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Wear behavior of SiC/PyC composite materials prepared by electromagnetic-field-assisted CVI

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Abstract: Silicon carbide/pyrolytic carbon (SiC/PyC) composite materials with excellent performance of self-lubrication and wear resistance were prepared on SiC substrates by electromagnetic-field-assisted chemical vapor infiltration (CVI). The composition and microstructure of the SiC/PyC materials were investigated in detail by XRD, SEM and EDS, etc. The effects of the deposition temperature on the section features and wear resistance of the SiC/PyC were studied. The results show that the PyC layers were deposited onto SiC substrates spontaneously at a lower deposition temperature. The SiC substrates deposited with PyC can significantly reduce the wear rate of the self-dual composite materials under dry sliding condition. The wear tests suggest that the SiC/PyC composite materials own a better wear resistance property when the deposition temperature is 800 °C, and the wear rate is about 64.6% of that without the deposition of PyC.

Key words: SiC/PyC composite materials; wear performance; self-lubricating; chemical vapor infiltration; interfacial adsorption

1 Introduction

Silicon carbide (SiC) ceramics materials with good characteristics such as good high-temperature strength, wear resistance, thermal stability, small thermal expansion coefficient, high thermal conductivity, high hardness, good chemical resistance and thermal shock resistance [1,2], have been increasingly widely used in the high technology and basic industries, such as insert bearing, sealing element, steam turbine rotor, and heat exchanger components [3,4], which are supposed to be the application prospect of structure materials that resist wear and corrosion. However, SiC under conditions of lubrication-free media can increase the material invalidation probability and in turn reduce the life of the material itself, easily leading to the increase of wear rate, due to the high friction coefficient of friction pair. In order to achieve the anti-wear property of SiC materials, relevant researchers tried the combination of SiC and lubricant. But traditional lubricant additives still cannot improve the lubrication, for the absence of fine contact boundary film in the process of wear and defects such as micro convex direct contact caused by the decrease of the lubrication medium, which greatly restrict the wide application in the high end field of cutting technology. Recently, primarily applied technologies such as compound sintering and molding technology of graphite/ silicon carbide ceramic, medium pore filling composite SiC ceramic technology, the second phase particle composite technology and composite silicon carbide ceramic coating technology, have been used to improve the friction and wear properties of SiC [5−8]. Researchers studied the tribological properties of C/C composites with various PyC microstructures. The results showed that the PyC with rough laminar structure exhibited the highest wear mass loss but the lowest fraction of oxidation abrasion, while the lowest friction coefficient and the highest fraction of oxidation abrasion were observed for the C/C composite with the smooth laminar structure [9]. All the preparation processes mentioned above can improve the friction and wear properties of SiC materials more or less. Nevertheless, they still cannot be able to satisfy the request of

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continuous self-lubrication under the extremely harsh operating mode condition due to the composition segregation of SiC substrate and the assistant filling composition, the bad match of compatibility and the thermal-expansion coefficient [10].

To improve the wear resistance and the self-lubricating property of SiC materials and realize the dynamic self-repairing function in the process of wear, appropriate amount of the PyC was introduced homogeneously into the matrix of SiC using an electromagnetic-field-assisted CVI at a lower deposition temperature. The morphology and composition distribution of the PyC in SiC hole at different deposition temperatures were characterized. The study on the preparation of the SiC/PyC via electromagnetic field-assisted CVI provides a theoretic reference for the preparation of new high temperature lubricating materials.

2 Experimental

Small specimens (50 mm×50 mm×6 mm) of SiC ceramic materials with a density of 2.65−2.75 g/cm^3, and a porosity of 15% and purity of greater than 99 % were used as substrates. These specimens (SiC matrix) were cleaned by ultrasonic wave with alcohol, and then put into the electric heating equipment of the electromagnetic-field-assisted CVI [11,12]. The SiC/PyC composite materials were developed on the SiC substrates using C_3H_6 (purity of 99.9%) as carbon source and N_2 as carriers and diluted gas (at a flow ratio of 1:1) in the absence of catalyst when the deposition temperature was 750−850 °C and the gas pressure of the system was in the range of 1−2 kPa in a homemade depositing furnace [13]. Archimedes principle was employed to measure the open porosity and density of the ceramic materials.

The tribological behaviour of the SiC/PyC composite materials against the self-dual carborundum grinding wheel was investigated on a vertical grinding wheel machine which could simulate the cutting operation. The counterpart disk panel was pure SiC with 250 mm in diameter and 25 mm in thickness (S3SL−250 Pedestal grinders). During the test, the disk surface sliding velocity was determined to be 2850 r/min (linear velocity of 37.3 m/s). The normal load of contact was 50 N/cm^2 and the total test time was 60 s. The wear volume loss of the SiC/PyC against SiC was investigated by per unit length at one sliding pass (calculated by the average result of three experiments). The morphology of the worn surface and cross-section of the SiC/PyC composite materials were observed by scanning electron microscope (SEM, FEI Quanta 200) attached with energy dispersive spectroscope (EDS). And the chemical composition was analyzed by D8−ADVANCE rotating anode X-ray diffraction (XRD).

3 Results and discussion

3.1 Physical properties and microstructure of SiC/PyC

The XRD patterns of the surface of the SiC/PyC are shown in Fig. 1.

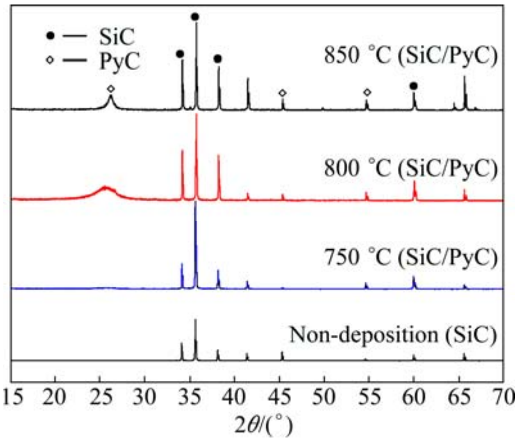

Fig. 1 XRD patterns of surface of SiC and SiC/PyC

It can be seen that the main crystal phase is SiC and its phase type is 6H. Furthermore, an obvious amorphous peak appears on the matrix of the SiC ceramic materials when they are deposited with the PyC. The phenomenon suggests that the PyC was deposited on the surface of the SiC material within the temperature range from 750 °C to 850 °C by electromagnetic-field-assisted method. The intensity of the characteristic diffraction peak and the amount of the crystallinity of the PyC on the surface of SiC/PyC increased gradually with the increase of the temperature.

The SEM images of cross-section of the SiC/PyC composite materials at different temperatures are shown in Fig. 2. It can be seen that the surface of the carbon layer on the boundary of the cross section of the micro porous and the section of the matrix material is smooth (Fig. 2 (a_1)). However, it is noticed that the PyC layer was deposited on the SiC at 750, 800 and 850 °C. The thickness of the interface layer of the PyC increases as the deposition temperature increases at the same time (Figs. 2(b_2)−(d_2)). A typical characteristic of the CVI process is that the PyC can combine with the SiC well without obvious interface and microcrack. From the EDS analysis results of the interfacial transition zone in each specimen in Fig. 2 and Table 1, it can be seen that with the increase of the elevated temperature, the carbon content on the interface of PyC and SiC increased whilst the Si content decreased. Table 2 for the open porosity and density of the ceramic materials shows that with the

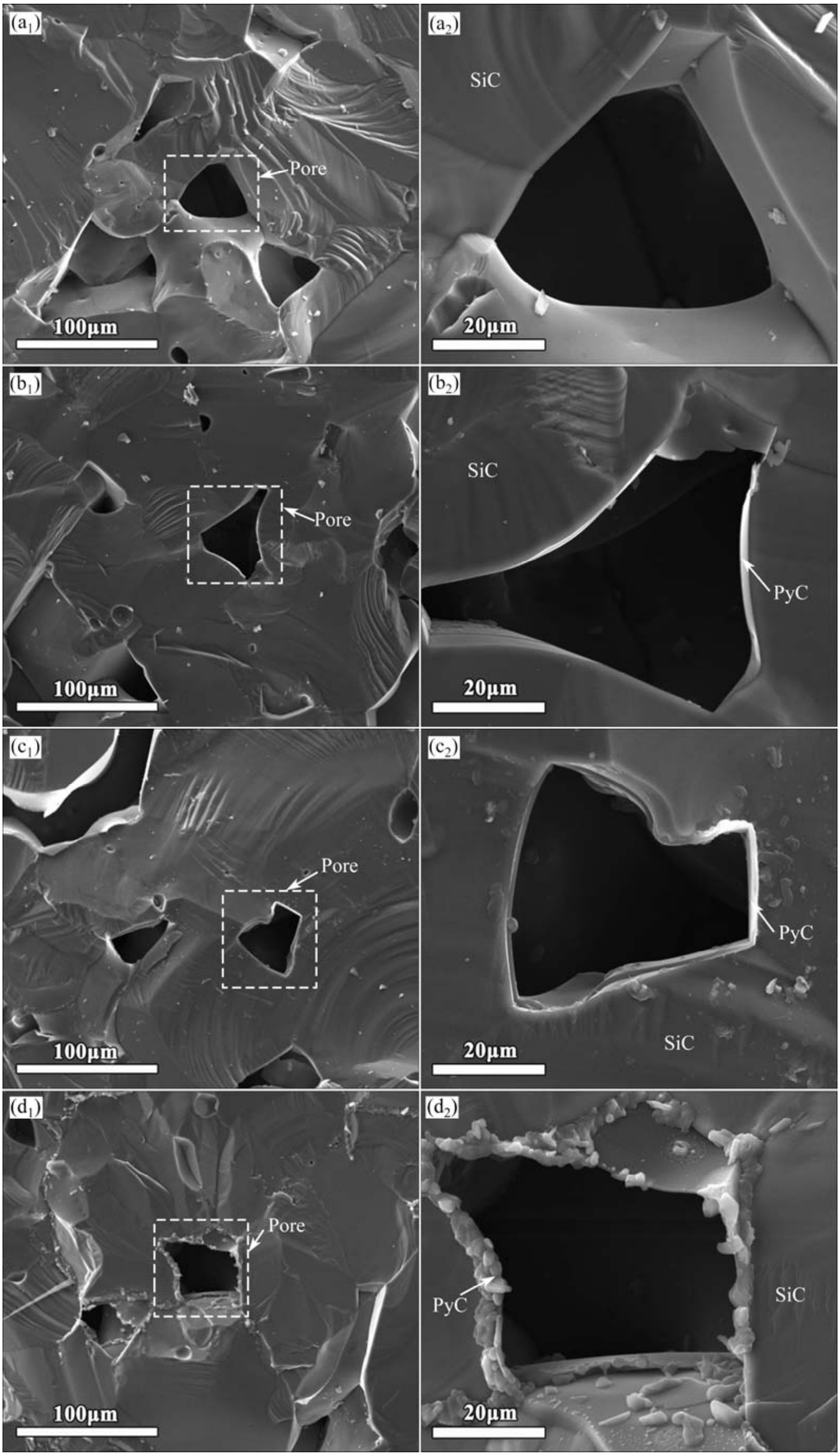

Fig. 2 SEM images of cross section of SiC/PyC composite materials: (a_1−d_1) Morphologies of cross section of pure SiC and PyC/SiC produced by CVI at 750, 800 and 850 °C, respectively; (a_2−d_2) Local area magnification images of (a_1−d_1), respectively

Table 1 EDS analysis results of tested specimen in interfacial transition zone in Fig. 2

Specimen	x(Si)/%	x(C)/%
SiC (No deposition)	42.32	57.68
SiC/PyC at 750 °C	24.58	75.42
SiC/PyC at 800 °C	19.00	81.00
SiC/PyC at 850 °C	14.16	85.54

Table 2 Open porosity and density of ceramic materials

Specimen	Open porosity/%	Density/(g·cm^{-3})
SiC (No deposition)	15.00	2.683
SiC/PyC at 750 °C	14.91	2.702
SiC/PyC at 800 °C	14.21	2.718
SiC/PyC at 850 °C	14.09	2.722

increase of temperature, the density of SiC/PyC increased and the porosity declined, which means the increasing amount of the PyC on the SiC substrate as well.

In the process of electromagnetic-field-assisted chemical vapor infiltration, a large number of the hydrocarbon groups are generated after propylene cracking, and then the hydrocarbon groups are aggregated on the surface of the SiC materials, which act as a conductive heat generator. Under the function of ancillary electromagnetic field [14−17], the aggregation is accelerated and attached to the SiC substrate as the paramagnetic charged groups, which move along the direction of resultant of the magnetic field, are formed after aggregation is polarized in the magnetic field. At the beginning of the adsorption, the C/Si interface shows a characteristic of gradient change as a result of chemical reaction between C and Si under the influence of SiC active growing point on the surface and the disruptive discharge of the charged groups [18]. From the analysis of its structure characteristics, it can be seen that the reason why the PyC and SiC are in a good combination is that the gradient change on the SiC/PyC interface can effectively reduce the thermal fatigue cracks caused by the excessive alternating thermal stress, rather than concentrated in a single interface point. The deposition temperature had a significant effect on the activation process of the PyC-deposition following the Arrhenius equation [19], the reaction rate of polarity charged groups in the activation process would increase exponentially and the PyC deposition volume also increased with the increase of temperature. It is typical mechanical mesh and physical adsorption concomitant model [20].

3.2 Effect of deposition temperature on wear rate of SiC/PyC under dry sliding condition

Figure 3 shows the effect of the deposition temperature on wear rate of the SiC/PyC under dry sliding condition. Figure 4 shows the SEM images of the worn surface of different samples. And the TEM morphologies of the wear debris particles of the pure SiC and the SiC/PyC are shown in Fig. 5.

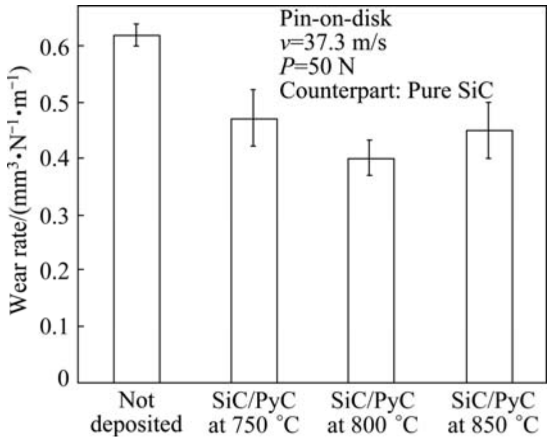

Fig. 3 Effect of deposition temperature on wear rate of SiC and SiC/PyC under dry sliding condition

As shown in Fig. 3, the wear rates of the SiC/PyC composite materials are lower than that of the matrix materials under the same condition of dry sliding. Among them, the wear rate of the matrix materials is 0.62 mm^3/(N·m), while that of SiC/PyC composite materials prepared at 800 °C is lower, about 64.6% of the former, only 0.40 mm^3/(N·m). The introduction of the PyC in SiC ceramics makes the interlayer slide easily when there is a shear stress between the SiC/PyC against the self-dual SiC grinding wheel. It shows that the formation of PyC films during wear process can effectively reduce the friction coefficient of friction pairs, correspondingly, the wear rate is decreased. The moderate and continuous PyC films transfer to SiC grinding to achieve the regulation of self-lubrication. The mechanism is similar to self-lubricating anti-friction effect of graphite in wear-resistant materials [21]. With the increase of deposition temperature, the deposition thickness of PyC also increases, which results in the decrease of adhesion strength between PyC and SiC substrate, thereby aggravates the delamination wear, so that the whole PyC blocks fall directly in the wear process and the wear rate increases.

Figure 4 shows that the specimen without the deposition of the PyC was gathered and isolated by fine wear debris particles filling the pores between the silicon carbide. The micro area of frictional film peeled, complete frictional films could not be seen, and the friction surface had obvious traces of shearing. This indicates that the main wear mechanism of SiC−SiC self dual without a lubricant is severe adhesive wear [22]. This is attributed to that the real contact area of no

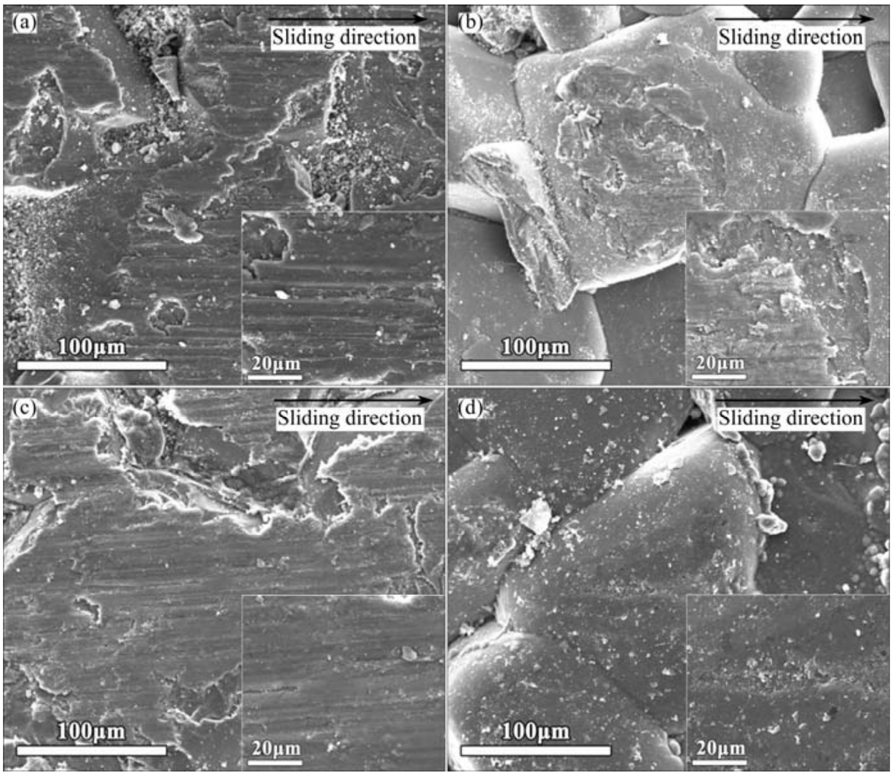

Fig. 4 SEM images of worn surface: Morphologies of surface of pure SiC (a), PyC/SiC produced by CVI at 750 °C (b), 800 °C (c) and 850 °C (d)

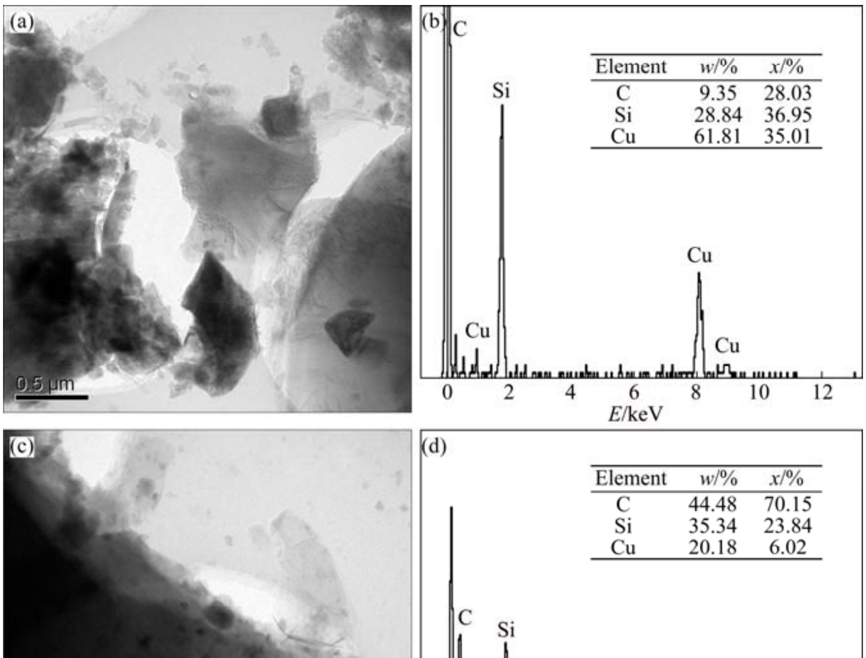

Fig. 5 TEM images (a, c) and EDS analysis (b, d) of debris particles of SiC and SiC/PyC: (a, b) Pure SiC; (c, d) PyC/SiC produced by CVI at 800 °C

lubricant SiC−SiC self-duality friction surface is small, causing significant impact abrasive wear and adhesive wear (Fig. 4(a)). On the worn surface of the SiC/PyC composite materials with the deposition temperature at 750 °C, it is visible that friction film covered on the surface of the SiC material is not dense enough, and there exist large bulk and cross (Fig. 4(b)). The friction film on the surface of the SiC/PyC composites with the deposition temperature at 800 °C is compact, uniform and complete, and there is no phenomenon of obvious scratches and large accumulation (Fig. 4(c)). Meanwhile, it can be obtained from the TEM image that the element C exists in the debris particles of the SiC/PyC (Fig. 5(c)), which are different from the debris particles of the pure SiC materials (Fig. 5(a)). And both the SiC and the elemental C are closely combined together.

The quality of friction film on the surface of the SiC/PyC composites with the deposition temperature at 850 °C becomes worse instead, and there are clear accumulation, stacking phenomena, and more aggregation of the wear debris particles (Fig. 4(d)). This is because the excess of PyC makes excessive friction film form and leads to abrasive dust accumulation, which results in the increase of wear rate instead.

By comparison, along the sliding direction, the PyC and SiC shedding mixture can be attached to the worn surface after roller compaction, which can regulate the wear effectively. Moreover, the PyC deposits in the holes of SiC forming a lubricating film to reduce the effects of the friction, and the wear mechanism of friction material shifts from impact wear and adhesion wear to abrasive wear and slight adhesive wear in the process of friction.

4 Conclusions

1) The wear-resistant PyC/SiC ceramic materials with self-lubricating property were prepared by electromagnetic-field-assisted chemical vapor infiltration at a lower deposition temperature. The combination of PyC and SiC shows better properties when the deposition temperature reaches 800 °C.

2) The wear rate of SiC sample without deposition of the PyC is 0.62 $mm^3/(N\cdot m)$, whereas that of SiC/PyC composite materials prepared at 800 °C is the minimal, only 0.40 $mm^3/(N\cdot m)$.

3) The wear mechanisms of SiC−SiC self dual without a lubricant are mainly impact wear and adhesive wear. And, the SiC/PyC and SiC wear mechanisms are mainly abrasive wear and mild adhesive wear when the PyC is deposited on the SiC substrate.

References

[1] KRENKEL W, HEIDENREICH B, RENZ R. C/C−SiC composites for advanced friction systems [J]. Adv Eng Mater, 2002, 4(7): 427−436.

[2] PREWO K M. Fiber-reinforced ceramics: New opportunities for composite materials [J]. American Ceramic Society Bulletin, 1989, 68(2): 395−400.

[3] HILLIG W B. Making ceramic composites by melt infiltration [J]. American Ceramic Society Bulletin, 1994, 73(4): 56−62.

[4] CHIANG Y M, MESSNER R P, TERWILLIGER C D. Reaction-formed silicon carbide [J]. Ceramic Engineering and Science Proceedings, 2003, 24(3): 375−381.

[5] KRENKEL W, BERNDT F. C/C−SiC Composites for space applications and advanced friction systems [J]. Mater Sci Eng A, 2005, 412(1−2): 177−181.

[6] SATO S, SERIZAWA H, ARAKI H, NODA T, KOHYAMA A. Temperature dependence of internal friction and elastic modulus of SiC/SiC composites [J]. J Alloys Compds, 2003, 355(1−2): 142−147.

[7] ZHANG Ya-ni, XU Yong-dong, LOU Jian-jun, ZHANG Li-tong, CHENG Lai-fei, CHEN Zhi-jun. The analysis of friction and wear performance of C/C−SiC composites [J]. Journal of Aeronautical Materials, 2005, 25(2): 49−54.

[8] MATTONI M A, YANG J Y, LEVI C G, ZOK F W. Effects of matrix porosity on the mechanical properties of a porous-matrix, all-oxide ceramic composite [J]. J Am Ceram Soc, 2001, 84(11): 2594−2602.

[9] YU S, ZHANG F Q, XIONG X, LI Y P, TANG N, KOIZUMI Y, CHIBA A. Tribological properties of carbon/carbon composites with various pyrolytic carbon microstructures [J]. Wear, 2013, 304(1−2): 103−108.

[10] KUMAR S, KUMAR A, SHUKLA A, DEVI G R , GUPTA A K. Investigation of thermal expansion of 3D-stitched C−SiC composites [J]. Journal of the European Ceramic Society, 2009, 29(13): 2849−2855.

[11] YU Xin-qi, REN O-xu, LU Zhan-quan. Application of silicon carbide in mechanical seals [J]. Hebei Journal of Industrial Science and Technology, 2005, 22(3): 134−137. (in Chinese)

[12] ZHOU Song-qing, XIAO Han-ning, LI Gui-yu. High-temperature friction and wear mechanisms of situ synthesis of silicon carbide−titanium boride ceramic composites [J]. Journal of the Chinese Ceramic Society, 2006, 34(2): 152−157. (in Chinese)

[13] TU Chuan-jun, HUANG Qi-zhong, ZHANG Ming-yu, ZHAO Xin-qi, CHEN Jiang-hua. Microstructures and formation mechanism of headstand pyrocarbon cones developed by electromagnetic-field-assisted CVD [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(10): 2569−2577.

[14] XIE Zhi-yong, HUANG Qi-zhong, SU Zhe-an, ZHANG Ming-yu, LIANG Jin-hua, HUANG Bo-yun. Preparation of C/C composites by CVI with multi-factor coupling physical fields and deposition mechanism [J]. Journal of Inorganic Materials, 2005, 20(5): 1201−1207. (in Chinese)

[15] ZHANG Ming-yu, SU Zhe-an, XIE Zhi-yong, CHEN Jian-xun, HUANG Qi-zhong. Microstructure of pyrocarbon with chemical vapor infiltration [J]. Procedia Engineering, 2012, 27: 847−854.

[16] ZHANG Ming-yu, WANG Li-ping, HUANG Qi-zhong, CHAI Li-yuan. Rapid chemical vapor infiltration of C/C composites [J]. Transactions of Nonferrous Metals Society of China, 2009, 19(6): 1436−1439.

[17] WENG Yung-chun, WENG Yung-jin, YANG Sen-yeu. A study on the application of electromagnetic-field-assisted magnetic soft mold photocuring imprinting technology in micro-structure gradient replication molding [J]. Microelectronic Engineering, 2012, 96: 76-81.

[18] XIE Zhi-yong, HUANG Qi-zhong, SU Zhe-an, ZHANG Fu-qin, HUANG Bo-yun. Preparation and mechanism of C/C composites via coupling physical field CVI [J]. Inorganic Materials, 2005, 20(5): 1201−1207.

[19] GAO Peng-zhao, XIAO Han-ning, WANG Hong-jie, JIN Zhi-hao. A study on the oxidation kinetics and mechanism of three-dimensional (3D) carbon fiber braid coated by gradient SiC [J]. Materials Chemistry and Physics, 2005, 93(1): 164−169.
[20] BOUCHARD E, LAVENAC J, ROUX J C. Pyrocarbon depositson a graphite surface observed by STM [J]. Adv Mater CVD, 2001, 7(3): 125−130.
[21] DU Jun, HE Jia-wen. The preparation of graphite-like carbon film and difference from diamond-like carbon film [J]. China Surface Engineering, 2005, 18(4): 6−8. (in Chinese)
[22] AXEN N, HUTCHING I M, JAEOBSON S. A model for the friction of multiphase materials in abrasion [J]. Tribology International, 1996, 29(6): 467−475.

电磁场辅助 CVI 沉积 SiC/PyC 复合材料的磨损性能

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摘 要：采用电磁场辅助 CVI 沉积在 SiC 陶瓷基体上沉积热解炭，制得具有自润滑性和耐磨性的 SiC/PyC 复合材料。利用 XRD、SEM 和 EDS 等手段对 SiC/PyC 材料的成分和显微结构进行表征，研究沉积温度对 SiC/PyC 材料的截面结构和耐磨性能的影响。结果表明，在较低温度下可将热解炭引入 SiC 基体，并可降低与自对偶材料在干滑动摩擦条件下的磨损率。磨损试验结果表明，在沉积温度为 800 °C 条件下制得的 SiC/PyC 材料具有较优的抗磨损性能，其磨损率为未沉积热解炭的 SiC 材料磨损率的 64.6%。

关键词：SiC/PyC 复合材料；磨损性能；自润滑；化学气相渗透；界面吸附

(Edited by Wei-ping CHEN)