JOURNAL OF MATERIALS SCIENCE **34** (1999) 827–834

The properties of carbon fibre/SiC composites fabricated through impregnation and pyrolysis of polycarbosilane

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Unidirectional carbon fibre reinforced SiC composites were prepared from four types of carbon fibres, PAN-based HSCF, pitch-based HMCF, CF50 and CF70, through nine cycles or twelve cycles of impregnation of polycarbosilane and subsequent pyrolysis at 1200 °C. The polycarbosilane-derived matrix was found to be β-SiC with a crystallite size of 1.95 nm. The mechanical properties of the composites were evaluated by four-point bending tests. The fracture behavior of each composite was investigated based on load-displacement curves and scanning electron microscope (SEM) observation of fracture surfaces of the specimens after tests. It was found that CF50/SiC and CF70/SiC exhibited high strength and non-brittle fracture mode with multiple matrix cracking and extensive fibre pullout, whereas HSCF/SiC and HMCF/SiC exhibited low strength and brittle fracture mode with almost no fibre pullout. The differences in the fracture modes of these carbon fibre/SiC composites were thought to be due to differences in interfacial bonding between carbon fibres and matrix. Values of flexural strengths of CF70/SiC and CF50/SiC were 967 MPa and 624 MPa, respectively, which were approximately 75% and 38% of the predicted values. The relatively lower strength of CF50/SiC, compared with CF70/SiC, was mainly attributed to the shear failure of CF50/SiC during bending tests. © *1999 Kluwer Academic Publishers*

1. Introduction

Silicon carbide ceramics have wide applications in various industrial fields because of their excellent high-temperature strength and modulus, low density, good oxidation resistance and high hardness etc. However, like all ceramic materials, they are generally notch-sensitive and low in toughness, hence they are unreliable as structural materials. Continuous fibre reinforced SiC composites have been demonstrated to be the most effective way for improving toughness [1–3].

Generally, there are several methods to fabricate fibre/SiC composites, such as chemical vapor infiltration (CVI) [4, 5], slurry infiltration combined with hot-pressing [2, 6, 7] and polymer-impregnation [8–10], etc. The feature of CVI is that the process can be conducted at about 1100 °C, much lower than the sintering temperature of SiC. Moreover, it can be applied to complex shapes with near-net-shape feature. However, the CVI process takes a very long time to densify the composites. Fibre/SiC composites can also be fabricated through slurry infiltration. Fibres have been infiltrated with a slurry of SiC and then hot-pressed at high temperature [5, 6]. This process is limited to simple shapes, and the samples have to be hot-pressed at very high temperatures near 1900 °C, which causes degradation of reinforcements [11]. One other method to prepare continuous fibre reinforced ceramic composites is to use a preceramic polymer, such as polycarbosilane, which is frequently used to fabricate ceramic fibre [12] or film [13]. This method is gaining increasing attention in recent years because of its low processing temperature and good shaping features. The preceramic polymer liquid with low viscosity, which can be obtained by dissolving in organic solvent [8, 9] or melting at elevated temperature [10], can be easily infiltrated into the fibre preform by using vacuum impregnation or pressure impregnation.

It is well demonstrated that the interface between fibre and matrix plays a key role in translating the mechanical properties of reinforcements to the mechanical properties of the ceramic matrix composites [3, 14, 15]. Weak interfaces are preferred in order to obtain high-performance fibre/ceramic composites which have high toughness and high strength. Possible interface bonding in composites includes interdiffusion, chemical bonding, reaction bonding and mechanical bonding, etc. [16], which strongly depend on processing conditions and the structure and properties of matrix and fibres, especially the surface structures of fibres. In designing fiber/ceramic systems, fibres, matrix and processing conditions should be carefully considered to diminish or avoid chemical bonding, reaction bonding

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and interdiffusion bonding. However, the mechanical bonding, which depends on the surface roughness of fibres and residual stresses in composites, cannot be avoided. In many cases, in order to reduce the interfacial bonding strength in ceramic matrix composites, carbon [4] or BN [17] was frequently coated on the surface of fibres. In carbon fibre reinforced SiC composites (CF/SiC), it is possible to tailor the interface by controlling the structure and surface structure of carbon fibres. There are a variety of commercially available carbon fibres from PAN-based high strength carbon fibres to pitch-based high modulus carbon fibres which show very different structures. However, these carbon fibres are produced mainly for resin matrix composites in which strong interfacial bonding is preferred. Therefore, it can be expected that these carbon fibres may show different behavior in ceramic matrix composites. There are still relatively few reports about the effects of different types of carbon fibres on the mechanical properties and fracture behavior of CF/SiC prepared from preceramic polymers. In this paper, the effects of different types of carbon fibres on the mechanical properties of CF/SiC composite materials, which were prepared through impregnation of polymer precursor of SiC, polycarbosilane (PCS), were investigated.

2. Experimental

2.1. Raw materials

Four types of continuous carbon fibres, PAN-based high strength carbon fibre (HSCF), pitch-based high modulus carbon fibre (HMCF) and ultra-high modulus carbon fibre CF50 and CF70, were used as the reinforcements. Some properties of these carbon fibres are shown in Table I. HSCF and HMCF, which were carbonized at below 1500 °C, had relatively low modulus, while CF50 and CF70, which were graphitized at above 2000 °C, showed much higher modulus than the other two types of carbon fibres. They were immersed in acetone to remove the sizing from the surface of fibres before being used in the processing of the composites.

Polycarbosilane (Type-UH, Nippon Carbon Co.) was used as the precursor of the SiC matrix, whose properties are shown in Table II (data by the maker). It can be directly pyrolysed to ceramic with a yielding of about 74% without curing. A toluene solution of PCS was used to impregnate carbon fibres to prepare SiC matrix composites.

2.2. Preparation process of CF/SiC

Continuous carbon fibres were wound unidirectionally on a metal frame and placed in a metal die. 50 wt % PCS toluene solution was poured into the metal die and infiltrated into the fibre preform and then pressed to remove excess solution. After drying at 80 °C, the prepregs were pyrolysed at 1200 °C in N_2 with a heating program of 5 °C/min to 300 °C, 1 °C/min to 800 °C, 5 °C/min to 1200 °C, holding at 1200 °C for 1 hour and then free cooling. The prepregs were then impregnated with 50 wt % PCS solution in vacuum, dried at 80 °C, and pyrolysed at 1200 °C in N_2 with the same heating program as described above. The impregnation in vacuum and pyrolysis process was repeated 8 times for HSCF and HMCF and 11 times for CF50 and CF70 to densify the composites. The sizes of the as-prepared composites were approximately 80 mm × 37 mm × 1 mm.

TABLE I Properties of as-received carbon fibres

Types of carbon fibres	Precursors of fibres	Density g/cm^3	Diameter μm	Tensile strength MPa	Tensile modulus GPa
HSCF	PAN	1.76	7.0	3830	240
HMCF	pitch	1.90	9.8	3350	277
CF50	pitch	2.14	9.4	3950	519
CF70	pitch	2.18	9.4	4200	700

TABLE II Properties of polycarbosilane (Type-UH)

Mean molecular weight	m.p.* °C	Chemical compositions wt % Si	C	H	O	N	SiC yield %
5000	partial ∼ 350	49.4	39.5	8.1	1.35	1.65	74

*Only partially melting at about 350 °C.

2.3. Evaluation of mechanical properties and microstructures of the composites

The volume fractions of fibre (V_f) in the composites were measured by scanning electron microscope (SEM) photography of cross-sections of the composites. The bulk density of the composites was obtained by measuring weight and sizes of the samples. The total porosity of the composites was then calculated from the density of the carbon fibres and SiC matrix, the composite bulk density, and the volume fraction of the fibre. Four-point bending tests were used to evaluate mechanical properties of the composites with a crosshead speed of 0.5 mm/min, a support span of 30 mm and a loading span of 10 mm, using a universal testing machine (AGS-5KND, Shimadzu, Japan). The sizes of specimens for flexural strength tests were about 3.5 mm in width, 1 mm in thickness and 40 mm in length. The load-displacement curves were recorded simultaneously by using load-cell and laser extensometer.

Fracture surfaces of the specimens after four-point bending tests were examined on the SEM. Crystallinity of the carbon fibres and the SiC matrix was analyzed using x-ray diffraction (XRD).

3. Results

3.1. Pyrolysis of polycarbosilane

Fig. 1 shows the thermal gravimetric analysis (TGA) of PCS pyrolysed in N_2. It is noted that the PCS lost about 6% of its weight at 70 °C–300 °C, due to evaporation of small molecules in the PCS. From 300 °C to 440 °C, the PCS had almost no change in weight. From 440 °C–800 °C, there was a remarkable weight loss, due to the decomposition of PCS. Above 800 °C, the weight of PCS residue showed almost no change, indicating that PCS had been changed to inorganic materials. The trend of the pyrolytic process of the PCS was similar to

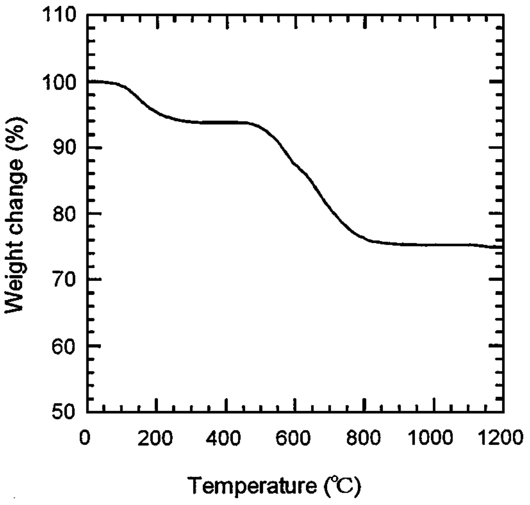

Figure 1 TGA curve of polycarbosilane in N_2.

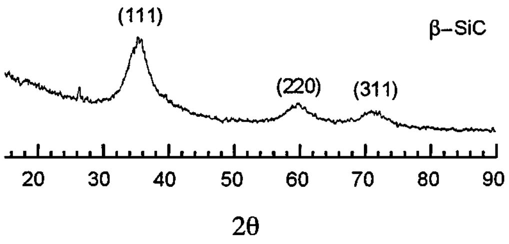

Figure 2 XRD pattern of pyrolytic residue of polycarbosilane.

those reported by other researchers [18, 19]. However, the PCS used here showed higher pyrolytic yield, because the PCS probably had a high average molecular weight and was well cross-linked.

Fig. 2 shows an XRD pattern of the pyrolytic residue of PCS treated at 1200 °C for 1 hour in N_2. The three broad peaks are considered to be (111), (220) and (311) peaks of β-SiC. It is apparent from the broad peaks that the β-SiC has a small crystallite size. The half-width of its (111) peak was measured quantitatively and the L_{111} crystallite size of β-SiC was calculated to be 1.91 nm according to the Scherrer equation. The L_{111} value was slightly smaller than the values obtained from other researchers [18, 19]. It is suggested that in PCS which cross-linked well, it is more difficult to stack the atoms in an orderly manner during pyrolysis. The peak at 26.6° was probably caused by silica. It still appeared in the 1400 °C-heat-treated samples, however, it was not detected in the 1600 °C-heat-treated samples which showed some weight loss. These phenomena suggested that there was silica and free carbon in the pyrolytic residue of PCS which had been well demonstrated in other types of PCS [18, 19].

3.2. Mechanical properties of the composites

HSCF/SiC and HMCF/SiC composites were prepared through a total of 9 cycles of impregnation of PCS, whereas CF50/SiC and CF70/SiC composites were prepared through a total of 12 cycles of impregnation of PCS as described in section 2.2. The mechanical properties of the composites were evaluated by four-point bending tests combined with load-displacement curves recorded simultaneously. The specimens for the bending tests were prepared with a thickness of 1 mm, in order to prevent the specimen from failing in a shear way. The obtained properties of the composites are shown in Table III. The matrix cracking stress was determined from the load at which deviation from linearity in the load-displacement curves occurred. The matrix cracking stresses of HSCF/SiC and HMCF/SiC are not listed in Table III, because these two composites failed in a brittle mode. The ultimate flexural strength was obtained from the peak load. The four kinds of CF/SiC composites in Table III can be classified into two groups. The first group of HSCF/SiC and HMCF/SiC failed in a brittle mode with flexural strength of 210 MPa and 275 MPa, respectively. The other group of CF50/SiC and CF70/SiC failed in a non-brittle fracture mode with ultimate flexural strength of 624 MPa and 967 MPa, respectively. Fig. 3 shows the load-displacement behavior of the composites. HSCF/SiC and HMCF/SiC exhibited perfectly linear load-displacement behavior up to the point of fracture. In contrast, the load-displacement behavior of CF50/SiC and CF70/SiC were markedly non-linear.

To elucidate the failure behavior of the composites, the specimens were observed by SEM after the bending tests. Fig. 4 shows the fracture surfaces of HSCF/SiC and HMCF/SiC. It is noted that both of HSCF/SiC and HMCF/SiC exhibited flat fracture surfaces with very short fibre pullout; notably HSCF/SiC showed a completely flat fracture surface. It has been well demonstrated that these phenomena were caused by strong interfacial bonding between carbon fibre and matrix. On the contrary, the fracture surfaces of CF50/SiC and CF70/SiC showed extensive fibre pullout which was demonstrated to be caused by weak interfacial bonding of CF/matrix [15, 16]. It was also found that there were many matrix cracks normal to the fibre axis direction on the tensile surface of the CF50/SiC and CF70/SiC after bending tests. Fig. 5 shows the matrix cracking on the surface and in the centre of CF70/SiC. CF50/SiC also exhibited similar phenomena. Matrix cracking has also been reported in many continuous fibre reinforced ceramic composites which exhibited high strength, and

TABLE III Mechanical properties of the composites

Composites	Apparent density (g/cm^3)	V_f (%)	Total porosity (%)	Matrix cracking stress (MPa)	Flexural strength (MPa)	Modulus (GPa)	Fracture mode
HSCF/SiC	1.74	67	13	—	220 ± 38	105	Brittle
HMCF/SiC	1.92	58	12	—	275 ± 51	121	Brittle
CF50/SiC	2.20	43	10.2	242 ± 50	624 ± 123	188	Non-brittle
CF70/SiC	2.28	33	9.6	268 ± 43	967 ± 62	207	Non-brittle

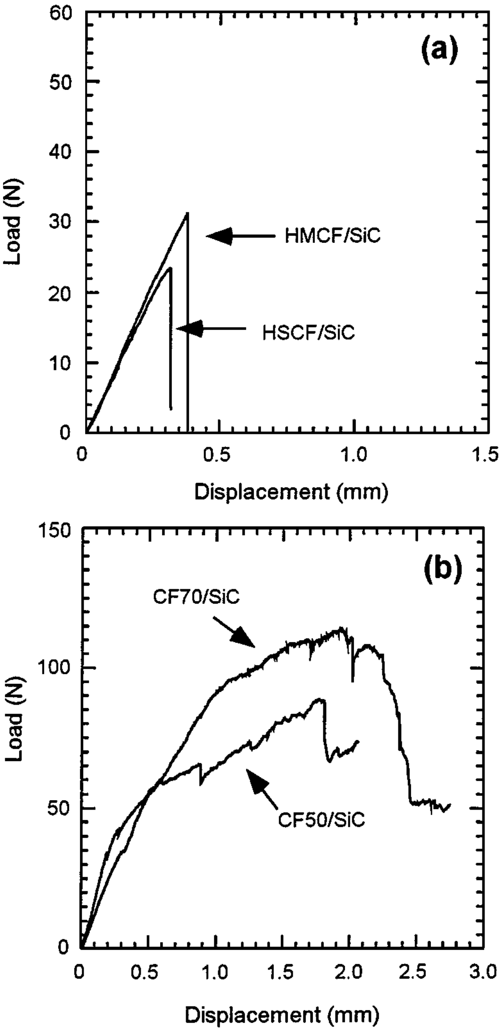

Figure 3 Load-displacement curves of HSCF/SiC and HMCF/SiC (a), CF50/SiC and CF70/SiC (b) in four-point bending tests.

have been treated theoretically by many researchers [3, 20, 21].

The ultimate tensile strength of ceramic matrix composites which exhibited matrix cracking and fibre pull-out was deduced theoretically by Curtin [22], as shown by the following formula,

$$\sigma_{UTS} = V_f \sigma_c \left(\frac{2}{m+1}\right)^{1/(m+1)} \left(\frac{m+1}{m+2}\right) \quad (1)$$

where V_f represents the fibre volume fraction, σ_c is the characteristic strength of fibre, m is the Weibull modulus of fibre strength distribution. The m of CF50 and CF70 were measured to be 3.53 and 4.06, respectively, by testing the monofilament strength of as-received fibres. Here we estimated approximately the ultimate tensile strength of CF50/SiC and CF70/SiC, assuming that σ_c was equal to the average strength of the fibres. The ultimate tensile strengths of CF50/SiC and CF70/SiC were then calculated to be 1176 MPa and 930 MPa, respectively.

It was reported that the flexural strengths are approximately 1.4 times greater than tensile strengths in continuous fibre reinforced ceramic matrix composites [23]. Therefore the predicted ultimate flexural strength of CF50/SiC and CF70/SiC were obtained as 1646 MPa and 1300 MPa, respectively. Compared with the measured values in Table III, it can be noted that the measured flexural strength of CF70/SiC was about 75% of the predicted value. The discrepancy between measured and predicted strengths of the composites may be caused by the damage of carbon fibre during processing of the composite. On the other hand, the flexural strength of CF50/SiC was only approximately 38% of

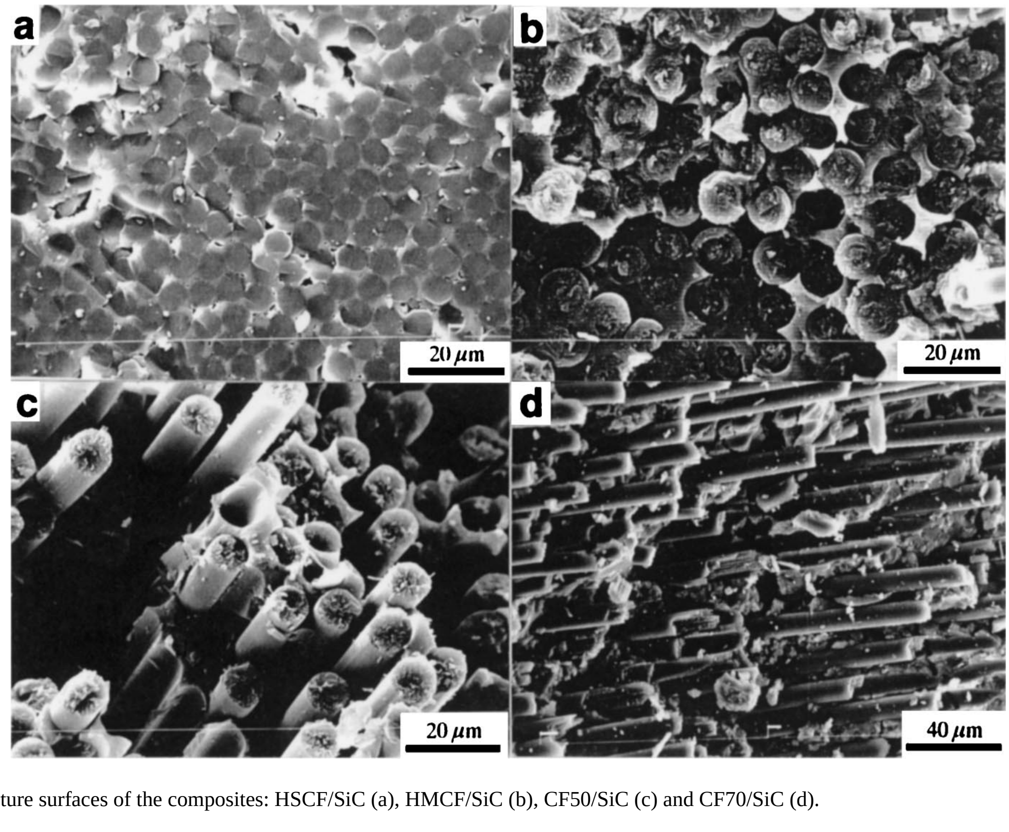

Figure 4 Fracture surfaces of the composites: HSCF/SiC (a), HMCF/SiC (b), CF50/SiC (c) and CF70/SiC (d).

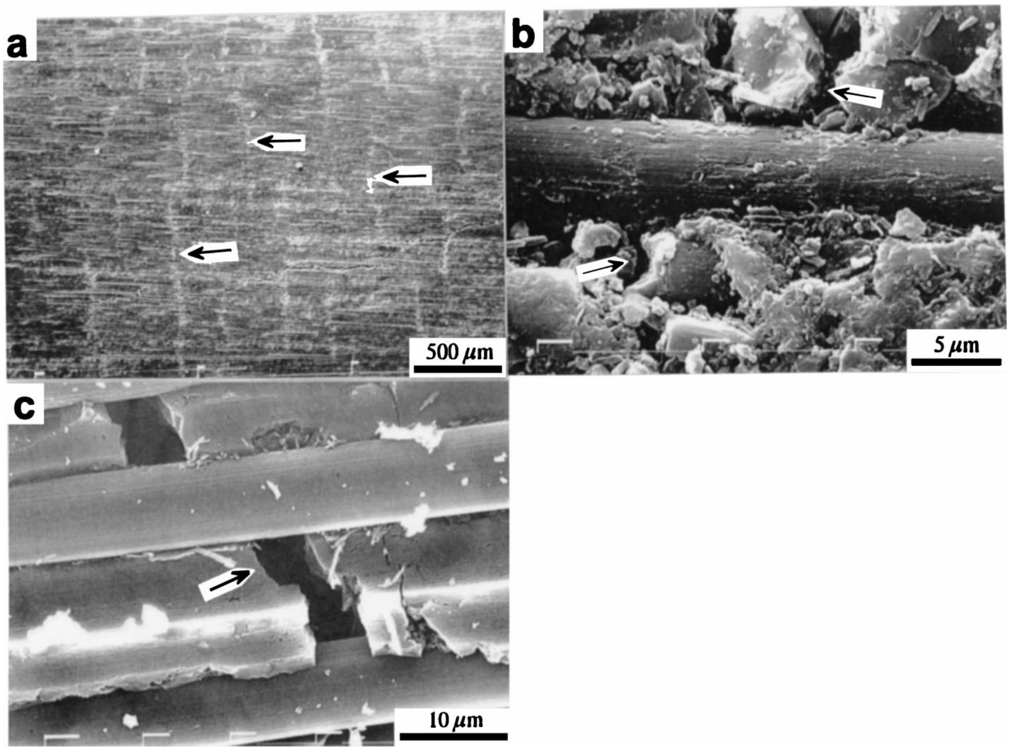

Figure 5 Matrix cracking occurred in CF70/SiC during four-point bending test: matrix cracking on the surface (a) (b), matrix cracking in the sample (c).

the predicted value. The main reason was that CF50/SiC failed in a shear way before tensile failure.

4. Discussion

It has been well demonstrated that interfacial properties between fibre and matrix play an important role in properties of ceramic matrix composites. In order to obtain high-performance ceramic matrix composites, weak interface bonding is necessary to resist catastrophic failure, caused by the matrix cracking, through interfacial debonding [3, 15, 16]. Interfacial strength can be evaluated by the morphology of the fracture surface; long fibre pullout indicates weak interfacial strength, as discussed above. The interfacial properties in composites are considered to be relative to the surface characteristic of fibres, microstructure of matrix and processing conditions of the composites. Since the same matrix and the same processing conditions were used in the preparation of all four kinds of CF/SiC composites, it is reasonable to consider that the differences of interfacial strength in these composites were caused by the difference of the surface characteristics of the carbon fibres, which depended strongly on the microstructures of these carbon fibres without special surface treatment.

Since HSCF and HMCF were fabricated at below 1500 °C, and CF50 and CF70 were fabricated at above 2000 °C, it is expected that their crystallinities and microstructures differ remarkably between the two groups of fibres. The (002) peaks of these carbon fibres as well as the peak of the internal standard silicon obtained by XRD are shown in Fig. 6. It is noted that the (002) peaks of HSCF and HMCF were broad, whereas those of CF50 and CF70 were much narrower and shifted to a higher angle. The lattice spacing d_{002} and the crystallite size of L_{c002}, which were calculated according to Gakushinhou [24], are shown in Table IV. It can be seen that the crystallinities of HSCF and HMCF were not well-developed with less stacking layers and bigger

TABLE IV The d_{002} and L_{c002} of carbon fibres

Carbon fibres	d_{002} (Å)	L_{c002} (Å)
HSCF	3.479	15
HMCF	3.476	22
CF50	3.418	200
CF70	3.395	230

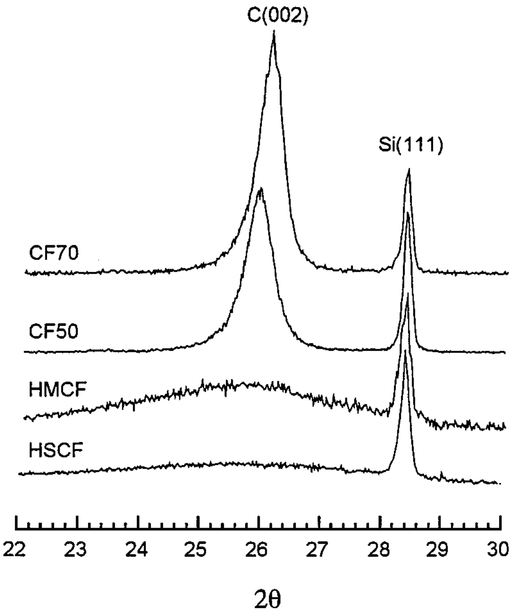

Figure 6 (002) peaks of the as-received carbon fibres.

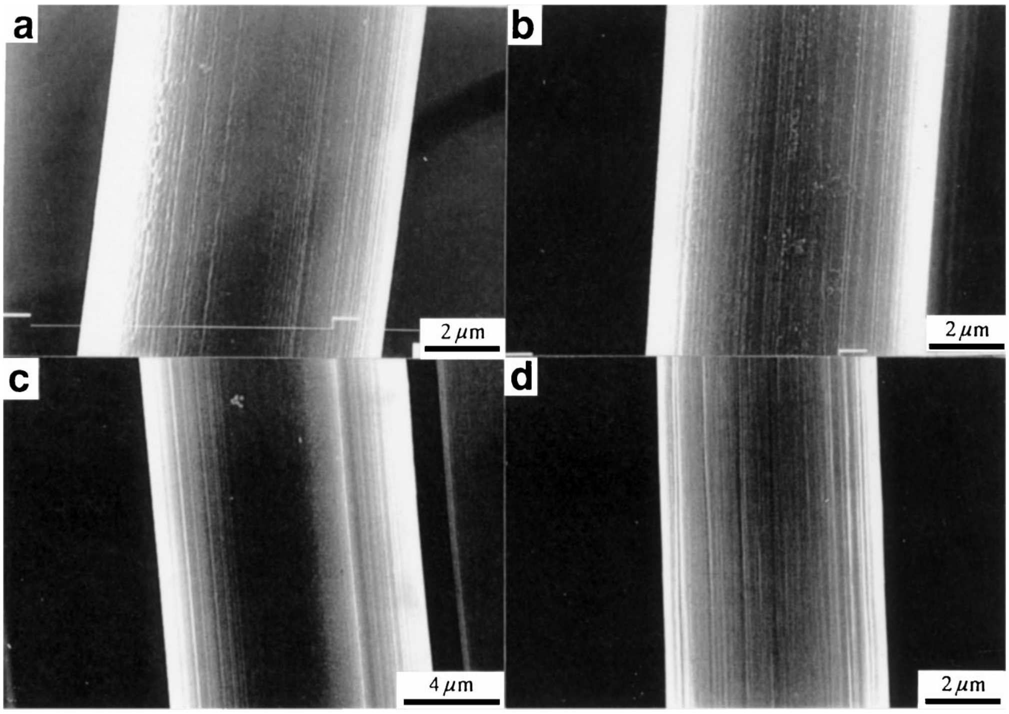

Figure 7 Surface morphologies of the carbon fibres: HSCF (a), HMCF (b), CF50 (c), and CF70 (d).

d_{002} spacing, whereas CF50 and CF70 were apparently highly-graphitized with large crystallite size and small d_{002} spacing. The difference in the crystallinity of the carbon fibres give rise to the difference in the surface structure and activity of the carbon fibres. Moreover, those carbon fibers fabricated below 1500 °C have more impurity elements, such as N, O, H, which are left by the precursors [25]. Therefore, HSCF and HMCF generally have more functional groups on their surfaces than CF50 and CF70, which were fabricated above 2000 °C. Fig. 7 shows the surface morphologies of the carbon fibres. It seems that the surfaces of CF50 and CF70 were somewhat smoother than those of HSCF and HMCF. The texture of the carbon fibres can be evaluated through examining transverse sections of the carbon fibres by SEM, as shown in Fig. 8. It is noted that HSCF has a relatively random structure, HMCF has an onion-like structure in its inner core and a radial structure in the outer layer, and both CF50 and CF70 have radial structure. From these results and observation of the carbon fibres, it seems that the surface properties of the carbon fibres were greatly affected by HTT or degree of graphitization of the carbon fibres. Those carbon fibres which are heat-treated at high temperatures and have high degree of graphitization tend to bond weakly with matrix. Because the four kinds of carbon fibres may be derived from different precursors, it is difficult to draw out a clear conclusion here.

The difference in the interfaces may start from the first impregnation-pyrolysis process. Because of the differences in their microstructures and their activities, the carbon fibres showed different behavior toward impregnation of PCS solution and the subsequent pyrolysis process. It is noted from Table III that the volume fractions of fibre (V_f) in HSCF/SiC and HMCF/SiC are much higher than those in CF50/SiC and CF70/SiC. The difference in V_f is thought to be due to the wetting ability and bonding strength between the carbon fibres and PCS. Fig. 9 shows the two different models of impregnation of PCS into the fibre preform. As the fibres were impregnated with PCS solution, HSCF and HMCF had better wettability with PCS solution than CF50 and CF70. After drying, it was observed that PCS was strongly bonded with HSCF and HMCF, but just weakly bonded with CF50 and CF70. Since the PCS-derived matrix was not well crystallized and contained silica, as described above, the matrix tend to be bonded well with those functional groups or active sites of HSCF and HMCF. Because CF50 and CF70 were much less active in their surfaces than HSCF and HMCF, the matrix was poorly bonded with CF50 and CF70, as verified by TEM observation [26]. After first cycle of impregnation, drying and pyrolysis, the shrinkage of PCS significantly diminished the fibre spacing in HSCF/SiC and HMCF/SiC, but not so significantly in CF50/SiC and CF70/SiC. At subsequent impregnation, PCS is more likely to infiltrate into the openings of matrix particles in HSCF/SiC and HMCF/SiC, but into the openings between fibre and matrix particles in CF50/SiC and CF70/SiC. As a result, the fiber spacing in HSCF/SiC and HMCF/SiC is smaller than that of CF50/SiC and CF70/SiC, that is, HSCF/SiC and HMCF/SiC have higher V_f than CF50/SiC and CF70/SiC. Consequently, HSCF/SiC and HMCF/SiC reached their high density after 9 cycles of impregnation, whereas CF50/SiC and CF70/SiC reached their high density after 12 cycles of impregnation. Further impregnation did not give an apparent increase in density, indicating many of the pores in the samples were closed.

From the above discussion, it can be found that the wettability of PCS solution to fibres is essential to the preparation of CF/SiC. The good wettability and the weak interface seem self-contradictory. In the four

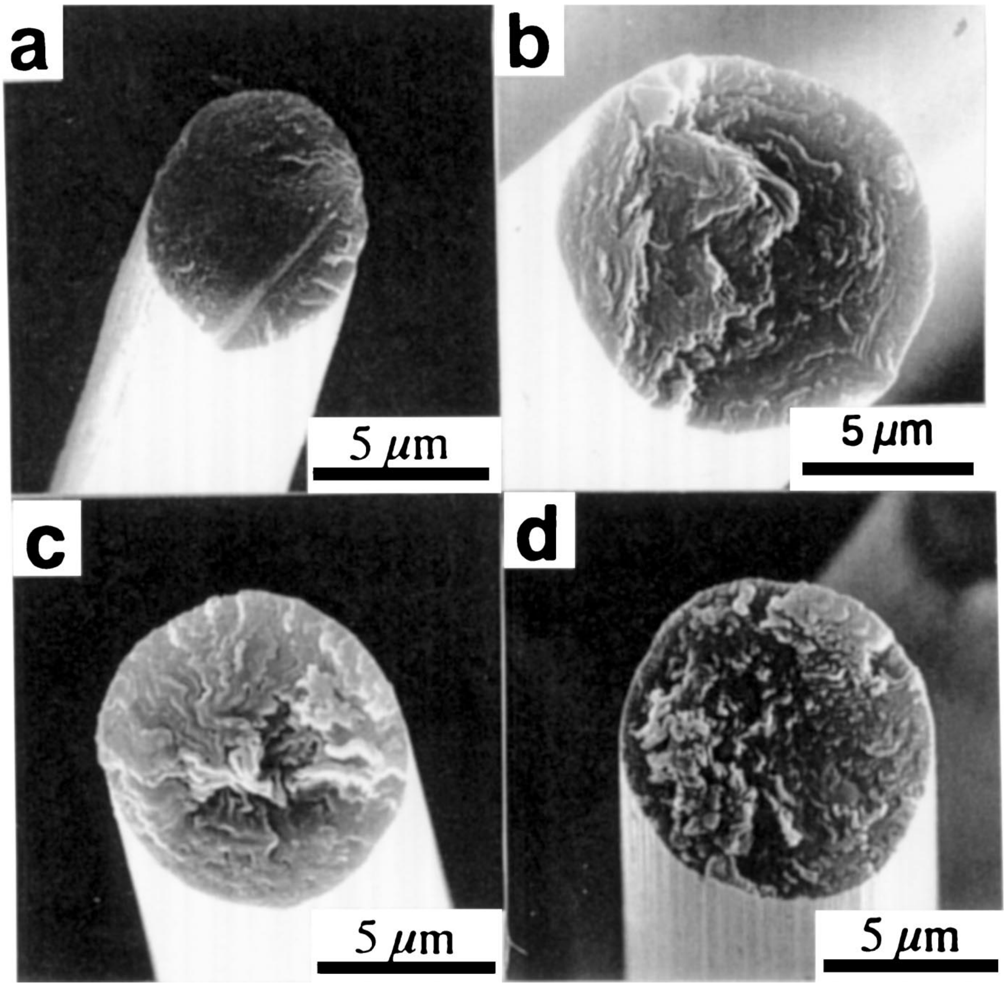

Figure 8 Transverse sections of the carbon fibres: HSCF (a), HMCF (b), CF50 (c), and CF70 (d).

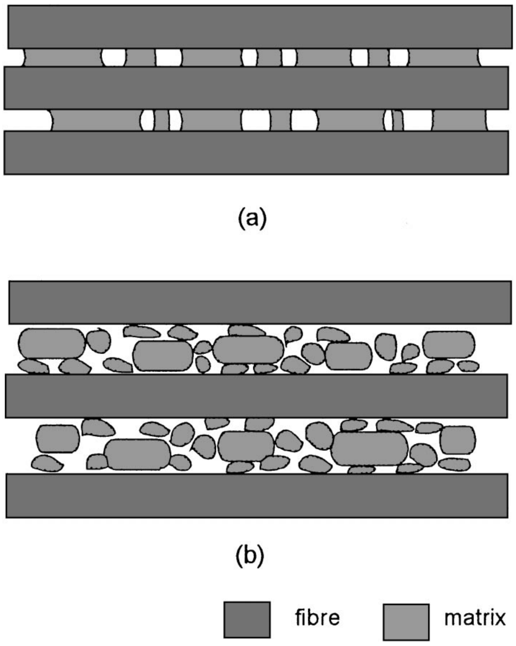

Figure 9 The model of impregnation of polycarbosilane into fibre tows: HSCF and HMCF (a), CF50 and CF70 (b). Large particles were formed in first impregnation, and small particles were formed in the subsequent impregnations.

types of carbon fibres used in the experiments, graphitized CF50 and CF70 were found to have adequate wettability and weak bond with the matrix.

Because HSCF/SiC and HMCF/SiC had strong interface bonding, cracking in the matrix can easily propagate across the interface between the carbon fibre and matrix, resulting in failure at low strain. On the other hand, the weak interfacial bonding in CF50/SiC and CF70/SiC resisted propagation of matrix cracks into the carbon fibres by debonding of the interface, although the cracks propagated throughout the matrix. After that, carbon fibres still supported the load through friction between fibres and matrix.

The four types of CF/SiC were divided into two groups. HSCF and HMCF belonged to the strong interfacial bonding group, and CF50 and CF70 belonged to the weak interfacial bonding group. Although HSCF/SiC and HMCF/SiC exhibited similar mechanical behavior in the current conditions, there was a degree of difference. From the fracture surfaces of HSCF and HMCF in Fig. 4, it is noted that the HSCF/SiC showed almost completely flat fracture surface, while HMCF/SiC showed some short fibre pullout although it could not resist the propagation of the matrix cracks. This difference indicates that HMCF/SiC had a relatively weak bonding interface compared with HSCF/SiC, and can be explained by their differences of crystallinity and microstrucures as described above.

The differences of interfacial properties of CF50/SiC and CF70/SiC, both of which exhibited multiple matrix cracking and extensive fibre pullout, had not been well understood here, because fibre pullout length and distribution had not been precisely measured in our experiments. Moreover, the shear failure of CF50/SiC during bending test made it difficult to compare the CF50/SiC and CF70/SiC.

5. Conclusions

Unidirectional carbon fibre reinforced SiC composites were prepared from four types of carbon fibres, HSCF, HMCF, CF50 and CF70, through nine cycles or twelve cycles of impregnation of polycarbosilane and subsequent pyrolysis at 1200 °C. Their mechanical properties and microstructures were evaluated. The following conclusions can be drawn from the present investigation:

(1) The matrix pyrolysed at 1200 °C in N_2 was β-SiC with crystallite size L_{111} of approximately 1.95 nm.

(2) CF50/SiC and CF70/SiC showed non-brittle fracture behavior with multiple matrix cracking and extensive fibre pullout, while HSCF/SiC and HMCF/SiC exhibited brittle fracture behavior, during four-point bending tests.

(3) CF70/SiC exhibited high flexural strength of approximately 967 MPa, which is about 75% of predicted strength. On the other hand, the flexural strength of CF50/SiC was 624 MPa, which was about 38% of predicted strength, because CF50/SiC failed in a shear way during bending tests.

(4) Differences in fracture behavior of the four types of CF/SiC were mainly attributed to the surfacial characteristics of the carbon fibres, which were strongly dependent on crystallinity of the carbon fibres or heat treatment temperatures. The graphitized carbon fibres (CF50 and CF70) were more adequate to be used as reinforcement of the CF/PCS-derived-SiC than the carbon fibres (HSCF and HMCF) treated below 1500 °C.

Acknowledgements

We thank Prof. B. Rand of Leeds University for useful discussions. We also thank Nippon Carbon Co. for providing polycarbosilane.

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Received 18 June 1997
and accepted 21 August 1998