Short Communication

Antioxidant Coating Composed of SiC on Carbon Fibers by Chemical Vapor Reaction

J. Hao[1, 2], J. Li[*1, 2], W. Shi[1, 2, 3], Y. Tan[1, 2], X. Ding[3]

[1]Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China
[2]School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China
[3]School of Mechanical and Power Engineering, Dalian Ocean University, Dalian 116023, China

Abstract

A silicon carbide (SiC) coating was prepared on the surface of carbon fibers by means of chemical vapor reaction (CVR) at different temperature. The phase, microstructure and oxidation behavior of the SiC coating prepared from 1 723 to 1 923 K were investigated. The SiC coating becomes thicker and the SiC grains grow with the increase in reaction temperature. The oxidation resistance of carbon fibers can be improved significantly by the SiC coating, and the oxidation resistance of the carbon fibers increases as the reaction temperature increases. The initial oxidation temperature of the SiC-coated carbon fibers prepared at 1 923 K is about 90 K higher than that of the uncoated carbon fibers. The apparent activation energy for the synthesis of the SiC coating by means of CVR is calculated based on the thickness of the SiC coating, which is about 118.06 KJ/mol.

Keywords: Carbon fibers, SiC, coating, oxidation behavior

I. Introduction

Advanced resin-based and carbon-based composites have been widely applied in numerous areas, due to their high specific strength, modulus, good chemical stability and low thermal expansion coefficient. Carbon fibers are the crucial reinforcement in these composites [1, 2]. However, their sensitivity to oxidation at high temperature restricts the application of carbon fibers in the above-mentioned composite materials. To prevent the oxidation of carbon fibers, a SiC coating has been prepared on the carbon fibers and the effectiveness of the oxidation resistance of the SiC coating has been investigated [3-5].

Up to now, many methods have been used to coat SiC on the surface of carbon fibers, such as precursor infiltration and pyrolysis (PIP) [6], carbothermal reduction [7] as well as chemical vapor deposition (CVD) [8,9]. However, these processes are complicated and costly, limiting their application in practical production. In recent years, in order to further reduce the preparation cost for SiC coatings, chemical vapor reaction (CVR) [10] has been developed as a novel method. Chemical vapor reaction method is a simple, feasible and low-cost method for preparing SiC coatings, which is based on the direct reaction of matrix carbon and silicon vapor to synthesize SiC.

In this paper, a silicon carbide coating was prepared on the surface of carbon fibers in the CVR process. The influence of the reaction temperature on the morphology and microstructure of carbon fibers with SiC coating was discussed. In addition, the oxidation behavior and the reaction kinetics for the synthesis of the SiC coating were also investigated and analyzed.

II. Experimental

(1) The preparation process of SiC coating

The carbon fibers used as substrates were commercial fibers (PAN carbon fibers, T300, Toray Company, Japan). The assembly for the CVR method is shown in Fig. 1. A graphite crucible was used as a container for Si evaporation. The Si sheet (industrial reagent, > 99.9 %) was put on the bottom of the graphite crucible, and the carbon fiber was placed above the Si sheet. The Si vapor was generated when the temperature exceeded 1 687 K. After that, the Si vapor reacts with the carbon on the fibers' surface to synthesize the SiC coating. The experiments were conducted under vacuum conditions and the holding time for the experiments was 20 min, followed by natural cooling to room temperature.

(2) Characterization of the carbon fibers

The phases of the samples were analyzed by means of X-ray diffraction (XRD) performed on a Bruker D8 Focus with CuKα monochromatic radiation (λ =0.15406 nm). The surface composition of carbon fibers was analyzed with an X-ray photoelectron diffraction spectrometer

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*   Corresponding author: lijiayan@dlut.edu.cn

(XPS, ESCALAB™ 250Xi). The morphology of the SiC-coated carbon fibers was characterized by means of field emission scanning electron microscopy (ZEISS SUPRA 55). The oxidation behavior of carbon fibers with or without SiC coating was studied with thermogravimetric analysis (DSC822/TGA, SDTA851, America). About 8 mg of carbon fibers were heated to 1 373 K in alumina crucibles. The oxidation agent was air and the heating rate of the temperature was about 10 K/min.
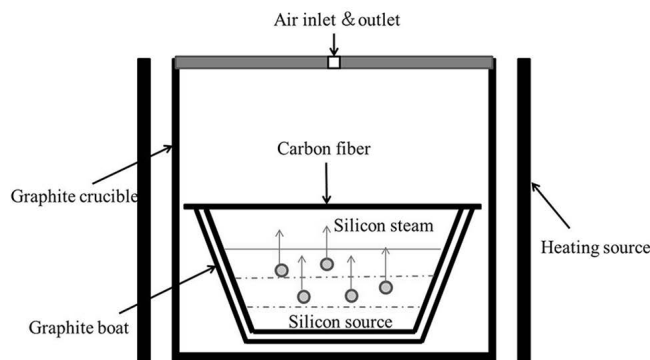

Fig. 1: Schematic diagram of the CVR process.

III. Results and Discussion

(1) Phase analysis by XRD

As shown in the XRD pattern (Fig. 2), the phase composites of fibers treated at different reaction temperature (1 723 K, 1 823 K and 923 K) were observed. The major peaks at approximately 26.4 and 43.0 and 53.6 deg correspond to the peaks of carbon [11]. Compared to the uncoated carbon fibers, the additional weak diffraction peaks appearing at 35.8, 41.3, 60.0, and 72.0 deg are attributed to cubic SiC phase (β-SiC) [12], which agrees with the standard JCPDS Card for β-SiC (No. 0029 – 1129). With increasing reaction temperature, the intensity of the β-SiC peaks increases, as shown in the inset for a magnified peak of β-SiC at 35.8 deg, and the peak intensity of the carbon phase decreases, which indicates that the Si vapor reacts directly with carbon from the carbon fibers and the SiC coating can be prepared on the fiber surface at a high temperature during the process of chemical vapor reaction.
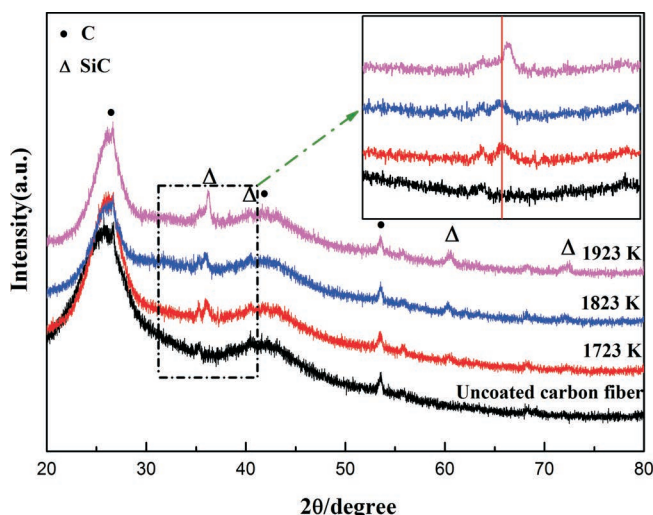

Fig. 2: XRD pattern of the carbon fibers.

(2) XPS characterization

As shown in Fig. 3, the chemical changes on the surface of carbon fibers were also analyzed in X-ray photoelectron spectroscopy spectra (XPS) with the binding energy ranging from 0 to 1 000 eV. For the uncoated carbon fibers, only two peaks for C1s (283.54 eV) and O1s (531.8 eV) are detected, which can be attributed to the oxidation of carbon fibers. After the CVR reaction, as shown in Fig. 3(b), two new peaks appear at 153.0 eV and 101.5 eV in the XPS spectra, correspond to the Si2s and Si2p, respectively. Furthermore, the increasing intensity of O1s peak indicates that the oxygen content is larger on the surface of the SiC-coated carbon fibers than that of the carbon fibers. During the preparation process for the SiC coating, an amorphous SiO_2 film is easily produced on the SiC coating surface, which can prevent carbon fibers from further oxidation in air. Fig. 3(c) and Fig. 3(d) show narrow scan spectra of the C1s and Si2p region of the SiC-coated carbon fibers. Particularly, the C1s spectrum on the surface of the carbon fibers can be divided into four components. The major components at 283.54 eV and 284.94 eV have been corresponded to carbon atoms in the C-Si bond and C-C bond [13–16], indicating the SiC phase was coated on carbon fibers surface by CVR reaction. This result is consistent with the Si2p core-level spectrum. The other two peaks at 286.12 eV and at 288.91 eV indicated the existence of a C-O bond and the functional groups -COOH. Moreover, the Si2p peaks can be divided into two peaks in the XPS spectrum, as shown in Fig. 3(d). The main peak at 101.46 eV is attributed to the silicon atoms in the Si-C bond, the other higher binding energy peak at 103.69 eV has been corresponded to silicon atoms in Si-O bond [13, 14, 17, 18], which confirms the formation of SiO_2 film on the SiC surface during the CVR process.

(3) Morphology of the carbon fibers

The surface SEM images of the carbon fibers are shown in Fig. 4. Fig. 4 (a) shows the surface of the uncoated carbon fibers, and it can be observed that the uncoated carbon fibers are clean with many strips or grooves on the surface and it conforms to the characteristics of PAN-based carbon fibers [19]. Fig 4 (b), (c), and (d) present the surface morphologies of the carbon fibers treated under the temperature of 1 723 K, 1 823 K, and 1 923 K, respectively. A uniform coating is obtained on carbon fibers with CVR treatment. Base on the combination of SEM analysis with XRD and XPS analysis, it can be concluded that the coating material is β-SiC. The SiC coating becomes coarse and some large SiC grains from 360 nm to 580 nm in size can be found on the fibers' surface, corresponding to the temperature from 1 723 K to 1 923 K respectively. Meanwhile, the coating surface is not continuous, and pores can be obtained on the SiC coating when the reaction temperature is above 1 823 K, which should be attributed to the growth of SiC crystalline. The diameters of the pores measure about 200 to 700 nm.
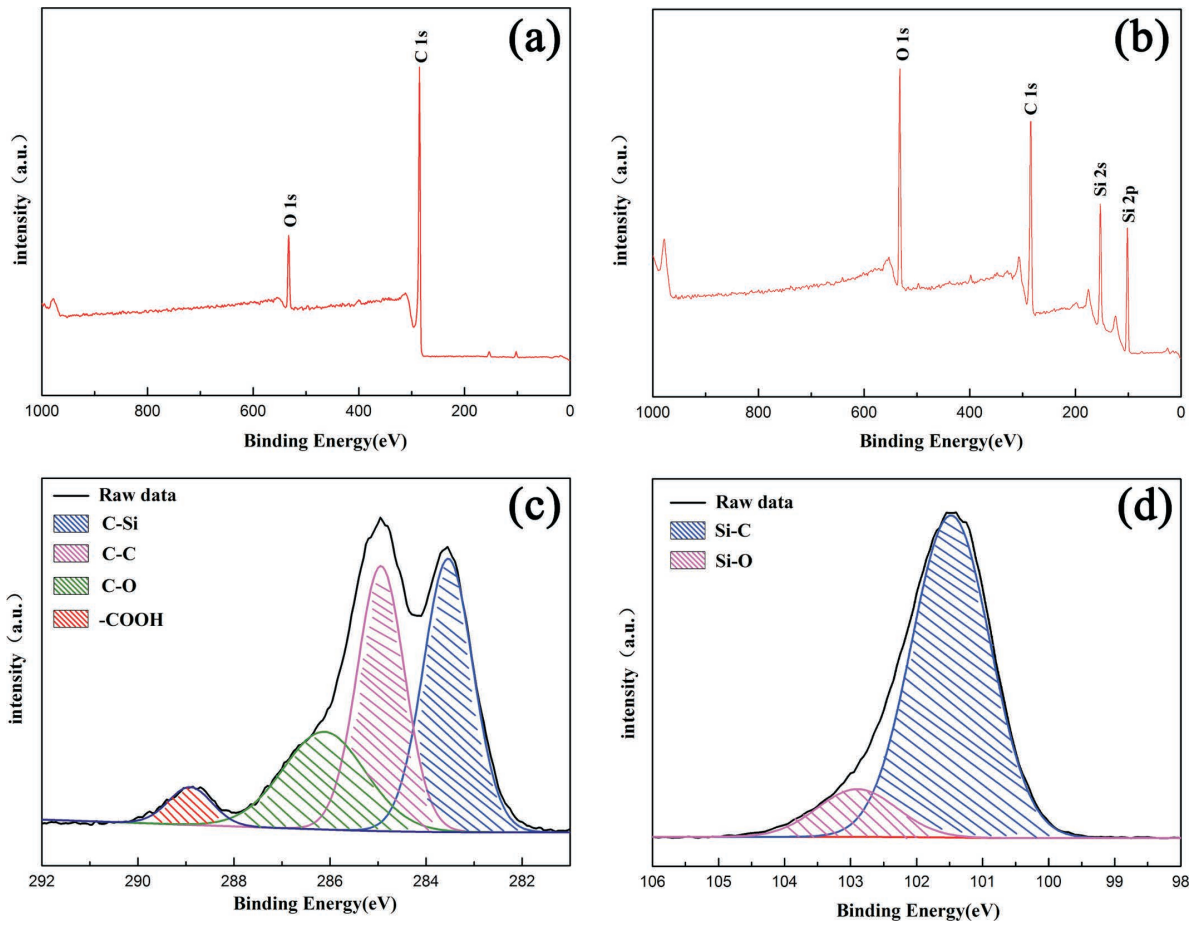
Fig. 3: XPS spectrum of the carbon fibers. (a) Survey XPS spectrum of uncoated carbon fiber; (b) Survey XPS spectrum of SiC carbon fiber prepared at 1 723 K; (c) C1s spectra of SiC carbon fiber prepared at 1 723 K; (d) Si2p spectra of SiC carbon fiber prepared at 1 723 K.
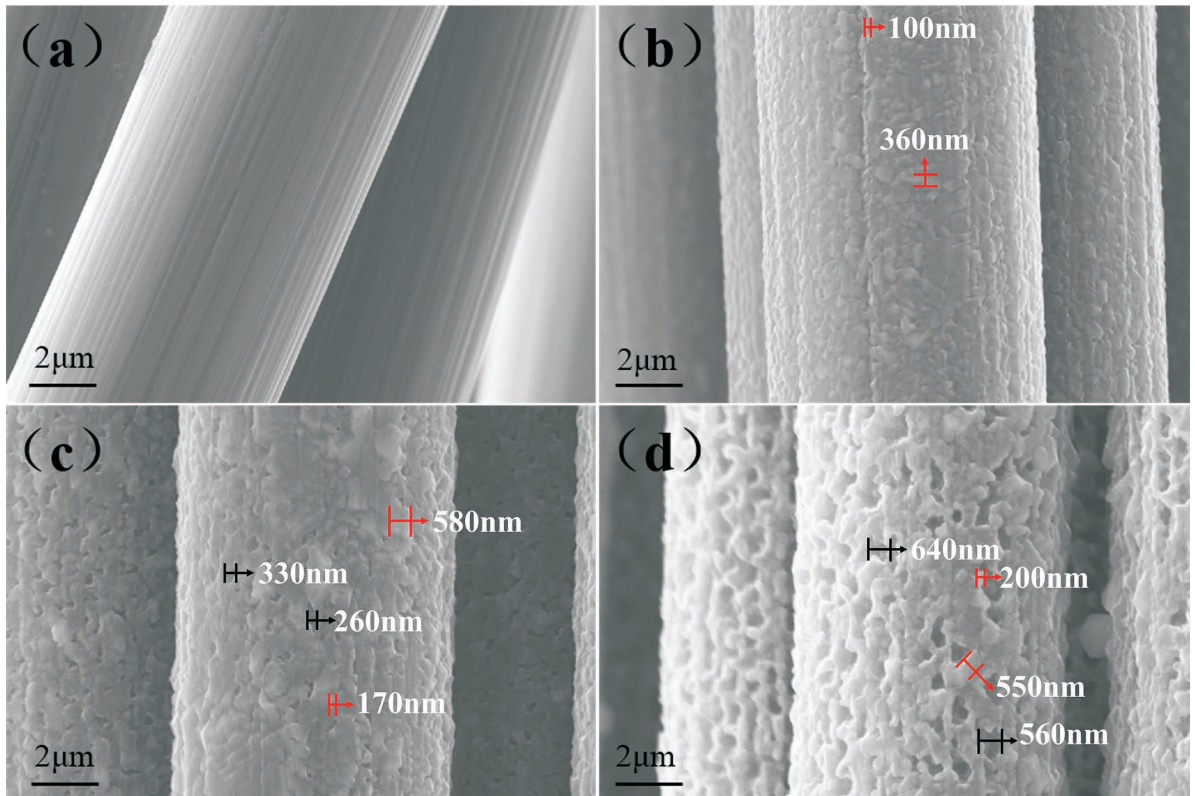

Fig. 4: The surface SEM images of carbon fibers prepared at different temperature. (a) uncoated carbon fibers; (b) 1 723 K; (c) 1 823 K; (d) 1 923 K.
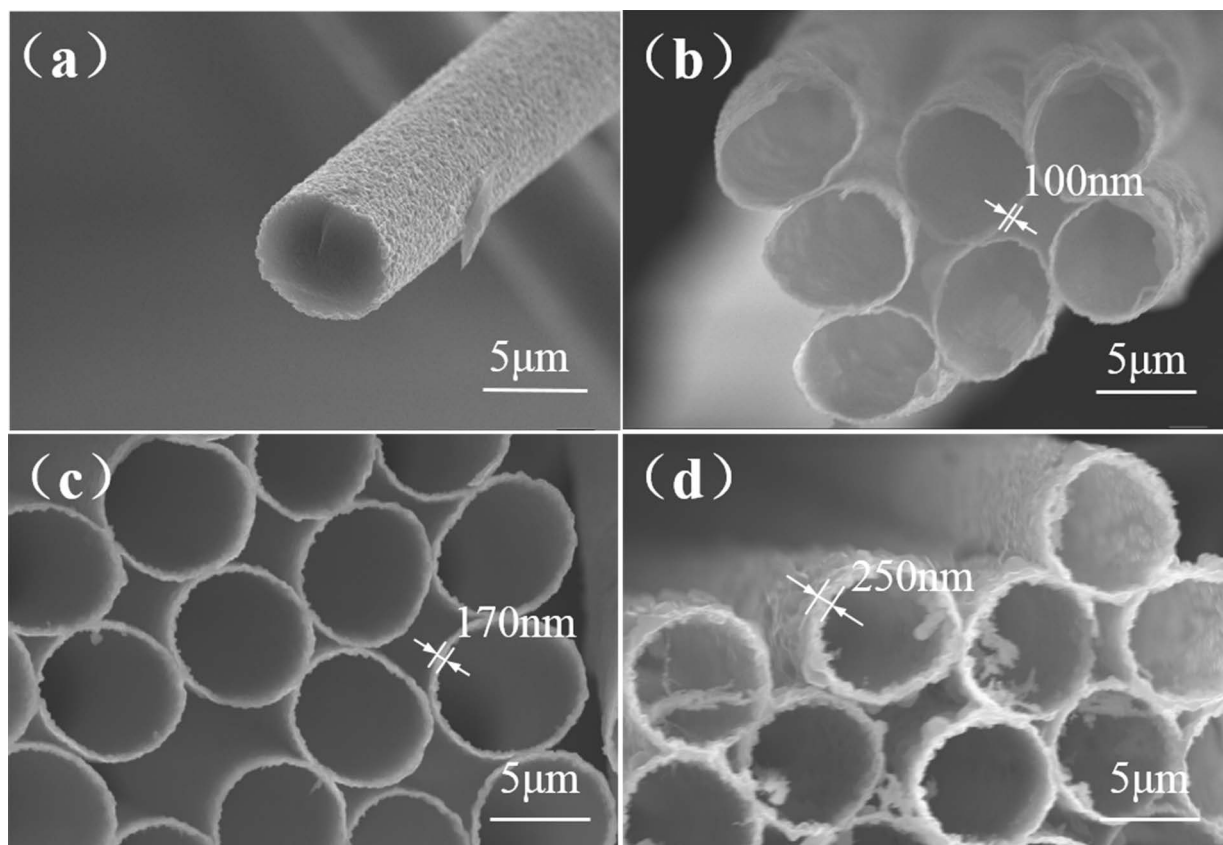
Fig. 5: The cross-section SEM images of carbon fibers prepared at (a) 1 823 K; and (b) 1 723 K; (c) 1 823 K; (d) 1 923 K after oxidization at 1 173 K for 2 h.

Fig. 5(a) presents the cross-section of the carbon fibers treated at 1 823 K. Furthermore, no obvious interfaces are found between the carbon fibers and the SiC coating, which indicates the good compatibility and adherence between the matrix and coating. Fig. 5 (b), (c) and (d) show the cross-section of the carbon fibers treated at 1 723 K, 1 823 K and 1 923 K after the oxidation process at 1 173 K for 2 h. It is observed that the carbon fibers had been consumed, leaving only the outer coating. The coating that was prepared is continuous and the thickness is uniform. It is also found that the thickness of the coating and the sizes of the SiC grains increase as the reaction temperature rises. The thickness of the SiC coating is approximately 100 nm at 1 723 K, 170 nm at 1 823 K and 250 nm at 1 923 K.

(4) The improvement of oxidation behavior

The oxidation behavior of carbon fibers was measured with a thermogravimetric (TG) analyzer with a heating rate of 10 K/min under flowing air and the oxidation behavior was analyzed as shown in Fig. 6. As generally known, the improvement of the initial oxidation temperature is a significant factor for expanding the application fields of carbon fibers. The initial oxidation temperature of carbon fiber increased from 850 K to 880 K, 910 K and 940 K respectively, correspond to the different reaction temperature at 1723 K, 1823 K and 1923 K. Compared to the uncoated carbon fibers, the initial oxidation temperature of the SiC-coated carbon fiber prepared at 1 723 K, 1 823 K and 1 923 K are increased by 30 K, 60 K and 90 K respectively, showing that the oxidation resistance can be improved with the SiC coating. The weight loss of the carbon fibers is about 100 % above 1 100 K, indicating

that all the carbon has oxidized to volatiles (CO_x) and is removed below 1 100 K. The mass loss rate of the carbon fibers coated with SiC decreases with the increasing reaction temperature, which should be attributed to the SiC residue after oxidation treatment. Furthermore, the oxidation rate should be represented by the slope of the TG curve between the initial oxidation temperature and the final oxidation temperature, and the value of the oxidation rate is also shown in Fig. 6. From the value of the curve slope, although the oxidation resistance of the SiC-coated carbon fiber prepared at 1 723 K and 1 823 K is improved owing to the increase of the initial oxidation temperature, the increasing oxidation rate between initial oxidation temperature and final oxidation temperature results in the reduction of oxidation resistance. Carbon fibers are used as a carbon source to react with Si and obtain SiC coating during CVR process, therefore, the surface structures of carbon fibers are damaged. It is known that the oxidation behavior of carbon fibers includes two segments, the diffusion of oxygen through the SiC layer [3] and the reaction between carbon and oxygen. When the diffusion rate is greater than the reaction rate, the oxidation rate is decided by the reaction rate. Therefore, the oxygen diffusion is very fast when the thin SiC coating is obtained at 1 723 K and 1 823 K and the oxidation reaction happens easily because of the damaged structure. So the oxidation rate is higher than that of the uncoated carbon fibers. When the reaction temperature is 1 923K, the SiC coating is about 250 nm, making the diffusion of oxygen difficult, so that the oxidation rate decreases to $3.7 \cdot 10^{-3}$/K.
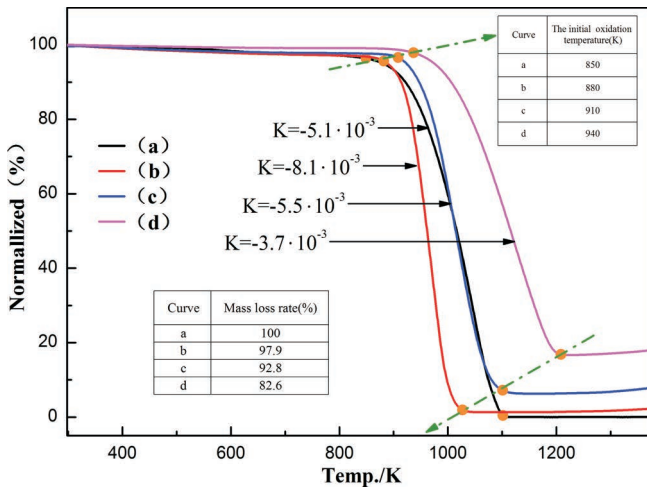
Fig. 6: Thermogravimetric curves of the oxidation with treatment at different reaction temperatures (a) uncoated carbon fibers; (b) 1 723 K; (c) 1 823 K; (d) 1 923 K.

(5) Apparent activation energy for the formation of the SiC coating

As generally known, the apparent activation energy for the formation of the SiC coating can be deduced from the deposition rate based on the law of Arrhenius [20]. The deposition rate can be calculated from the average thickness of SiC coating, which can be calculated from the change of mass after the oxidation process. Therefore, a geometrical model of the SiC-coated carbon fiber is built for calculating the average thickness of the SiC coating as shown in Fig. 7, where d is the diameter of the carbon fiber (7 μm), d' is the residual diameter of the carbon fiber after CVR treatment, D is the diameter of the SiC-coated carbon fiber, t is the thickness of the SiC coating.
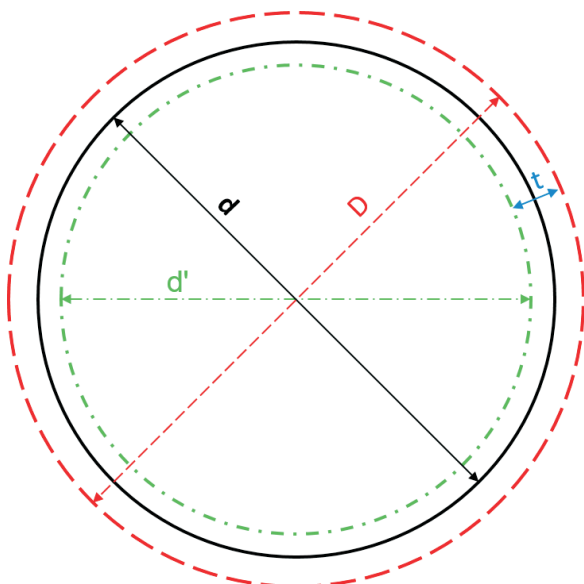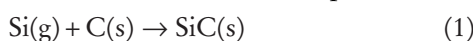

Fig. 7: Geometrical model of the SiC-coated carbon fiber.

In the process of calculation, it is assumed that the carbon fibers have a uniform diameter and their total length is L. Reaction (1) is considered in the chemical vapor reaction.

$$Si(g) + C(s) \rightarrow SiC(s) \tag{1}$$

According to Reaction (1), for preparation of 1 mol SiC, 1 mol Si and 1 mol C are consumed. The change of the vol-

ume and mass during the reaction process can be described as Eq. (2) and Eq. (3).

$$V_{SiC} = \frac{\frac{M_{SiC}}{\rho_{SiC}}}{\frac{M_C}{pC}} V_C \tag{2}$$

$$m_{SiC} = \frac{M_{SiC}}{M_C} m_c \tag{3}$$

where V_{SiC} and m_{SiC} are the volume and mass of the SiC generated, V_C and m_c are the volume and mass of the carbon fiber consumed, M_{SiC} and M_C are the molecular weight of SiC and carbon, ϱ_{SiC} and ϱ_C are the density of SiC(3.22 g/cm^3) and carbon fiber (1.76 g/cm^3). m_{SiC} is the residual mass after the oxidation reaction at 1 173 K for 2 h. Then, after chemical vapor reaction treatment, the volume of the residual carbon fiber can be described as follows:

$$V_{RC} = \frac{m - m_{SiC}}{\rho_C} = \frac{\pi d'^2 L}{4} \tag{4}$$

where V_{RC} is the volume of the residual carbon fiber after chemical vapor reaction treatment, m is the total mass of the SiC coating and the residual carbon fiber after chemical vapor reaction treatment. Then we can use Eq. (4) to derive the relationship between d and d'. The volume of the carbon fiber consumed and the volume of the SiC generated can be described as Eq. (5) and Eq. (6) with L.

$$V_C = \frac{\pi d^2 L - \pi d'^2 L}{4} \tag{5}$$

$$V_{SiC} = \frac{\pi D^2 L - \pi d'^2 L}{4} (D = d' + 2t) \tag{6}$$

Table 1: Deposition rate of SiC coating at different reaction temperature

Treatment temperature(/K)	The thickness of the SiC coating(/nm)	Deposition rate of the SiC coating(nm/s)
1 723	97	0.081
1 823	172	0.144
1 923	226	0.189

According to Eq. (2), (5), and (6), we can calculate the average thickness of the SiC coating (t), as shown in Table 1. The calculated results agree with the measured thickness in Fig. 5(a), (b) and (c). The relationship of deposition rate with reaction temperature may comply with the law of Arrhenius, as shown in Eq. (7).

$$k = A\exp(-E_\alpha/RT) \tag{7}$$

where k is the deposition rate of the SiC coating, A is a constant, E_α is the apparent activation energy, R is the gas constant, and T is the deposition temperature. Fig. 8 shows the Arrhenius plot of the relationship of logarithm of deposition rate versus reciprocal temperature. The activation energy can be determined based on the slope. In this case, it is found to be about 118.06 KJ/mol.
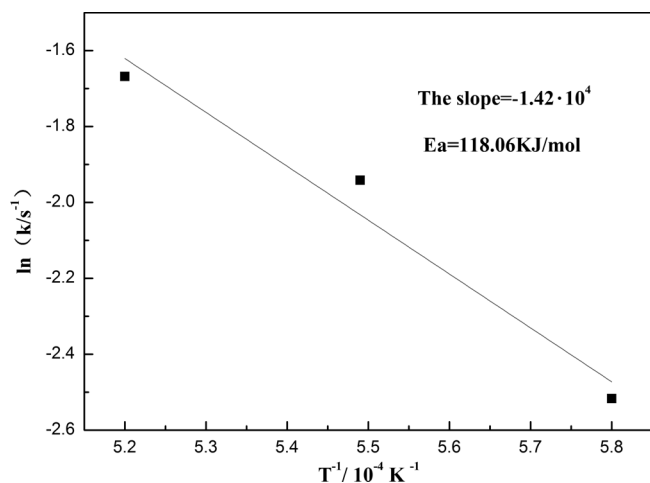
The slope=-1.42·10⁴

Ea=118.06KJ/mol

Fig. 8: Arrhenius plots of the formation of the SiC coating.

IV. Conclusions

A SiC coating is synthesized on the surface of carbon fibers by means of CVR. The thickness of the SiC coating increases and the SiC grains are coarsened with the elevation of the reaction temperature. The apparent activation energy for the synthesis of the SiC coating is about 118.06 KJ/mol.

The oxidation resistance of carbon fibers can be significantly improved by the SiC coating. The initial oxidation temperature of the SiC-coated carbon fibers prepared at 1 923 K is about 90 K higher than that of the uncoated carbon fibers.

Acknowledgements

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