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Mechanical properties improvement of carbon/carbon composites by two different matrixes

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Abstract Carbon/carbon (C/C) composites with two different matrixes of pitch carbon and pyrolytic carbon were fabricated using 2-dimensional (2D) carbon felts preform. In order to study the effects of matrixes on mechanical properties, C/C composites with single matrix of pitch carbon were prepared. The mechanical properties were tested on CMT5304-30KN universal testing machine. Polarization microscope and scanning electron microscope were used to investigate the microstructures and fracture surface of C/C composites. It was resulted that the flexural strength of C/C composites with two matrixes was improved by 96% compared with that of C/C composites with single matrix. Meanwhile, better toughness was also obtained with two matrixes. For the composites, multilayer microstructures were generated after filling up of voids caused during carbonization of mesophase pitch by pyrolytic carbon. The multilayer microstructures were beneficial to the improvement of mechanical properties of C/C composites, especially the toughness. More energy could be dissipated during mechanical tests while cracks might extend along multiple paths, such as the interface between fiber and matrix or the interface between different matrixes.

Introduction

Carbon/carbon (C/C) composites have superior characteristics, such as low density, high strength, high thermal conductivity, and low thermal expansion coefficient together with good frictional performance, so they are widely applied in different fields [1–3].

Nevertheless, low toughness and brittle fracture behaviors of C/C composites limit their further usage as structural materials. The mechanical properties mainly depend on microstructures of composites, so the study on microstructures of C/C composites is getting much more important. Researches have been done on this [4–8]. Reznik studied the microstructures and mechanical properties of C/C composites with multilayered pyrocarbon matrix and revealed the effects of microstructures on mechanical properties of composites [9]. It was resulted that C/C composites with multilayered pyrocarbon matrix exhibited non-brittle fracture behavior in association with a relatively high flexural strength. Lu found a method to improve toughness of C/C composites by intercalating bromine into graphite microcrystal of pyrocarbon [10]. After intercalation, a tough-like fracture mode was obtained and the flexural modulus and deflection was increased by 10 and 18%, respectively. Lee [11] used filler material (SiC powder) for modifying microstructure of C/C composites, and it was effective for enhancing mechanical strength which was increased by more than 100%. In the work of Chollon, flexural strength and interlaminar shear strength of C/C composites were significantly increased by the addition of fillers, such as carbon black and colloidal graphite which were introduced into composites [12]. Kowbel reported that 300% increase in interlaminar strength and 250% increase in interlaminar shear strength were found in the case of C/C composites made with a whiskerized fabric [13]. Liu showed that mechanical property of C/C composites was improved by using fillers including expanded graphite and vapor-grown spiral carbon fiber as second reinforcement in carbon matrix [14]. Li [15] revealed that the flexural strength, modulus and interlaminar shear strength of C/C

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composites containing 5 wt% carbon nanotubes were increased by 21.5, 33.5, and 40.7%, respectively. Gao prepared C/C composites containing zirconium and showed that zirconium could improve interface bonding and enhance mechanical property of the composites [16].

Researchers [17, 18] have found that the multilayer microstructures may improve toughness of composites. Zhu [19] revealed that bending strength of C/SiC composites with pyrolytic carbon layer was enhanced remarkably to 247 MPa and the composites exhibited a typical non-brittle fracture behavior, as the bending strength of composites without pyrolytic carbon layer was only 46 MPa. The studies of Taguchi [20] demonstrated that both the flexural and tensile strength of SiC/SiC composites with SiC/C multilayer were approximately 10% higher than composites fabricated without SiC/C layer. In the above researches, multilayer was applied into C/SiC composites and good mechanical properties were obtained, while the toughening of C/C composites by multilayer microstructure has scarcely been studied. Therefore, matrix modification was applied as means of toughening C/C composites in this work. C/C composites with two different carbon matrixes of pitch carbon and pyrolytic carbon were fabricated by impregnation/carbonization technique and chemical vapor infiltration (CVI), thus two layers of matrixes were obtained to improve the toughness of composites.

Experimental

Raw materials

2-Dimensional (2D) carbon felts were used as preform for preparation of C/C composites. The preform with density of 0.4 g/cm^3 was fabricated by repeatedly overlapping the layers of 0° non-woven fiber cloth, short-cut fiber web, and 90° non-woven fiber cloth with needle-punching step-by-step. The mesophase pitch (Mitsubishi Gas Chemical, Japan) was used as precursor. Table 1 shows the properties of mesophase pitch.

Sample preparation

C/C composites with two matrixes were fabricated by two processes of impregnation/carbonization technique and CVI in sequence. In impregnation/carbonization technique, first, the preform was placed in a steel container and covered by fine mesophase pitch powder. After temperature was raised to 653–673 K, nitrogen was filled into the container until the pressure reached 0.5 MPa and held for 1–2 h. Then, carbonization proceeded in a resistance furnace with nitrogen as protective gas. After four cycles of impregnation/carbonization, CVI was applied for subsequent densification of the samples. The process proceeded in a CVI furnace at 1,273–1,373 K with methane as precursor and nitrogen as diluted gas. For comparison, C/C composites with single matrix of pitch carbon were fabricated by multi-cycle impregnation/carbonization. C/C composites with two matrixes were marked as CC-1 and composites with single matrix were marked as CC-2.

Mechanical property tests

Three-point bending property was tested on CMT5304-30KN universal testing machine, conducted at loading speed of 0.5 mm/min and support span of 40 mm length. The size of specimens was 55 mm × 10 mm × 4 mm. The number of specimens was not less than five for every test point. The flexural strength and modulus were calculated according to the formulas listed below:

$$\sigma_f = \frac{3PS}{2bh^2}, \tag{1}$$

$$E_f = \frac{\Delta P_f S^3}{4bh^3 \Delta f}, \tag{2}$$

where, σ_f is flexural strength, E_f is flexural modulus, P is the maximum of load, S is span, b is the width of specimen, h is the height of specimen, and $\Delta P_f/\Delta f$ is the slope of load–displacement curve.

The fracture toughness was tested with the specimen of 35 mm × 5 mm × 2.5 mm (Fig. 1) according to Single-Edge-Notched-Beam (SENB) three-point bending method. The span was 20 mm, loading speed was 0.2 mm/min, and the width of the notch was lower than 0.1 mm. The fracture toughness K_{IC} was calculated according to formulas 3 and 4.

$$K_{IC} = \left(\frac{P_Q S}{bW^{\frac{3}{2}}}\right) f\left({}^{n}/_{W}\right) \tag{3}$$

$$f\left({}^{n}/_{W}\right) = \frac{3\left(n/W\right)^{1/2}\left[1.99 - \left(n/W\right)\left(1 - n/W\right) \times \left(2.15 - 3.93n/W + 2.7n^2/W^2\right)\right]}{2\left(1 + 2{}^{n}/_{W}\right)\left(1 - {}^{n}/_{W}\right)^{3/2}} \tag{4}$$

Table 1 The properties of mesophase pitch

Material	Softening point (K)	Volume density (g cm^{-3})	Mesophase content (%)	*C/H* mol ratio
Mesophase pitch	548–568	0.65	100	1.56–1.72

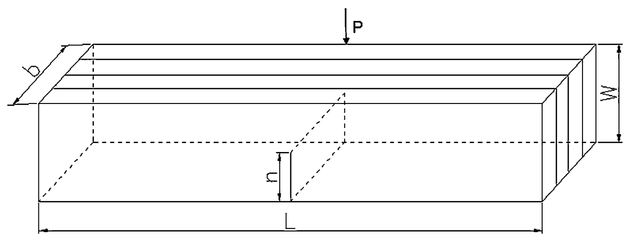

Fig. 1 The schematic of fracture toughness specimen (*P* the load, *b* the width of specimen, *W* the height of specimen, *n* the depth of notch, *L* the length of specimen)

where, K_{IC} is fracture toughness, P_Q is the cracking threshold, S is the span, b is the width of specimen, W is the height of specimen, and n is the depth of notch.

Microscopic morphology

The samples were mounted in epoxy resin and ground on four grades of silicon carbide paper (400, 600, 800, and 1,200 grits) in the order, then polished with diamond polishing slurries. Finally, the samples were observed under Leica DMLP optical microscope. The fracture surface observation was carried out using JSM6460 and JSM6700 scanning electron microscopes (SEM).

Results and discussion

The microstructures

The microstructures of C/C composites with two matrixes are presented in Fig. 2. It is shown that the carbon matrixes consist of two different components of pitch carbons and pyrolytic carbons, which fill among carbon fibers. The pitch carbons are composed of mainly small domains and mosaic texture, which are classified according to the dimension of optical activity textures [21], as shown in Fig. 2a. Among pitch carbons are the pyrolytic carbons (Fig. 2b), which are smooth laminar carbon textures. It is found that the pyrolytic carbons are darker than the pitch carbon matrixes under polarized light, which indicates the optical activity of smooth laminar carbon textures is lower than that of the pitch carbons.

Figure 2c shows the pyrolytic carbons grown on the surface of pitch carbons. The pyramidal smooth laminar pyrolytic carbons have a compact coherence with pitch carbons. From Fig. 2d, it can be seen that the pyrolytic carbons deposited on pitch carbons can be divided into three layers: small granular pyrolytic carbon, pyramidal pyrolytic carbon, and large particle pyrolytic carbon. Close to pitch-based carbons, the pyrolytic carbons are small

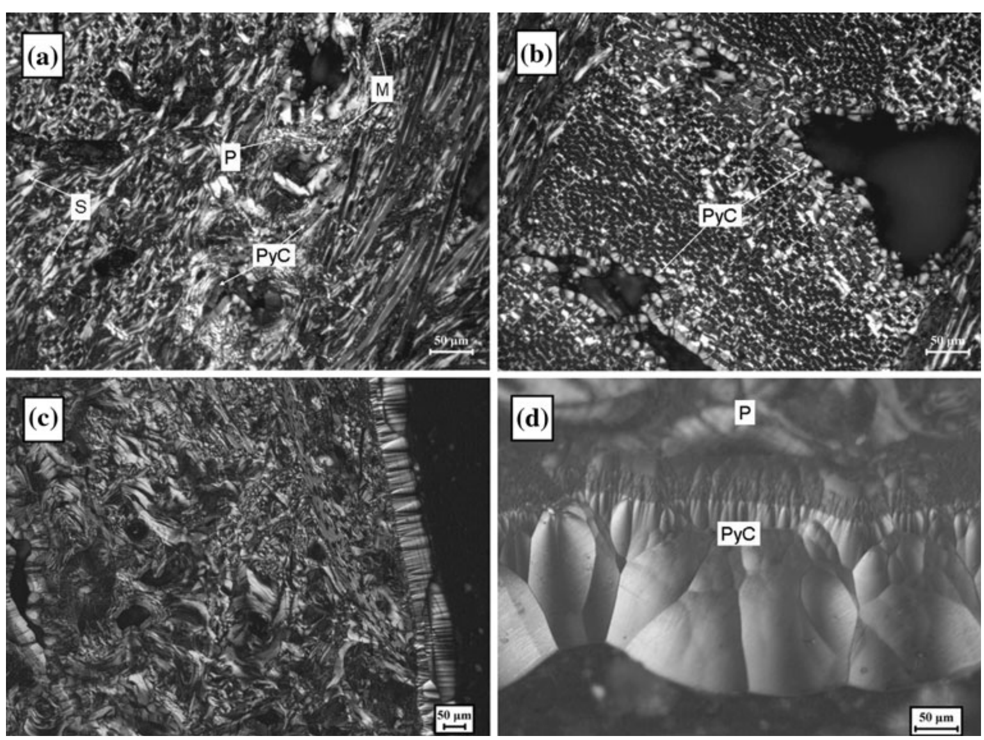

Fig. 2 The microstructures of C/C composites with two matrixes fabricated using 2D carbon felts (*P* pitch-based carbons, *PyC* pyrolytic carbons, *S* small domains, *M* mosaic texture)

granular, with proceeding of deposition, the microstructures transfer into large laminar textures. It is deduced that the pitch carbons exert inducting effects for deposition of pyrolytic carbons. The gradient microstructures indicate that pyrolytic carbons may well fill up the voids generated after impregnation/carbonization because of the small granular pyrolytic carbon close to the pitch carbons.

Figure 3 shows the typical SEM micrographs of two different matrixes of CC-1. It can be seen that the pyrolytic carbons deposited between fiber and pitch carbons or among pitch carbons are about 1 μm. From Fig. 3b, the magnification of Fig. 3a, it is seen that the pyrolytic carbons are smooth lamellar textures. After impregnation/carbonization, voids generated during carbonization due to volatilization of small molecular supply space for deposition of pyrolytic carbons. Pyrolytic carbons fill up these voids producing the hybrid matrixes which enhance the C/C composites. From Fig. 3c, an obvious interface phase with lamellar textures can be seen between pyrolytic carbon and pitch carbon, it is different with pitch carbon and pyrolytic carbon.

Figure 4 shows the pyrolytic carbons deposited around carbon fiber. The pyrolytic carbons close to carbon fiber with about 4 μm are low-texture. As grown apart from fiber, pyrolytic carbons transfer to media-texture.

It can be concluded that carbon matrixes of CC-1 consist of pitch carbons and pyrolytic carbons. The pitch carbons can be divided into small domains and mosaic texture while the pyrolytic carbons contain low-texture and media-texture carbon. The different interface between fiber and matrix or between different matrixes can be obtained and observed. The mixed microstructures are beneficial to the improvement of mechanical properties of C/C composites, especially the toughness. The reasons will be explained below.

The mechanical properties

Table 2 lists the mechanical properties of CC-1 and CC-2, respectively. It is shown that C/C composites with two matrixes exhibit much better mechanical properties than the composites with single matrix. The flexural strength of CC-1 is increased to 118.91 MPa compared with 60.74 MPa of CC-2, i.e. the value of flexural strength increases by 96%, although the flexural modulus of CC-1 is lower than CC-2. The fracture toughness of CC-1 is also much higher than CC-2, as shown in Table 2.

The flexural load–displacement curves of C/C composites are shown in Fig. 5. It is also the direct evidence that CC-1 has higher flexural strength and pseudo-plastic

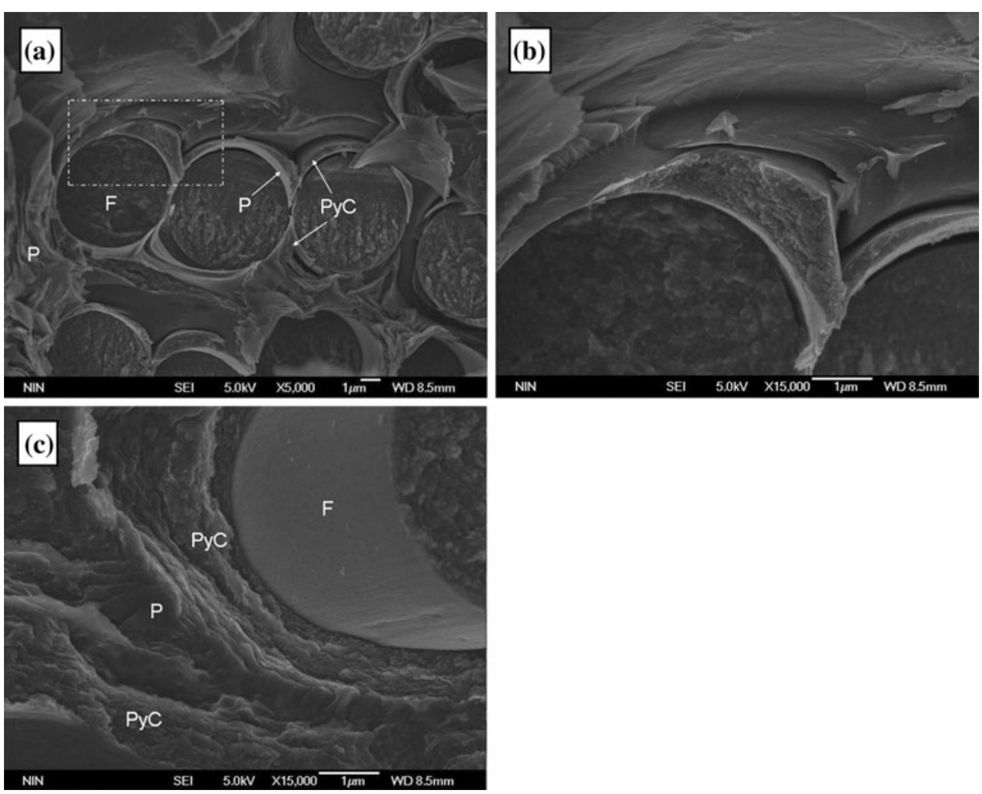

Fig. 3 The microstructure of C/C composites with two matrixes (*F* fiber, *P* pitch-based carbons, *PyC* pyrolytic carbons)

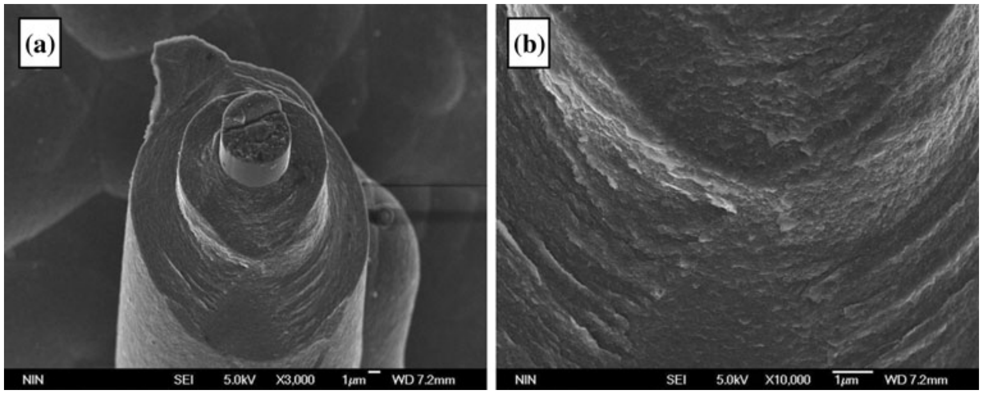

Fig. 4 The pyrolytic carbon microstructure of CC-1

Table 2 The mechanical properties of C/C composites fabricated by different processes

Sample	Density (g cm^{-3})	Flexural modulus (GPa)	Flexural strength (MPa)	K_{IC} (MPa m$^{1/2}$)
CC-1	1.67	11.35	118.91	3.54
CC-2	1.64	19.44	60.74	2.11

behavior, while CC-2 presents brittle behavior. The load–displacement curve of CC-2 can be divided into two segments: linear rise and linear decrease of load. The load decreases perpendicularly leading to catastrophic failure of sample as load goes up to the maximum value, which indicates brittle fracture occurs in CC-2. On the contrary, CC-1 has good toughness. The load–displacement curve in Fig. 5 can be divided into three segments: linear rise of load, non-linear rise of load, and a plateau region with a small range of displacement, stepped decrease of load, which correspond to three stages: matrix elastic deformation, appearing and extending of cracks among matrix, fiber debonding from matrix and fiber (or multi-interlayer) pull-out, respectively [22]. The load decreases in step-style but not perpendicularly after the maximum value, which demonstrates good toughness of CC-1.

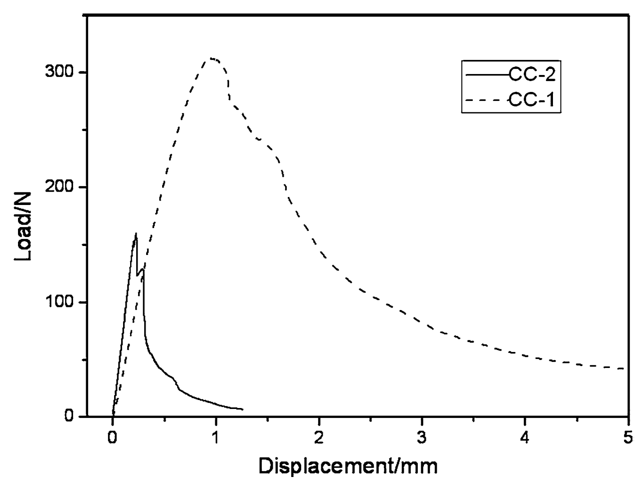

Fig. 5 The load–displacement curve of C/C composites fabricated by different processes

The fracture surface

From the fracture surface shown in Fig. 6, CC-1 is deduced to present better toughness than CC-2 because surface of the former is rougher than that of the later. CC-2 has strong interface bonding between fibers and pitch carbon as few fiber pull-out and gaps between them are observed. While the much rougher fracture surface of CC-1 demonstrates the composites present pseudo-plastic behaviors and good toughness.

Figure 7 shows the fracture surfaces of samples after fracture toughness tests. The bottom half of the photograph is flat surface cut by wire cutting machine. Typical pseudo-plastic characters of pull-out of long bundles of fibers can be seen in Fig. 7a, bundles of fibers also twine on the fracture surface. It is tempting to speculate that CC-1 presents good toughness. While the fracture surface of CC-2 is very flat indicating brittle behaviors of the sample. The different fracture behaviors can also be verified by the macro photograph of fracture toughness samples shown in Fig. 8. After test, CC-1 is still linked by some fibers and matrixes, while CC-2 ruptures into two separated parts.

From Fig. 5 and Table 2, the mechanical properties of CC-1 and CC-2, it is concluded that C/C composites with two different matrixes have higher flexural strength and fracture toughness. The fracture mechanism of C/C composites depends not only on the matrix and fibers, but the interface between them also plays an important role on it [22]. Due to the two matrixes, different interfaces between

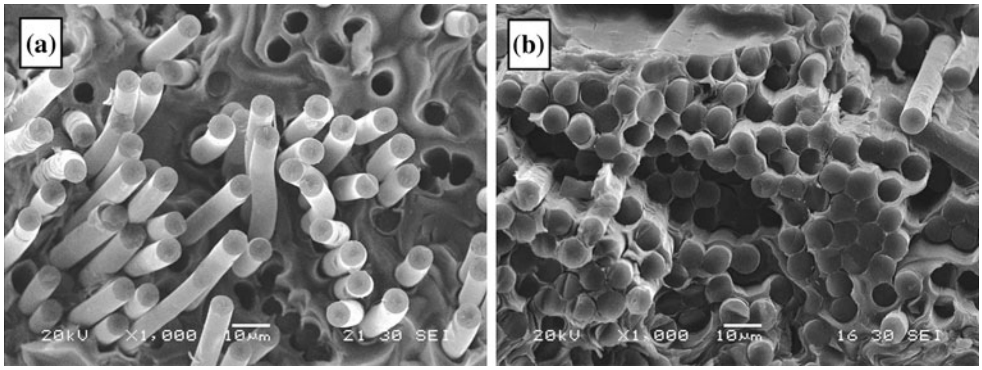

Fig. 6 The fracture surface of flexural specimens (**a** CC-1, **b** CC-2)

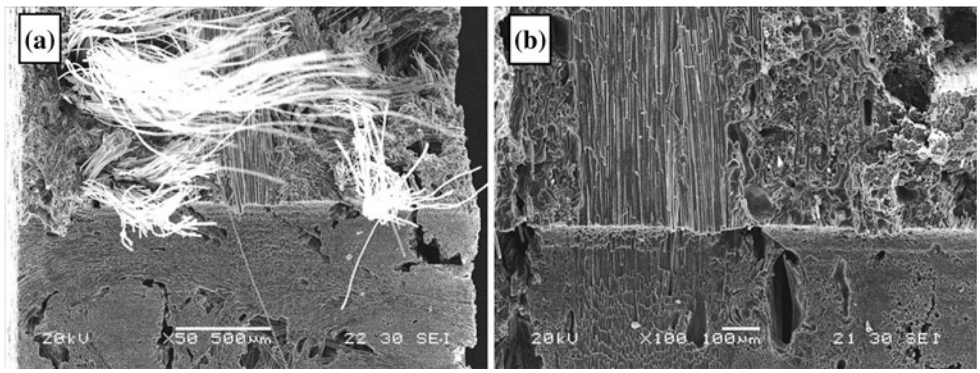

Fig. 7 The fracture surface of samples after fracture toughness tests (**a** CC-1, **b** CC-2)

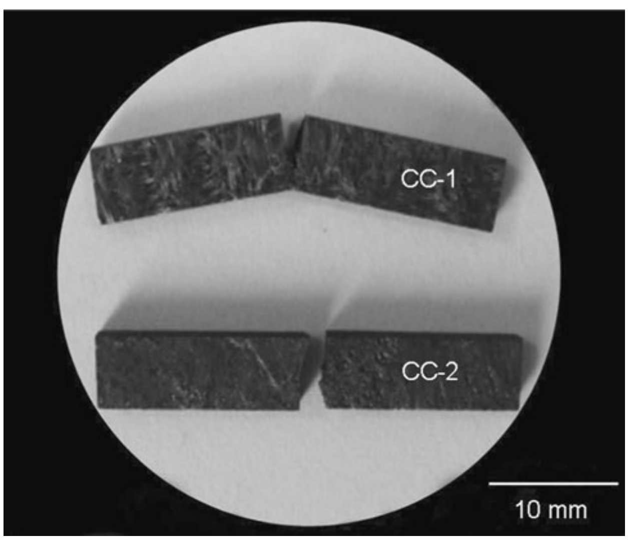

Fig. 8 The macro photograph of samples after fracture toughness tests

fiber and matrix or between different matrixes are obtained. The complex microstructures are useful to improve mechanical properties of C/C composites. Fracture surface of CC-1 shows a complex morphology with lots of fibers pull-out and fractured matrix (Fig. 9a). Meanwhile in Fig. 9b, cracks between different matrixes are observed, and they also can be observed between fiber and matrix or in single matrix (Fig. 9c). All these phenomenons improve the mechanical properties of C/C composites, particularly the toughness property.

During the mechanical tests of C/C composites, as load increases to some extent, cracks appear in the matrix of C/C composites, then spread to interface of fiber and matrix as load increases continuously. For CC-2, as cracks extend immediately to the fiber from matrix, they are not deflected along fiber/matrix interface due to the tight conjunction of fiber and matrix. Therefore, as load reaches the maximum value, fibers are sheared off by cracks and sample ruptures completely, brittle fracture behaviors are obtained. While for CC-1, the complex matrix constituents and interface described before supply paths for extending of cracks during tests. The non-brittle fracture behaviors are related to the multiple crack deflections. As cracks appear among matrixes, they spread along the interface of two different matrixes or the interface of fiber and matrix, and then cause debonding and fracturing of matrixes or fiber pull-out (Fig. 9b, d). Cracks also can extend along matrix perpendicular to fiber (Fig. 9c). These complex extension paths of cracks dissipate energy during

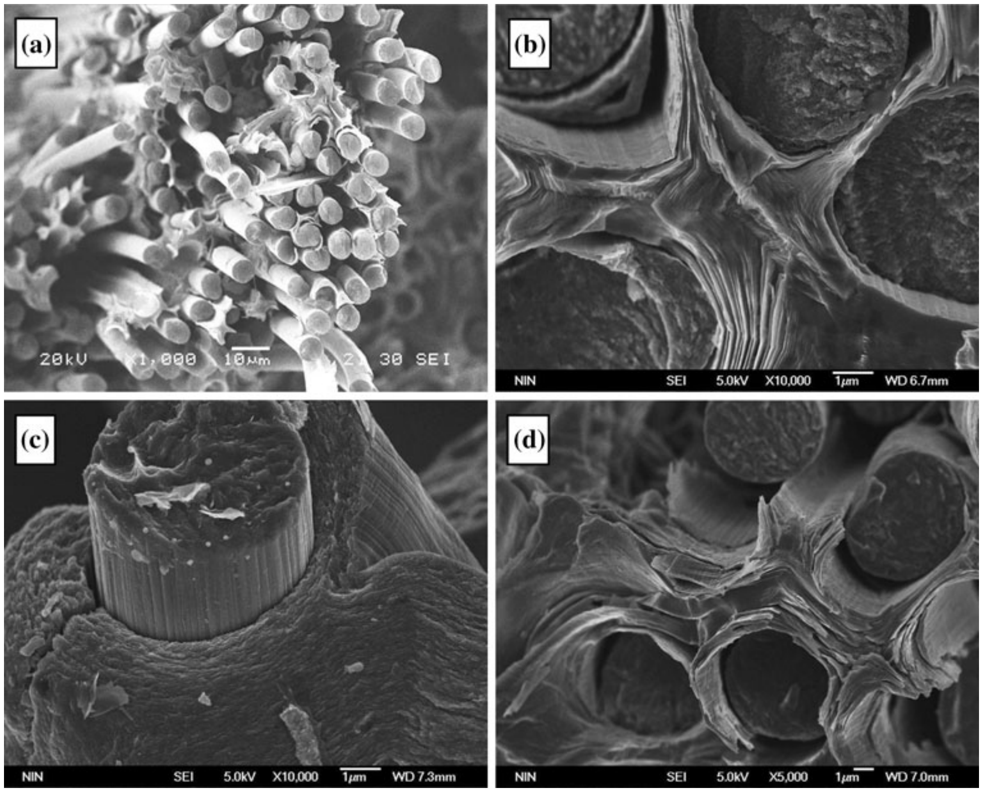

Fig. 9 The flexural fracture surfaces of CC-1

mechanical tests leading to high bending property and good toughness.

Conclusions

Two different matrixes of pitch carbons and pyrolytic carbons have significant effects on improving mechanical properties of C/C composites. It is concluded that C/C composites with two matrixes exhibit super mechanical properties such as high bending strength and fracture toughness. Compared with C/C composites with single matrix, the flexural strength and fracture toughness are increased by 96 and 67%, respectively. The bending load against displacement curve is characteristic of pronounced pseudo-plastic deformation. The SEM morphologies of fracture surface also prove that C/C composites with two matrixes present pseudo-plastic fracture character. Pyrolytic carbons deposit between fiber and pitch carbons or among pitch carbons, they fill up the voids generated by volatilization of small molecular and swelling of matrix during carbonization, thus C/C composites with multilayer microstructure are obtained. This character of microstructure improves the mechanical properties of C/C composites, especially toughness, as cracks spread along multiple paths dissipating energy during mechanical tests.

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