm × 5 mm × 30 mm with the notch depth to sample height ratio of 0.5.

The microstructure observation and composition analysis were carried out in a conventional transmission electron microscope (Model JEM-2010) equipped with LINK-ISIS energy-dispersive X-ray spectrometer (EDS). For structural analysis of the grains and phase boundaries as well as intergranular phases, the high-resolution TEM imaging technique (HRTEM) was applied. In addition, the fracture surfaces of the samples were observed by a scanning electron microscopy (SEM), and the phases in the samples were identified by X-ray diffractometer (XRD).

3 RESULTS AND DISCUSSION

3.1 Mechanical properties of the composite

The densities and mechanical properties of the composites are summarized in Table 1, which shows that the composite with uncoated fibers have been densified at the temperature as low as 1 750 ℃ and the densities increased with the sintering temperature. The density of the composites sintered at 1 850 ℃ achieved 95.6% of the theoretical density. These results show that the increase of the sintering temperature is helpful to the densification, which is good agreement with the sintering theory on ceramics. In addition, the interlaminar shear strength is improved with the sintering temperature in accordance with the density, which is considered to be primarily due to the strengthening of the fiber/matrix interface resulting from the increase of sintering temperature. However, the variation of the mechanical properties is not agreement with that of the density or interlaminar shear strength. Increasing the sintering temperature from 1 750 ℃ to 1 800 ℃, the flexural strength and fracture toughness increased by 22.8% and 35.3%, respectively, apart from the improvement in density. However, irrespective of the improvement in density and interlaminar shear strength, the flexural strength and fracture toughness of the composite sintered at 1 850 ℃ decreased by 17.6% and 36.7%, respectively, as compared with that of the composite sintered at 1 800 ℃, which can be explained by the change of the fiber/matrix interface. In comparison with the composite sintered at 1 850 ℃ with uncoated fibers, the composite sintered at 1 850 ℃ with P_yC-coated fibers exhibited much better flexural strength and fracture

Table 1   Densities and mechanical properties of the composites tested

Fiber coating	Sintering temperature /℃	Flexural strength /MPa	Fracture toughness /MPa·m$^{1/2}$	Interlaminar shear strength /MPa	Density /g·cm^{-3}	Relative density /%
none	1750	563.2	15.3	31.2	2.32	92.8
none	1800	691.6	20.7	39.8	2.34	93.6
none	1850	569.7	13.1	44.3	2.39	95.6
P$_y$C	1850	723.5	18.8	37.1	2.32	92.8

toughness in spite of the decrease in density and interlaminar shear strength (Table 1), which indicated that fiber coating shows remarkable effect on the mechanical properties.

3.2 Microstructures of the composites

Fig. 1 presents the microstructures of the composites. It was found that the matrixes in the composites primarily consist of fine equiaxed grains with average size about 1.0 μm and some finer grains of about 100 ~ 300 nm in size. In combination with the XRD pattern in which no AlN peaks were identified, the EDS results revealed that the large grains mainly containing Si and C should be the starting SiC grains (Fig. 2 (a)) and the fines containing a lot of Al and N besides Si and C should be SiC-AlN solid solution grains(Fig. 2(b)). The bright phase in Fig. 1 proved to be the grain-boundary-phase and fiber/matrix interphase, whose EDS and SAD patterns are presented in Fig. 2(c). It can be presumed that the reaction among the Y$_2$O$_3$, AlN, and PCS may be responsible for the formation of the liquid-phase, which is distributed at the grain boundaries and the fiber/matrix interface mainly in the amorphous form. The pyrolysis products of the PCS in the present study are mainly comprised of β-SiC microcrystallines as well as some amorphous Si-O-C, SiO$_2$ and free-C. It can be proposed that the AlN-SiC solid solution is formed by the processes of the reaction between AlN and the pyrolysis products of the PCS, dissolution of the AlN and SiC and precipitation of the AlN dissolved in the grain-boundary-phase on the surface of the SiC microcrystalline. These uniform solidsolution grains, mainly distributed in the grain-boundary-phase can strengthen the grain-boundary-phase and suppress the growth of the SiC grains as well as improve the fiber/matrix interfacial bonding.

The studies on the interfaces showed that several types of interfaces were identified in the composites. One is the SiC/SiC interface, which is very clean and no grain-boundary-phase can be observed as shown in Fig. 3(a). The second is the interface between the SiC and the grain-boundary-phase shown in Fig. 3(b), and the third is the interface between solid solution grain and the grain-boundary-phase shown in Fig. 4. Comparing with the interface in Fig. 3(b), the interface in Fig. 4 is unclear and tortuous, which can also confirm that the processes of reaction-dissolution-precipitation are responsible for the formation of the SiC-AlN solid solution. Of all the interfaces in the matrix, the interfaces shown in Fig. 3(b) and Fig. 4 are predominant, which revealed that the composites were densified through the liquid-phase-sintering mechanism. In addition, another interface, namely fiber/matrix interface, can be observed in the composites, which will be discussed in details later.

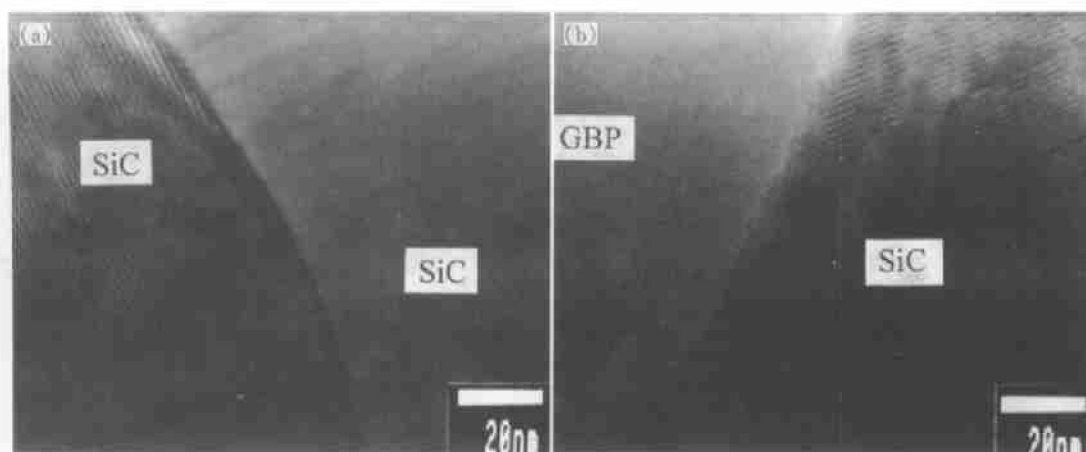### 3.3 Fracture behavior of the composites

Fig. 5 shows the fiber/matrix interfaces

**Fig. 1**   TEM image of the composite sintered at 1800 ℃
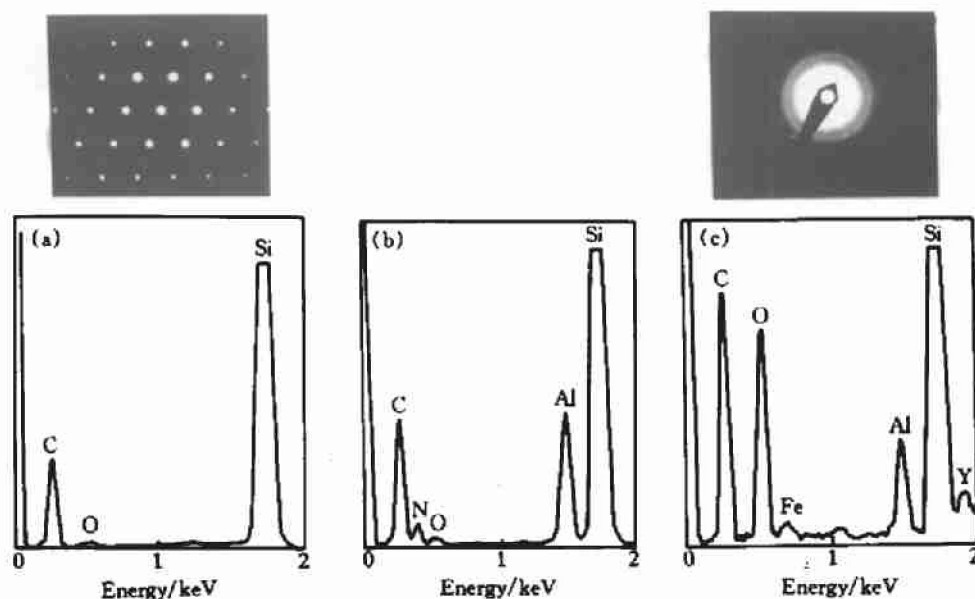
Fig.2   SAD and EDS pattern of the
large grains (a), fine grains (b) and grain-boundary-phase (c) in Fig.1

Fig.3   HRTEM images of the interfaces
between SiC grains (a) and SiC grain and grain-boundary-phase(GBP) (b)

in the composite sintered at 1 850 ℃ with un- coated or coated fibers. It was observed that the fiber/matrix interface in the composite sintered at 1 800 ℃ with uncoated fibers is made of uni- form carbon-rich grain-boundary-phase with a certain of thickness (Fig. 1). Wh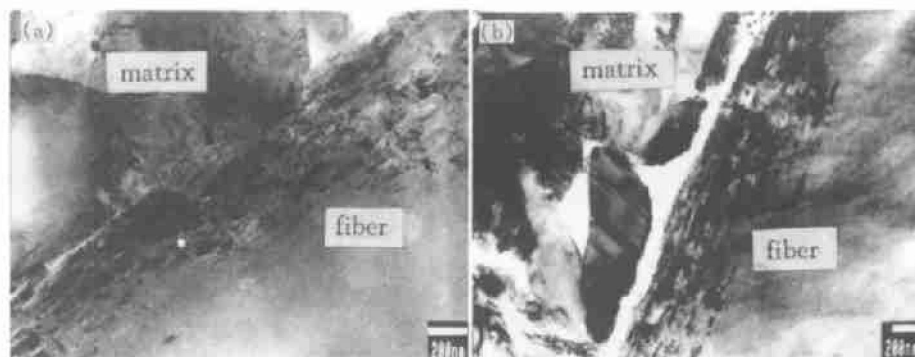ereas in the composite sintered at 1 850 ℃ with uncoated fibers, the interface is very narrow and little in- terphase can be observed, which may be at- tributed to the discrepancy in inter-diffusion a- mong the grain-boundary-phase fiber and the matrix. It is well known that the fiber/matrix interfacial characteristics play a critical role in controlling the properties of the composites,
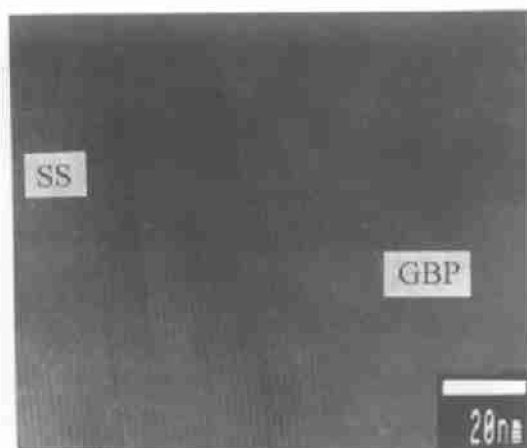
Fig. 4 HRTEM image of the interface
between solid solution (SS) and
grain-boundary-phase (GBP)

so the discrepancy in mechanical properties may
be explained by the variation of the fiber/matrix
interface[13,14]. The fiber/matrix interfacial
bonding in the composites sintered at 1 800 ℃ is
believed to be desirable, therefore, the compos-
ite exhibits tough behavior and excellent me-
chanical properties, which can be proved by the
fracture surface of the composite shown in Fig. 6
(a). However, the composite sintered at
1 850 ℃ shows brittle behavior (Fig. 6(b)) and
degraded mechanical properties as compared with
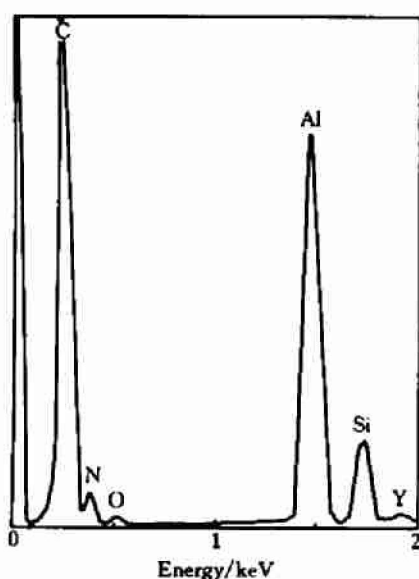the composite sintered at 1 800 ℃, which can be

rationalized on the basis of a strongly bonded
fiber/matrix interface in combination with
greater degradation of the fibers resulting from
higher temperature. The present of Al, N, O,
Y and Si elements in the fibers are detected by
EDS, as shown in Fig. 7, which reveals the oc-
currence of the inter-diffusion among the fiber,
matrix and the grain-boundary-phase. And it can
be thought that the inter-diffusion in the com-
posite sintered at 1 850 ℃ is serious compared
with that in the composite sintered at 1 800 ℃,
which is the critical reason for the decrease in the
mechanical properties of the composites. The
fiber/matrix interface in composites with P_yC-
coated fibers, which is distinct from the compos-
ite with uncoated fibers, is a broad region con-
sisting of carbon-rich interphase (Fig. 5(b)). It
decreased not only the fiber/matrix interfacial
bonding (decrease in interlaminar shear
strength), but limited the diffusion of the grain-
boundary-phase into the fibers which is primarily
responsible for the deterioration of the fibers.
Fig. 8 depicts the Al and Y atomic distribution in
the matrix, fiber and interphase. It was con-
cluded that the diffusion of the grain-boundary-
phase into the fibers in the composite with P_yC-
coated fiber was limited effectively as compared
with the composite with uncoated fibers. So, in
combination with the decreased fiber/matrix in-
terfacial bonding, the composite with P_yC-coated
fibers displayed much better mechanical proper-
ties and tough behavior(Fig. 9).

Fig. 5 TEM images of the composites
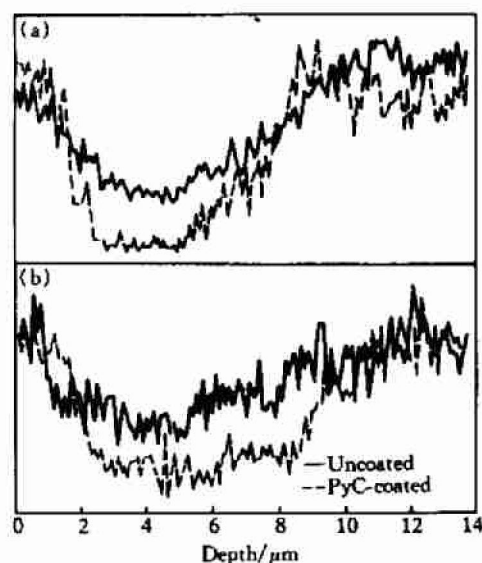sintered at 1 850 ℃ with uncoated fibers (a) and coated fibers (b)
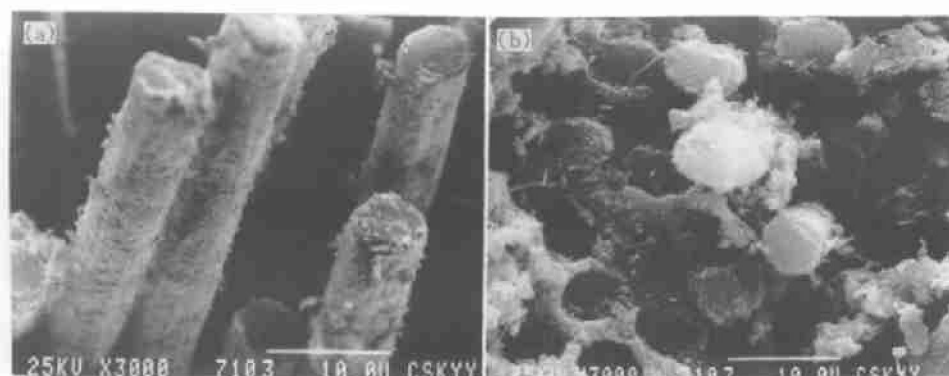
Fig.6 Fracture surfaces of the
composites sintered at 1 800 ℃ (a) and 1850 ℃ (b) with uncoated fibers

Fig.7 EDS pattern of the fibers
in the composite sintered
at 1 850 ℃ with uncoated fibers

Fig.8 Atomic concentration profile
for the composite sintered at 1 850 ℃
with uncoated or P_yC-coated fibers

(a)—Al element; (b)—Y element.

Note the region from 2 to 8 μm in depth refers to the fiber.

4 CONCLUSIONS

The C_f/SiC composites were prepared by polymeric precursor pyrolysis-hot pressing sintering with AlN and Y_2O_3 as sintering additives. During the sintering, Y_2O_3 reacted with the pyrolysis products of the PCS and the oxides on the surface of the AlN and SiC grains, forming the liquid-phase assisting in the densifcation of the composites. So, the composite sintered at the temperature of 1 750 ℃ showed higher density

and better mechanical properties. On increasing the sintering temperature to 1 800 ℃, the flexural strength and fracture toughness of the composite were substantially improved up to 691. 6 MPa and 20. 7 MPa·$m^{1/2}$, respectively, and the composite exhibited tough behavior. This could be explained by the desirable fiber/matrix interfacial bonding resulting from the formation of the
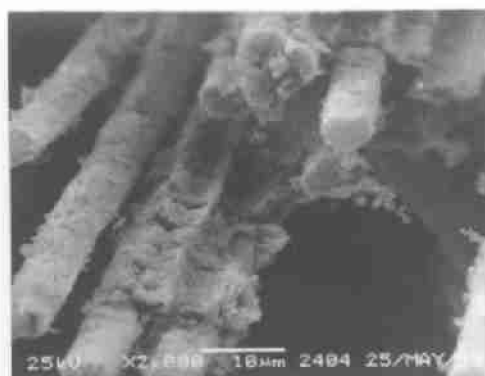
Fig.9 Fracture surface of the
composite with coated fibers

carbon-rich fiber/matrix interphase containing a
certain number of SiC-AlN solid solution grains.
However the composite sintered at 1 850 ℃
showed a degraded mechanical properties and a
typical brittle behavior, which may be rational-
ized on the basis of the relatively strongly bonded
fiber/matrix interface and the serious degrada-
tion of the fibers. In the case of the composite
with P_yC-coated fibers, owing to the presence of
the broad interface region, which decreased not
only the fiber/matrix interfacial bonding, but al-
so limited the diffusion of the grain-boundary-
phase into the fibers, the composite exhibited
better mechanical properties. All the results in-
dicated that the fiber/matrix interface played a
critical role in controlling the mechanical proper-
ties.

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