

# Manufacture of carbon fiber reinforced SiC composites by a hybrid process combining TiN filler infiltration and precursor impregnation and pyrolysis

Y Y Yang, W S Lin, J J Wang

**Abstract**—Three-dimensional carbon fiber reinforced silicon carbide composites (3D C<sub>f</sub>/SiC) were manufactured by a hybrid process combining TiN filler infiltration and precursor impregnation and pyrolysis (PIP). The mixture of polycarbosilane and divinylbenzene (DVB) was used as precursor of silicon carbide. TiN nano powders were used as the inert filler, resulting in enhancing the infiltration efficiency of PIP process and decreasing the open porosity of the Cf/SiC composites. The bending strength of the composite was 208 MPa when the TiN content was 6 wt%, much higher than that of the composite without filler (127 MPa).

**Index Terms**—Carbon fiber; Ceramics; Filler; Precursor impregnation and pyrolysis

## I. INTRODUCTION

In the past decade, SiC based matrix composite reinforced by the carbon fiber or silicon carbide fiber has been developed as an advanced composite because of its excellent mechanical properties, high thermal shock resistance and low density [1-4].

Many methods to manufacture carbon fiber reinforced SiC composites (Cf/SiC) had been reported in literatures [5-8]. Compared with other techniques, such as chemical vapor infiltration (CVI), or reactive melting infiltration (RMI), precursor infiltration and pyrolysis (PIP) processes were particularly developed recently because of its low cost of fabrication and feasibility for large-scale components with complex shapes [9-11].

In the PIP process, a ceramic precursor was dispersed in a solution before it was infiltrated into the fiber preforms. The precursor was then converted into ceramic phase in the pyrolysis process. However, it is difficult to achieve highly densified ceramics by this method because of the high volume shrinkage in the polymer-ceramic conversion. Therefore, repeated PIP cycles for densification were necessary, making the process time-consuming [11].

A new technique was developed to overcome this problem recently. In this process, some inorganic fillers were mixed with organo-metallic precursors and infiltrated into the fiber preforms to reduce the excessive shrinkage in the ceramic conversion process [11-17]. Several papers have reported an effective way to manufacture the SiC matrix composites with low porosity by introducing titanium silicon carbide

(Ti<sub>3</sub>SiC<sub>2</sub>) particles as the inert filler into the PCS precursor [12-14]. Al<sub>2</sub>O<sub>3</sub>, ZrC and TiSi<sub>2</sub> were also reported as the fillers to compensate the volume decrease during the PIP process and improve the infiltration efficiency of the composites [15-17].

Titanium nitride (TiN) was used for many engineering applications owing to its high mechanical properties, good thermal conductivity, and excellent corrosion resistance [18]. However, up to now, little concentration was given on the mechanical properties of Cf/SiC composites using TiN particles as filler. In the present work, polycarbosilane (PCS) and nano TiN powders were used as the precursor and filler, respectively. The mixed slurries of nano-TiN and PCS solvent were used in PIP process to manufacture three-dimensional carbon fiber reinforced silicon carbide composites (3D C<sub>f</sub>/SiC). Microstructure and phase variation as well as mechanical properties of the composites were investigated.

## II. MATERIALS AND METHODS

Carbon fibers (T300SC, Toray, Tokyo, Japan) were used to fabricate carbon fiber preforms. The carbon fiber were braided to be a three-dimensional (3D C<sub>f</sub>) preforms by a four-step process with fiber volume fraction of about 40%, which was technically supported by Jiangsu Tianniao High Technology Company (Jiangsu, China). The carbon fiber preforms were first deposited with PyC interphases by CVI method. The source gas for PyC was ethane, and the deposition conditions were 3 kPa and 1050 °C. Thickness of PyC layer is about 0.2 μm.

The obtained preforms were then densified by PIP process. The mixed slurries were composed of PCS, TiN and divinylbenzene (DVB), which were used as the precursor, filler and solvent, respectively. Nano-TiN powders (averaged size of 20 nm) were mixed with PCS powders (prepared in our laboratory with the molecular weight about 1300 and soften point about 210 °C) and DVB by ball-milling for 48 h to form homogenous slurries. The mass ratios of PCS and nano-SiC in the slurries were listed in Table 1.

The preforms were infiltrated with the mixture slurries under vacuum (10<sup>-2</sup>Pa) and then DVB was vacuumed away using a vacuum pump. Afterwards, the samples were dried at 80 °C for 6 h in a vacuum and then pyrolyzed at 1200 °C for 30 min under nitrogen atmosphere. The infiltration of the slurries and pyrolysis of the samples make up one cycle. Each sample was subjected to several PIP cycles until the weight-increase of the final composites were less than 1 wt%. After each PIP cycle, the weight-increase of each sample was measured by an electronic balance, the measurement accuracy of which is up to 0.1mg. Fig. 1 shows the flow chart for the preparation of composites via PIP route.

**Yayun Yang**, School of Materials Engineering, Shanghai University of Engineering Science, Shanghai, China, Mobile No.86-13262796801,

**Wensong Lin**, School of Materials Engineering, Shanghai University of Engineering Science, Shanghai, China, Mobile No.86-18917250639,

**Jingjing Wang**, School of Materials Engineering, Shanghai University of Engineering Science, Shanghai, China, Mobile No.86-18615428867,

# Manufacture of carbon fiber reinforced SiC composites by a hybrid process combining TiN filler infiltration and precursor impregnation and pyrolysis

Table 1 Compositions of the mixed slurries

Sample	Nano TiN /g	PCS /g	DVB /g	Nano TiN / wt%
A	0	50	35	0
B	1.5	50	35	3
C	3.0	50	35	6
D	4.5	50	35	9

The density of the samples was measured in kerosene by Archimedes's method. The apparent density ( $\rho_a$ ) and open porosity ( $\theta$ ) of the samples were calculated by the following equations:

$$\rho_a = \frac{m_1 \rho_k}{m_2 - m_3} \quad \text{and} \quad \theta = \frac{m_2 - m_1}{m_2 - m_3} \times 100\%$$

Where  $\rho_k$  is the density of kerosene,  $m_1$  is the weight of dry sample in the air,  $m_2$  and  $m_3$  are the weights of the sample in the air and in kerosene, respectively, after it had been immersed in kerosene for 24 h.

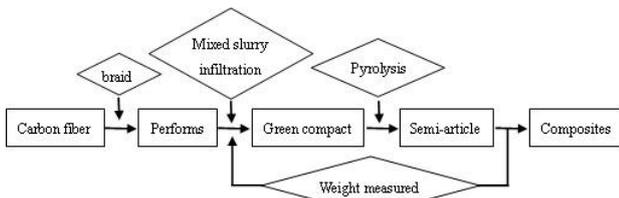


Fig. 1. The flow chart of the composites preparation process.

Bending strength was measured using a three-point-bending test with a span of 30 mm by a universal testing machine (Instron-5860, Instron Corp., MA), following the guidelines of ASTM standard C1341. Five specimens with the dimension of 40 mm × 5 mm × 4 mm were used for the test to get the average value of the bending strength of the same sample. The loading rate was 0.5 mm/min. The bending strength ( $\sigma$ ) is calculated by the following equation [15]:

$$\sigma = \frac{3FL}{2wt^2}$$

where F is the maximal applied force, L is the support span (30 mm), w is the width (5 mm), and t is the thickness (4 mm) of the specimen.

The phases presented in the composites were characterized by X-ray diffraction (X'Pert Pro, PANalytical, Netherlands) with Cu K $\alpha$  radiation using a step size of 0.01° for the 2 $\theta$  range 10°-100°. The morphology of fracture surfaces and polished section of the samples were studied by a scanning electron microscopy (Hitachi S3400, Japan).

## III. RESULTS AND DISCUSSION

### A. Density and Open Porosity

Fig. 2 shows the weight-increase of samples versus the number of PIP cycles for 3D C<sub>f</sub>/SiC composites with different content of TiN filler in the slurries. It was observed that the rate of weight-increase for all the composites slowed down with the increase in the amount of PIP cycles. The amount of PIP cycles for these composites not able to be infiltrated more slurries (weight-increase is less than 1 wt%) decreases from 14 to 8 as the TiN content vary from 0 to 9 wt%, indicating that the incorporation of TiN powders in the slurries improves the infiltration efficiency remarkably.

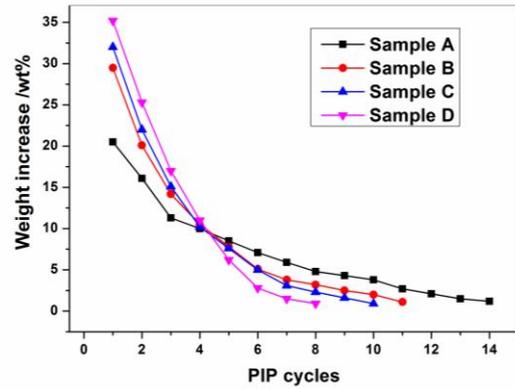


Fig. 2. The weight-increase of samples versus number of PIP cycles for 3D C<sub>f</sub>/SiC composites

### B. Mechanical Properties and Microstructure

Properties of the 3D C<sub>f</sub>/SiC composites were listed in Table 2. It can be seen that the maximum flexural strength (208MPa, Sample C) of the composites was achieved when the TiN content in the slurries is 6 wt%, much higher than that of the Sample A (127MPa).

Table 2 Properties of four kinds of 3D C<sub>f</sub>/SiC composites

Sample	Density / gcm <sup>-3</sup>	Open porosity / %	Bending strength / MPa	Elastic modulus / GPa
A	1.91	9.73	127	98
B	2.06	4.04	150	106
C	2.12	2.05	208	130
D	2.05	6.13	161	112

Typical load-displacement curves of the bending strength test for all composites were plotted in Fig. 3. As displayed in Fig. 3, all the composites showed an elastic deformation at the beginning of the loading, zigzag rise with increase of the load till the maximum value reached. Afterward the bending stress fell off gradually, which is typical for the fiber reinforced ceramic matrix composites. It also can be seen from Fig. 3 that the sample A shows the lowest bending strength and shortest displacement before the sample is failed, revealed that TiN filler can enhance the bending strength and improve the failure toughness of the composites.

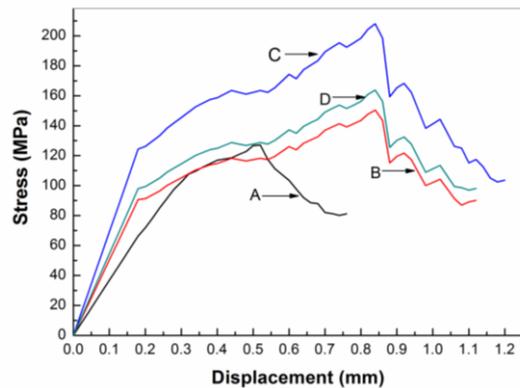


Fig. 3. Bending load/displacement curves of 3D C<sub>f</sub>/SiC composites

The typical fracture surface morphologies of the various composites were shown in Fig. 4. As seen from Fig. 4, the fracture surface of the composites without filler (Sample A) are relatively plain, and large pores are obvious, owing to the volume shrinkage of PCS during the pyrolysis, while the fracture surfaces of the Sample C with 6 wt% TiN filler exhibit long fibers pull-out.

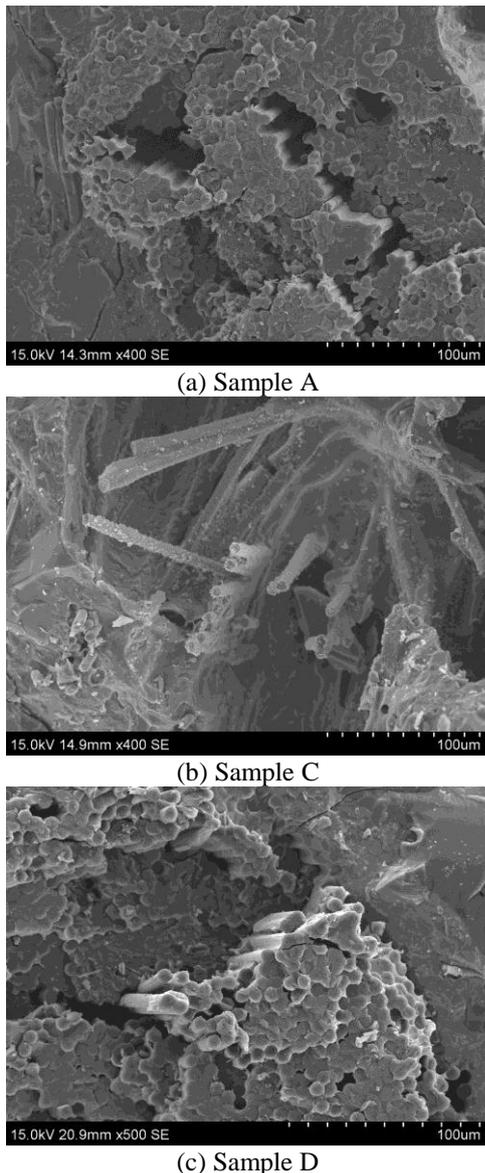


Fig. 4. The fracture surface morphologies of 3D C<sub>f</sub>/SiC composites

It can be concluded from the data listed in Table 2 that the bending strengths of the composites increase firstly and then decrease as the TiN content in the slurries increase from 0 to 9 wt%. This experiment result may be attributed to the following reasons. Firstly, the Sample A manufactured by PIP process without filler had a low relative density and high porosity because of its low ceramic yield of the precursor for SiC. Fourteen PIP cycles were not enough to make the composites fully densify. However, after so many PIP cycles, pores left behind come to be closed. As these isolated pores could hardly be further filled in the following infiltration process, a loose matrix is formed eventually.

TiN nanometer powders in the slurries can fill in the pores existed in the space between the fibers and act as the nuclei for the transformation of PCS to SiC matrix, resulting in a decrease of the porosity in the composites. As can be seen from Fig.4b, the fracture surface morphologies of Sample C, of which the filler content is 6 wt%, a dense matrix was formed because of the TiN powders dispersing in the SiC substrate.

As the content of TiN powders increase up to be 9 wt%, the slurry becomes more viscous and difficult to infiltrate into the

carbon fiber performs. Furthermore, large amount of TiN particles in the slurries may aggregate together, resulting in some micro-pores existed in the matrix after the PIP process, and thus composite degradation. It could be seen from Fig.4c that some narrow voids between fiber bundles existed in Sample D.

Therefore, it can be concluded that the appropriate TiN content can effectively improve the infiltration efficiency, increase the density and enhance the bending strength of the composites during the infiltration and PIP process.

The XRD pattern of Sample D was shown in Fig.5. The major phase in the composite was SiC, and a little amount of TiN was also found. Carbon could be observed from the XRD pattern, which possibly comes from pyrolytic carbon and/or carbon fiber, suggested that no reaction happened between TiN and pyrolytic carbon during the heat treatment in this experiments.

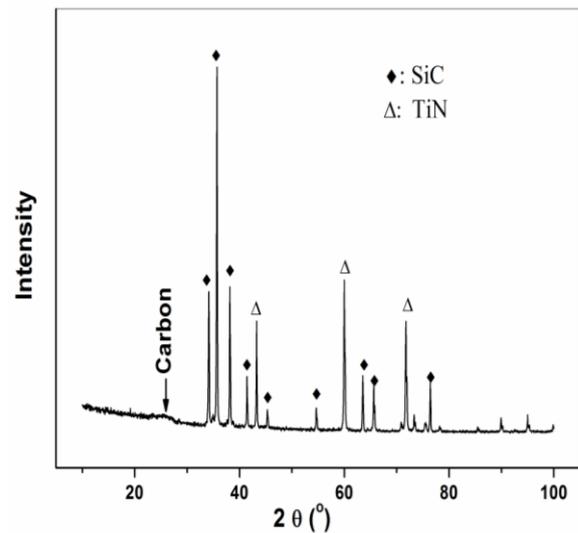


Fig.5 The XRD pattern of Sample D

#### IV. CONCLUSION

3D C<sub>f</sub>/SiC composites were prepared by a hybrid process combining infiltration with TiN powder filler and PIP process. The results indicated that the appropriate TiN content mixed in the infiltration slurries improved the infiltration efficiency of C<sub>f</sub>/SiC composites, and the TiN nanopowders can compensate for volume shrinkage of PCS in the PIP process and make the dense matrix formed. The bending strengths of the composites increase firstly and then decrease as the TiN content increase from 0 to 9 wt%. The maximum bending strength reaches 208 MPa when the content of TiN powders in the slurries is 6 wt%, which is 63 % higher than that of the composites without the filler (127MPa).

#### ACKNOWLEDGMENT

Authors appreciate the financial support of Innovation Program of Shanghai Municipal Education Commission (No. 13ZZ133) and Innovative Research Project for Graduate Students in Shanghai University of Engineering Science (No. 15KY0506).

# Manufacture of carbon fiber reinforced SiC composites by a hybrid process combining TiN filler infiltration and precursor impregnation and pyrolysis

## REFERENCES

- [1] R Naslain, Design, "preparation and properties of non-oxide CMCs for application in engines and nuclear reactors: an overview," *Compos. Sci.Technol.*, vol. 64, 2004, pp. 155-170.
- [2] Yang W, Noda T, Araki H, Yu J, Kohyama A, "Mechanical properties of several advanced Tyranno-SA fiber-reinforced CVI-SiC matrix composites," *Mater. Sci. Eng. A*, vol.345, 2003, pp. 28-35.
- [3] R.M. Rocha, C.A.A. Cairo, M.L.A. Graca, "Formation of carbon fiber reinforced ceramic matrix composites with polysiloxane/silicon derived matrix," *Mater. Sci. Eng. A*, vol.437, 2006, pp. 268-273.
- [4] J. Magnant, R. Pailler, Y. Le Petitcorps, L. Maillé, A. Guette, J. Marthe, E. Philippe, Y. Katoh, S.M. Dong, A. Kohyama, "A novel processing technique of silicon carbide-based ceramic composites for high temperature applications," *Ceram. Trans.*, vol.144, 2002, pp. 77-86.
- [5] R. R. Naslain, R. Pailler, X. Bourrat, S. Bertrand, F. Heurtevent, P. Dupel, F. Lamouroux, "Synthesis of highly tailored ceramic matrix composites by pressure-pulsed CVI, *Solid State Ionics*," vol.141-142, 2001, pp. 41-548.
- [6] H. Mei, Q. Bai, T. Ji, H. Li, L. Cheng, "Effect of carbon nanotubes electrophoretically-deposited on reinforcing carbon fibers on the strength and toughness of C/SiC composites," *Compos. Sci. Technol.*, vol.103, 2014, pp. 94-99.
- [7] Y. Wang, X. Zhu, L. Zhang, L. Cheng, "C/C-SiC-ZrC composites fabricated by reactive melt infiltration with  $\text{Si}_{0.87}\text{Zr}_{0.13}$  alloy," *Ceram. Int.*, vol.38, 2012, pp. 4337-4343
- [8] J. Jiang, S. Wang, W. Li, Z. Chen, Y. Zhu, "Preparation of 3D  $\text{C}_f/\text{ZrC-SiC}$  composites by joint processes of PIP and RMI," *Mater. Sci. Eng. A*, vol.607, 2014, pp. 334-340
- [9] X. Yang, C. Feng, "Effects of ZrC coating on mechanical properties of PIP-C/SiC composites," *J. Alloys Comp.*, vol.632(2015)263-268.
- [10] L. Q. Duan, Q. S. Ma, "Effect of pyrolysis temperature on the pore structure evolution of polysiloxane-derived ceramics," *Ceram. Int.*, vol.38(2012), 2667-2671.
- [11] Z. Wang, L. Gao, Y. Ding, B. Wu, H. Zhou, P. He, S. "Dong, Microstructure observation and analysis of 3D carbon fiber reinforced SiC-based composites fabricated through filler enhanced polymer infiltration and pyrolysis," *Ceram. Int.*, vol.38, 2012, pp. 535-540.
- [12] Y. Mu, W. Zhou, Y. Hu, Y. Qing, F. Luo, D. Zhu, "Improvement of mechanical and dielectric properties of PIP-SiC<sub>f</sub>/SiC composites by using Ti<sub>3</sub>SiC<sub>2</sub> as inert filler," *Ceram. Int.*, vol.41, 2015, pp. 4199-4206
- [13] X. M. Fan, X. W. Yin, L. Wang, "Processing, microstructure and ablation behavior of C/SiC-Ti<sub>3</sub>SiC<sub>2</sub> composites fabricated by liquid silicon infiltration," *Corros. Sci.*, vol.74, 2013, pp. 98-105.
- [14] J. S. Yang, S. M. Dong, P. He, "Fabrication and properties of C<sub>f</sub>/Ti<sub>3</sub>SiC<sub>2</sub>-SiC composites using Ti<sub>3</sub>SiC<sub>2</sub> as inert filler," *Key Eng. Mater.*, 512-515, 2012, pp. 681-684.
- [15] Y. Mu, W. Zhou, H. Wang, C. Wang, Y. Qing, "Mechanical and dielectric properties of 2.5 D SiC<sub>f</sub>/SiC-Al<sub>2</sub>O<sub>3</sub> composites prepared via precursor infiltration and pyrolysis," *Mater. Sci. Eng. A*, vol.596, 2014, pp. 64-70.
- [16] L. Maillé, S. Le Ber, M.A. Dourges, R. Pailler, A. Guette, J. Roger, "Manufacturing of ceramic matrix composite using a hybrid process combining TiSi<sub>2</sub> active filler infiltration and preceramic impregnation and pyrolysis," *J. Eur. Ceram. Soc.*, vol.34, 2014, pp. 189-195.
- [17] L. Zhang, S. Dong, H. Zhou, Y. Kan, F. Zhou, Z. Wang, "3D C<sub>f</sub>/ZrC-SiC composites fabricated with ZrC nanoparticles and ZrSi<sub>2</sub> alloy," *Ceram. Int.* vol.40, 2014, pp. 11795-11801.
- [18] U.W. Bläß, T. Barsukova, M. R. Schwarz, A. Köhler, C. Schimpf, I. A. Petruscha, U. Mühle, D. Rafaja, E. Kroke, "Bulk titanium nitride ceramics – Significant enhancement of hardness by silicon nitride addition, nanostructuring and high pressure sintering," *J. Eur. Ceram. Soc.*, vol.35, 2015, pp.2733-2744.

**Yayun Yang**, postgraduate majoring in Materials Science and Engineering, whose research work focused in the field of ceramic matrix composites.

**Wensong Lin**, the corresponding author, Ph.D and professor majoring in Materials Science and Engineering, whose research work focused in the field of ceramic and metal matrix composites.

**Jingjing Wang**, postgraduate majoring in Materials Science and Engineering, whose research work focused in the field of ceramic matrix composites.