Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 695–700
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Mechanical properties and microstructures of C_f/SiC–ZrC composites using T700SC carbon fibers as reinforcements

Z. Wang [a,b], S.M. Dong [a,b,*], Y.S. Ding [a,b], X.Y. Zhang [a,b], H.J. Zhou [a,c], J.S. Yang [a,c], B. Lu [a,c]

[a] *Structural Ceramics and Composites Engineering Research Center, Shanghai Institute of Ceramics Chinese Academy of Sciences, Shanghai 200050, PR China*
[b] *State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics Chinese Academy of Sciences, Shanghai 200050, PR China*
[c] *School of Graduate, Chinese Academy of Sciences, Beijing 100039, PR China*

Received 24 March 2010; received in revised form 1 April 2010; accepted 25 September 2010
Available online 25 November 2010

Abstract

C_f/SiC–ZrC composites were fabricated through mold-pressing and polymer infiltration and pyrolysis (PIP) process using T700SC carbon fibers as reinforcements. The effects of interphases on the mechanical properties and microstructures of composites were studied. Composite showed brittle fracture behavior and low bending stress of 81 ± 24 MPa when no interphase was deposited on the fiber surface. With the deposition of a PyC/SiC interphase, composite showed typical non-brittle fracture behavior and the bending stress increased to 401 ± 64 MPa and a large amount of pulled-out fibers could be observed on the fracture surface. Meanwhile, it could also be concluded from the microstructures of the composites that the existed interphases had a great hindering effect on the infiltration of ZrC into the intra-bundle zones in the slurry infiltration process. The TEM analysis results showed that the carbon fibers were almost not eroded and the brittle fracture behavior may be mainly ascribed to the strong bonding between fibers and matrix.

Keywords: B. Composites; Interfaces; C. Mechanical Properties

1. Introduction

Due to their excellent high temperature performances, much attention was focused on the development of composites consisting of SiC matrix in the past decades, such as C_f/SiC and SiC_f/SiC composites [1,2]. However, the maximum use temperatures of silicon based ceramics are limited to about 1600 °C due to the onset of active oxidation in dry air and even lower temperatures in water vapor environments. Development of structural materials is therefore of great importance, for use in oxidizing and rapid heating environments above 1600 °C [3]. Two potential approaches may be chosen to develop fiber-reinforced ceramic composites that perform at ultra-high temperatures (>1500 °C) under oxidative conditions, namely (a) utilizing existing carbon-fiber-reinforced carbon-matrix composites (C/C) or carbon-fiber-reinforced silicon carbide matrix composites (C/SiC) coated by thick (>100 μm) ultra-high temperature ceramic (UHTC) coatings; (b) replacing the carbon or silicon carbide matrices of such composites with an ultra-high temperature matrix [4]. Introduction of UHTCs into C_f/SiC composites allows these composites to be used as potential candidates for extreme environments associated with the hypersonic flight and rocket propulsion due to their retained strength and ablation resistance at high temperatures [5]. UHTCs based on the carbides, nitrides and borides of group IV_B and V_B transition metals have received a considerable attention, due to their unique combination of properties such as high melting temperature and hardness, high electrical and thermal conductivity and chemical inertness against molten metals. Among the family of UHTCs, due to their high melting temperatures and relatively low density, zirconium-bearing UHTCs are of great interest. Meanwhile, the oxide scale formed in the ablation process can effectively reduce the diffusion rate of oxidizing atmosphere toward the composite.

* Corresponding author at: Structural Ceramics and Composites Engineering Research Center, Shanghai Institute of Ceramics Chinese Academy of Sciences, 1295 Dingxi Road Shanghai 200050, PR China.
Tel.: +86 21 5241 4324; fax: +86 21 5241 3903.
E-mail address: smdong@mail.sic.ac.cn (S.M. Dong).

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.09.048

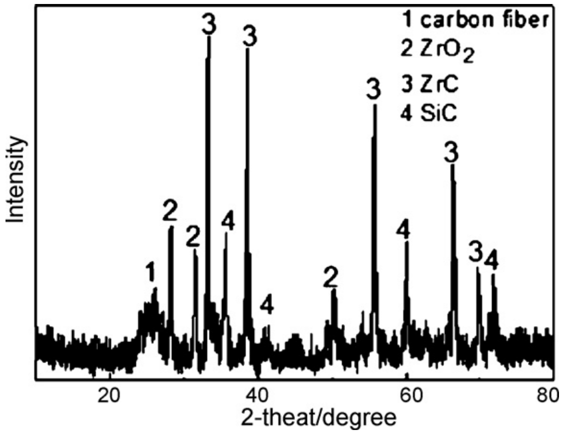

Fig. 1. XRD pattern of C_f/SiC–ZrC composite.

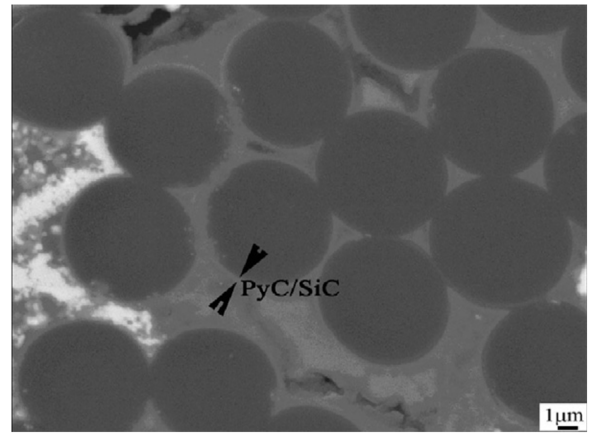

Fig. 3. Influence of interphase on microstructure of carbon fiber distribution.

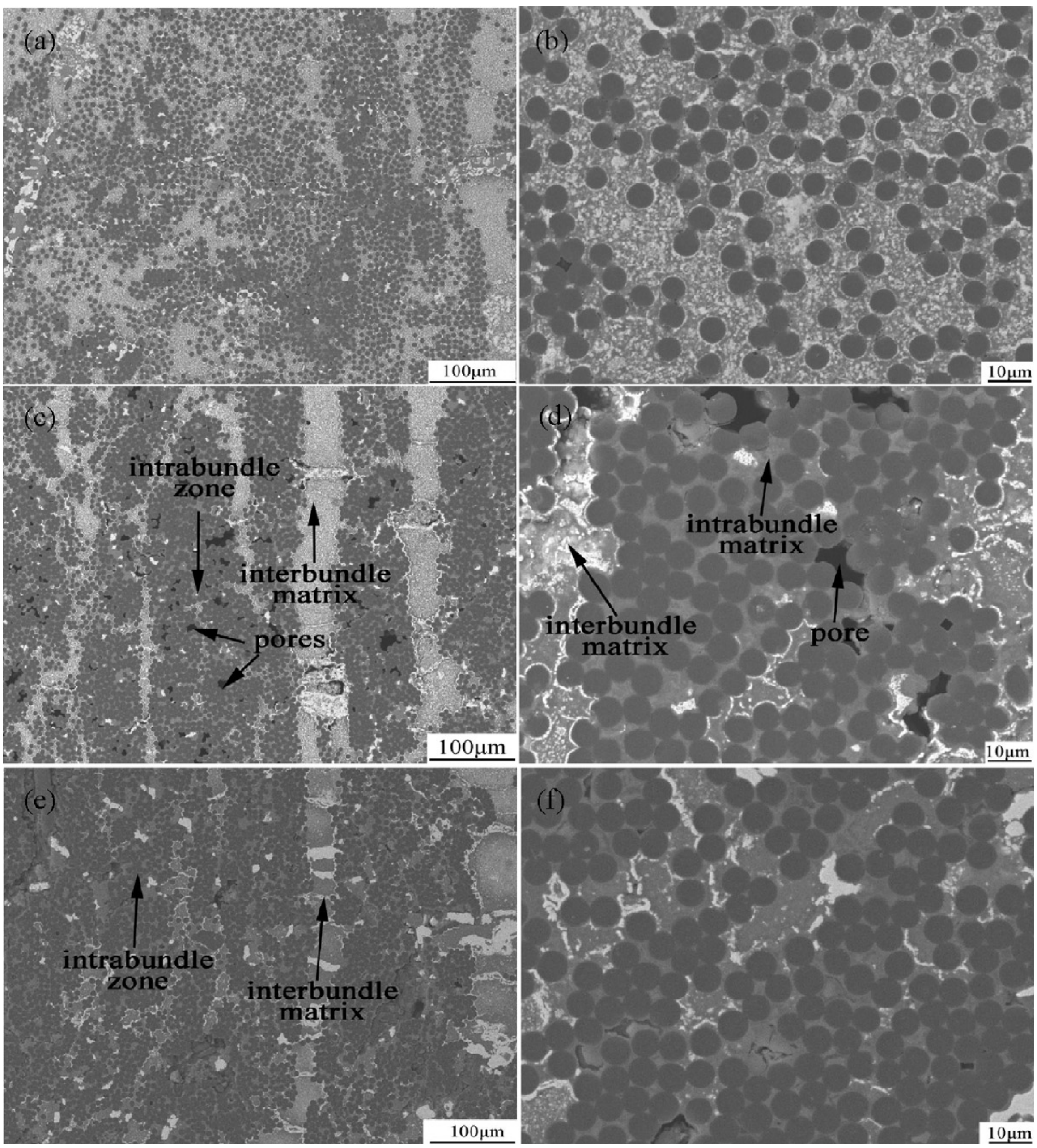

Fig. 2. SEM micrographs on the polished cross-section of C_f/SiC–ZrC composites using T700SC carbon fibers as reinforcements (a,b: none; c,d: PyC; e,f: PyC/SiC).

For continuous fiber reinforced ceramic matrix composites (CFCMCs), fiber/matrix interfaces are critical on determining the performance of the materials [6], as the properties of fiber/matrix interfaces determine the mechanical behavior of brittle-matrix composites [7,8]. It has been postulated that the best interphase materials might be those with a layered crystal structure (PyC, h-BN) or a layered microstructure, such as $(PyC\text{-}SiC)_n$ and $(BN\text{-}SiC)_n$, the layers being deposited parallel to the fiber surface weakly bonded to one another but strongly adherent to the fiber surface [9,10]. Furthermore, when interphases are deposited on the fiber surfaces, they cannot only provide a weak bond between the fiber and the matrix but also protect the fiber reinforcements from being damaged, which will lead to excellent mechanical properties of composites.

The aim of the present work is to study the properties and microstructures of C_f/SiC–ZrC composites with different interphases fabricated by mold-pressing and PIP process.

2. Experimental procedure

T700SC carbon fibers (Toray, Tokyo, Japan) were used as the reinforcements of the composites, the properties of carbon fibers were listed in Table 1. Carbon fibers were first wound to graphite frames to form fiber sheets and some were coated with PyC or PyC/SiC interphase by forced pressure-pulsed chemical vapor infiltration (FP-CVI) [11]. Commercially available ZrC powders were mixed with PCS (National University of Defense Technology, Changsha, China) with weight ratio of 50%:50%, using xylene as solvent to form homogenous dispersed slurry. Fiber sheets were impregnated with the aforementioned slurry. After the impregnation, the sheets were dried, cut to the desired size and placed into the graphite die to prepare unidirectional C_f/SiC–ZrC composites. The graphite die was then heated to about 200 °C in a hot-pressing furnace and pressure (about 5 MPa) was applied to control the thickness of samples at temperature somewhat higher than the softening temperature of PCS. Formed samples were further densified by several repetitions of impregnation and pyrolysis of PCS. More detailed experimental procedure was described elsewhere [12].

Densities and open porosities were measured by Archimedes' method. As the compositions of the matrix are complex, only the density and open porosity were listed, the relative density was not mentioned here. The samples were cut and ground into 4 mm × 2 mm × 40 mm specimens for three-point-bending test in an Instron-5566 testing machine, with a crosshead speed of 0.5 mm/min and a span of 24 mm. The compositions of composites were characterized by X-ray diffraction (XRD) with Cu Kα radiation. The microstructures of composites were characterized by electron probe micro-analyzer (EPMA, JXA-800) and field emission transmission electron microscopy (FETEM, TEM2010) equipped with EDS.

Table 1
Properties of T700SC carbon fibers.

Carbon fiber	Number of filament (K)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Density (g/cm^3)
T700SC	12	4900	230	2.1	1.8

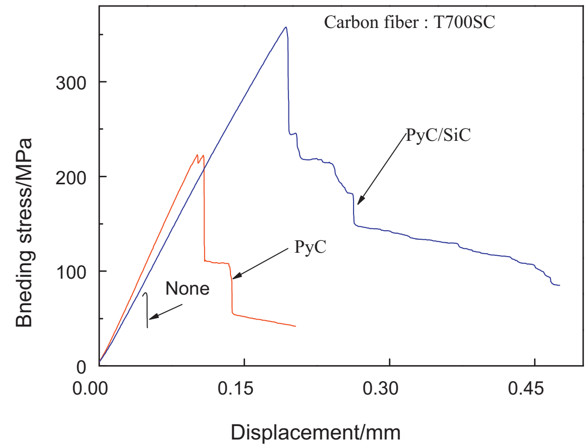

Fig. 4. Bending stress/displacement curves of C_f/SiC–ZrC composites with different interphases.

3. Results and discussion

The XRD pattern of composite fabricated using the as-received T700SC carbon fibers as reinforcements is plotted in Fig. 1. It can be concluded from the diffraction peaks that the main phases existing in the composite are carbon fibers, ZrC, SiC and ZrO_2. Due to the low crystallinity of carbon fibers, the intensity of their diffraction peak at about 26.7° is relatively weak. ZrC was introduced in the slurry impregnation process. As a result of low oxidation resistance of ZrC [13], when contacted with air, some ZrO_2 has been formed at the surface of nano-ZrC particles and SiC in the composite came from the pyrolysis of PCS.

Physical and mechanical properties of C_f/SiC–ZrC composites with different interphases are summarized in Table 2. It can be observed that when there is no interphase deposited on the surface of carbon fibers, the composite has a much higher density (2.66 g/cm^3) than those of composites with interphases (2.26 g/cm^3 and 2.37 g/cm^3, respectively, for composites with PyC and PyC/SiC). Meanwhile, as far as the mechanical properties of composites are concerned, they are greatly improved when interphases have been deposited on the fiber surfaces. The bending stress of composite with PyC/SiC interphase is 401 ± 64 MPa while that of composite without interphase is 81 ± 24 MPa.

Table 2
Properties of C_f/SiC–ZrC composites with different interphases.

Interphase	Fiber fraction (vol%)	ZrC fraction (vol%)	Density (g/cm^3)	Open porosity (%)	Bending stress (MPa)	Elastic modulus (GPa)
None	36	18	2.66	4.3	81 ± 24	91 ± 12
PyC	38	13	2.26	7.8	226 ± 26	115 ± 17
PyC/SiC	39	14	2.37	7.3	401 ± 64	104 ± 10

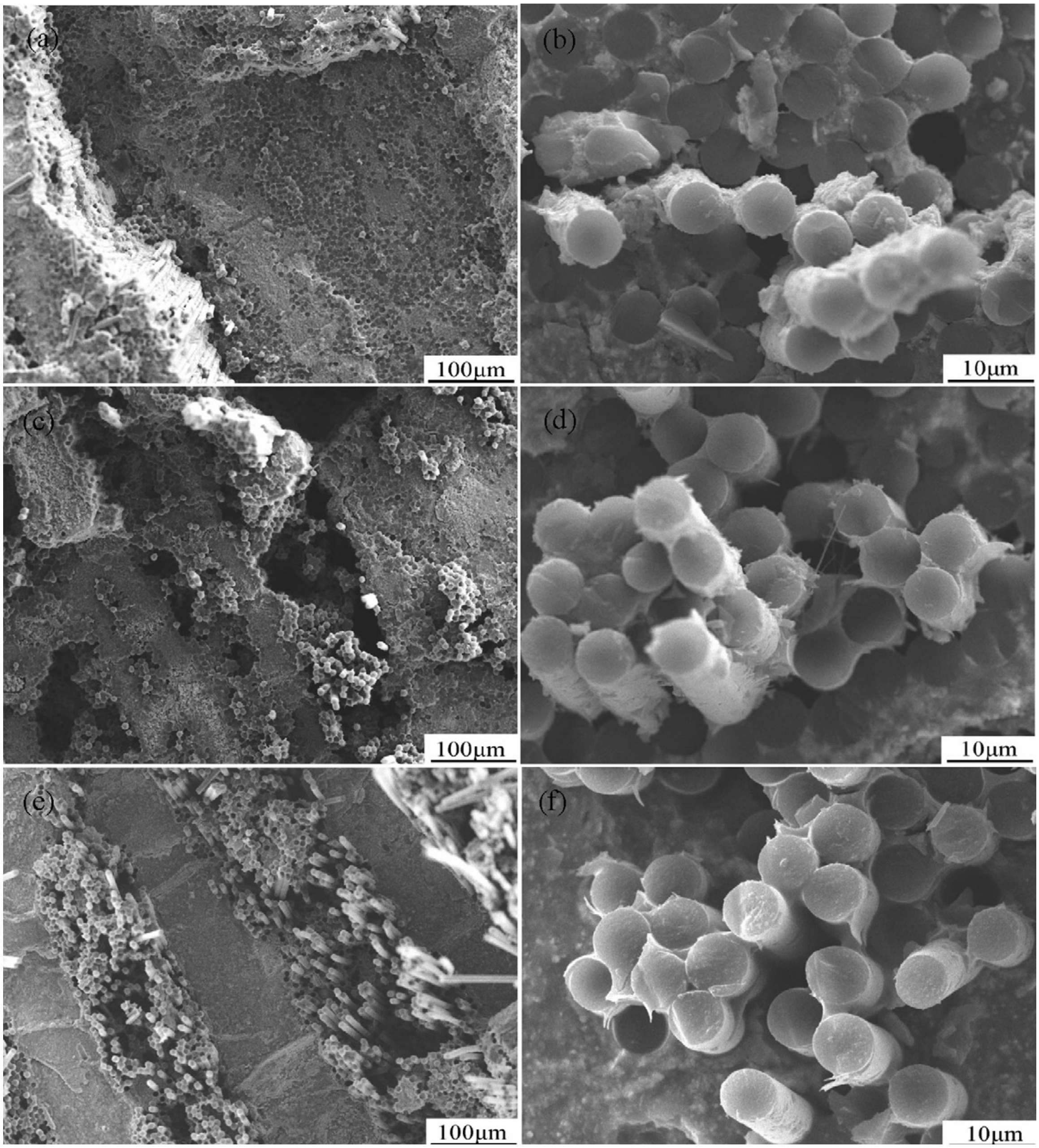

Fig. 5. SEM micrographs on the fracture surfaces of C_f/SiC–ZrC composites using T700SC carbon fibers as reinforcements (a,b: none; c,d: PyC; e,f: PyC/SiC).

The SEM micrographs on the polished cross-section of C_f/SiC–ZrC composites with different interphases are shown in Fig. 2. It can be observed that when no interphases were deposited on the surface, the fiber reinforcements and ZrC particles (with white contrast) were dispersed homogenously in composite. After interphases were deposited, there are obvious inter-bundle matrix zones existing in the composites and the inter-bundle matrix is relatively dense. In the fabrication process, pressures were applied to control the thickness of the samples at ~200 °C (somewhat higher than the softening temperature of PCS). Therefore, the slurry on the surface of carbon fiber bundles can move freely and fill the void existing in the inter-bundle zones. However, as far as intra-bundle zones were concerned, some more micro-pores can be found. There are 12,000 fiber filaments in each fiber bundle used in the experiment and the spaces between fiber filaments are small as a result of the small diameter of carbon fibers. When interphases were deposited on the fiber surface, filaments would be stack to each other by the interphase (the white rings around carbon fibers shown in Fig. 3) and result in a tight structure. In the slurry impregnation process, the hindering effect of tight fiber bundles was much more obvious than that of loose ones, consequently, more ZrC can be infiltrated into the intra-bundle zones of undeposited carbon fiber bundles and a more homogenous microstructure can be obtained. Nevertheless, most of the intra-bundle spaces of deposited bundles were filled with PCS in the infiltration process. Volume shrinkage accompanied in the PCS pyrolysis and crystallization

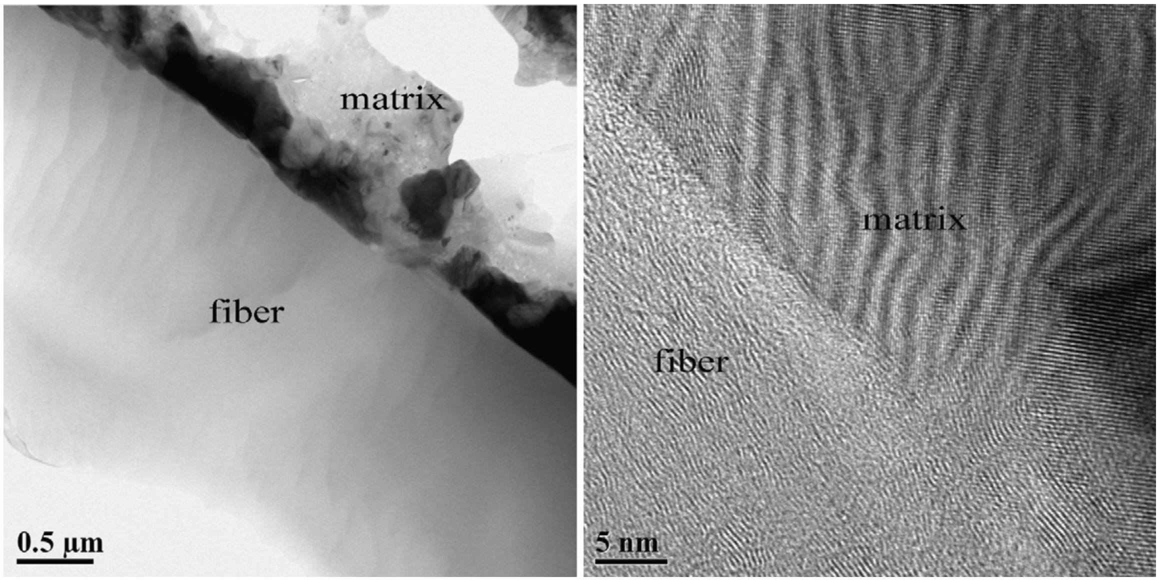

Fig. 6. TEM images of composites fabricated from carbon fibers without interphase.

process may account for the existence of intra-bundle-pores of composites with interphases. Though some pores can be filled in the following PIP process, there are still some closed pores remained. During PIP process, the micro-pores left in the matrix would decrease in size when PIP cycles proceeded. When the pores were small enough, it was difficult for the viscous polymer to fill into the consolidated body effectively [14].

Fig. 4 shows the bending stress–displacement curves of composites with different interphases. As it can be concluded from these curves that when no interphase was deposited, composite showed brittle fracture behavior while those with interphases showed typical non-brittle fracture behavior as it could be expected. With the deposition of interphases, mechanical properties including elastic modulus and bending stress greatly increased.

In consistence with the brittle fracture behavior of composite without interphase, no obvious fiber pull-out can be observed on the fracture surface, as shown in Fig. 5a and b. With the deposition of an interphase on the fiber surface, both the amount and the length of pulled-out fibers increase, especially for composite with PyC/SiC interphase. It can also be observed from the morphologies of pull-out fiber surfaces, when no interphase was deposited, that the surfaces of pulled-out fibers are much coarser. This noticeable difference may be accounted by the bonding strength. It has been documented that fiber/matrix interfacial characteristics plays a crucial role in determining the mechanical properties of CFRCMCs. Weak fiber/matrix interfacial bonding in a brittle matrix composite facilitates toughening mechanism such as interfacial debondingand fiber pull-out. In contrast, a strong interfacial bonding tends to cause the crack propagate straightly through the fibers and result in low fracture toughness [15]. When no interphases were deposited, strong interfacial bonding may occur and limit the deflection of crack in the damaging process.

In order to better understand the reasons for the brittle fracture behavior of composite with uncoated carbon fibers, TEM was applied to investigate the interfacial zone between the fibers and matrix, as shown in Fig. 6. No obvious reaction zones can be found from both transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) micrographs, which means that carbon fiber reinforcements were not eroded in the fabrication process and that the brittle fracture behavior of composite with uncoated carbon fiber reinforcements was mainly caused by the strong bonding between fibers and matrix. It is well known that too strong bonding between fiber reinforcements and matrix will hinder the deflection of cracks in the propagation process and result in brittle fracture behavior.

4. Conclusions

Interphases exert great effects on both microstructures and properties of C_f/SiC–ZrC composites fabricated through mold-pressing and PIP process.

1. When there is no interphase deposited on the surface of carbon fibers, composite possesses a much higher density and the dispersions of carbon fiber reinforcements and ZrC particles are much more homogeneous than those with interphases. When interphases were deposited, there are obvious inter-bundle matrix zones and ZrC existed mainly in inter-bundle matrix.
2. The addition of interphases can greatly improve the mechanical properties of composites. The bending stress and elastic modulus of composites with PyC/SiC interphase were 401 ± 64 MPa and 104 ± 10 GPa while those of composites without interphase were 81 ± 24 MPa and 91 ± 12 GPa. As a result of the weak bonding of interphases, composite with interphases showed typical non-brittle fracture behavior.

3. The brittle fracture behavior of C_f/SiC–ZrC composite without interphases may be mainly ascribed to the strong bonding between fibers and matrix.

Acknowledgments

Authors appreciate the financial support of the National High technology Research and development Program of China (863 Program) under Project No. 2006AA03Z565 and Knowledge Innovation Program of the Chinese Academy of Sciences. Authors also thank Professor Fangfang Xu from Shanghai Institute of Ceramics Chinese Academy of Sciences for his useful help in the analysis of TEM results.

References

[1] R.R. Naslain, SiC-matrix composites: nonbrittle ceramics for thermo-structural application, International Journal of Applied Ceramic Technology 2 (2) (2005) 75–84.
[2] S.M. Dong, Y. Katoh, A. Kohyama, Preparation of SiC/SiC composites by hot pressing, using Tyranno-SA fiber as reinforcement, Journal of the American Ceramic Society 86 (1) (2003) 26–32.
[3] E. Wuchina, M. Opeka, S. Causey, K. Buesking, J. Spain, A. Cull, J. Routbort, F. Guitierrez-Mora, Designing for ultrahigh-temperature applications: the mechanical and thermal properties of HfB_2, HfCx, HfNx, and alpha Hf(N), Journal of Materials Science 39 (19) (2004) 5939–5949.
[4] J.M.Y. Blum, H. Kleebe, Low temperature, low pressure fabrication of ultra high temperature ceramics (UHTCs), Technical reports, ADA456577, 2006.
[5] S.F. Tang, J.Y. Deng, S.J. Wang, W.C. Liu, K. Yang, Ablation behaviors of ultra-high temperature ceramic composites, Materials Science and Engineering A—Structural Materials Properties Microstructure and Processing 465 (2007) 1–7.
[6] W. Yang, H. Araki, A. Kohyama, H. Suzuki, T. Noda, Effects of SiC sub-layer on mechanical properties of Tyranno-SA/SiC composites with multiple interlayers, Ceramics International 31 (4) (2005) 525–531.
[7] R.J. Kerans, R.S. Hay, N.J. Pagano, T.A. Parthasarathy, The role of the fiber matrix interface in ceramic composites, American Ceramic Society Bulletin 68 (2) (1989) 429–442.
[8] F. Rebillat, J. Lamon, R. Naslain, E. Lara-Curzio, M.K. Ferber, T.M. Besmann, Properties of multilayered interphases in SiC/SiC chemical-vapor-infiltrated composites with ‘‘weak’’ and ‘‘strong’’ interfaces, Journal of the American Ceramic Society 81 (9) (1998) 2315–2326.
[9] R. Naslain, Design, preparation and properties of non-oxide CMCs for application in engines and nuclear reactors: an overview, Composites Science and Technology 64 (2) (2004) 155–170.
[10] R.R. Naslain, The design of the fibre–matrix interfacial zone in ceramic matrix composites, Composites Part A—Applied Science and Manufacturing 29 (9–10) (1998) 1145–1155.
[11] Q. Zhou, S.M. Dong, X.Y. Zhang, Y.S. Ding, Z.R. Huang, D.L. Jiang, Synthesis of the fiber coating by FP-CVI process, High-Performance Ceramics IV 336–338 (Parts 1–3) (2007) 1307–1309.
[12] Z. Wang, S.M. Dong, X.Y. Zhang, H.J. Zhou, D.X. Wu, Q. Zhou, D.L. Jiang, Fabrication and properties of C-f/SiC–ZrC composites, Journal of the American Ceramic Society 91 (10) (2008) 3434–3436.
[13] A. Bellucci, D. Gozzi, T. Kimura, T. Noda, S. Otani, Zirconia growth on zirconium carbide single crystals by oxidation, Surface & Coatings Technology 197 (2–3) (2005) 294–302.
[14] S.M. Dong, Y. Katoh, A. Kohyama, S.T. Schwab, L.L. Snead, Microstructural evolution and mechanical performances of SiC/SiC composites by polymer impregnation/microwave pyrolysis (PIMP) process, Ceramics International 28 (8) (2002) 899–905.
[15] Q.S. Ma, Z.H. Chen, W.W. Zheng, H.F. Hu, Processing and characterization of three-dimensional carbon fiber-reinforced Si–O–C composites via precursor pyrolysis, Materials Science and Engineering A—Structural Materials Properties Microstructure and Processing 352 (1–2) (2003) 212–216.