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ARTICLE

Effect of Reaction Pressure on Synthesis and Microstructure of SiC Coating on Carbon Fiber

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Abstract: The SiC coating on carbon fiber was synthesized via an in-situ reaction method using silicon powder as silicon source, and the effect of reaction pressure on the synthesis, microstructure, and oxidation resistance of SiC coating was investigated. The results show that SiC coating synthesized at the atmospheric pressure is loose and porous; numerous SiC nanowires are formed on it. In comparison, the SiC coating synthesized at the low pressure is uniform and dense. The isothermal oxidation test shows that the SiC coating synthesized at the low pressure has better oxidation resistance than the one synthesized at the atmospheric pressure, because the dense and uniform SiC coating can prevent oxygen from contacting with carbon fiber more effectively. Based on the experiment results, the growth mechanism of SiC coating influenced by the reaction pressure was proposed. At the atmospheric pressure, the kinetic energies of deposition particles are too low to overcome the shadowing effect, causing the formation of porous SiC coating. By contrast, the deposition particles have higher kinetic energies and surface diffusion rate on the surface of carbon fiber at the low pressure, thereby forming a uniform and dense SiC coating.

Key words: reaction pressure; carbon fiber; in-situ reaction; SiC coating; oxidation resistance

Silicon carbide (SiC) has a wide range of applications due to its excellent properties, such as good mechanical properties, good corrosion resistance, and high-temperature thermal stability. Particularly, SiC is suited for coating on carbon materials owing to the good chemical compatibility and similar thermal expansion coefficients between SiC and carbon[1,2]. The common methods to synthesize SiC coating on carbon materials include chemical vapor deposition (CVD)[3,4], pyrolysis of precursor[5], and in-situ reaction method[6]. CVD can fabricate a uniform and dense coating on carbon substrate. However, environmental-unfriendly precursors and special equipment restrict its application. The pyrolysis of precursor needs expensive precursors, such as polycarbosilane, and requires several times of immersion and pyrolysis.

The in-situ reaction method has been adopted to synthesize SiC coating on carbon materials by many researchers. Kang et al[7] prepared SiC coating on carbon fiber using silicon powder and graphite powder as raw materials. Dong et al[8] produced silicon vapor via the mixture of Si and Cu powders at 1200~1300 °C, and fabricated SiC coating by the reaction between silicon vapor and carbon fiber. Generally, SiC with different morphologies have different properties, and should be applied to different fields. For instance, SiC nanowire is commonly used in the photoluminescence and field emission due to its large surface area and the quantum confinement effect[9,10]. A dense and uniform SiC coating has low oxygen permeability, which can act as a thermal barrier at high temperature[11,12]. Therefore, it is believed that the preparation of the SiC coating with a desired morphology by adjusting the experiment parameters can broaden the application of SiC greatly.

According to the previous reports, the SiC nanowires are likely formed under an argon atmosphere[13,14], and a dense and uniform SiC coating preferentially grow at a low pressure[8,15]. It is assumed that the reaction pressure may have great influence on the growth behavior of SiC coating on carbon materials, thereby affecting its microstructure and properties. However, the effect of reaction pressure on the formation of SiC coating is rarely investigated. In this research, SiC coating was synthesized on carbon fiber by the in-situ reaction method, and the effect of reaction pressure on the growth

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behavior, microstructures, and oxidation resistance of SiC coating was investigated.

1 Experiment

Commercial M40J PAN-based carbon fiber (Toray Industries) and commercial silicon powder (Tianjin Kermel Chemical Reagent Co., Ltd) were used as the raw materials. Firstly, the silicon powder (5.0 g) was added into a graphite crucible, and then the carbon fiber was fixed on the top of the silicon powder. Secondly, the graphite crucible was placed into an electric resistance furnace. Thirdly, the furnace was heated to 1300~1500 °C at the atmospheric pressure (the furnace was filled with argon with flow rate of 1 L/min) or at the low pressure (the vapor pressure of the furnace was about 100 Pa) for 5 h. Finally, the furnace was cooled down. The experimental setup is illustrated in Fig. 1. The specimens obtained under the atmospheric pressure and the low pressure were named as APs and LPs, respectively.

The crystalline phase measurements were conducted using X-ray diffraction (XRD, Rigaku Dmax/2550 18KW) with Cu Kα source with a wavelength λ of 0.1542 nm. The morphologies of the products were observed using scanning electron microscopy (SEM, FEI Quanta 250 FEG). The isothermal oxidation test was conducted in an electric-resistance furnace. The mass change of the products was investigated by an electronic balance.

2 Results and Discussion

2.1 Morphologies and microstructures of SiC-coated carbon fiber synthesized at atmospheric pressure

Fig. 2 shows XRD patterns of AP specimens. A strong diffraction peak at around 2θ=26° is associated with the (002) plane of graphite (JCPDS No.75-1621), which is derived from the carbon fiber. Besides, three diffraction peaks at around 2θ= 36°, 60°, and 72° are related to the (111), (220), and (311) planes of the 3C-SiC (JCPDS No. 29-1129), respectively. Other crystalline phase such as silicon cannot be detected, suggesting that no unreacted silicon remains on the surface of carbon fiber. At 1300 °C, the diffraction peak of SiC can barely be observed, suggesting that the reaction temperature is too low to produce a large amount of SiC. As the reaction temperature increases, the relative intensity of diffraction peak of SiC is increased, which is ascribed to the intensive chemical reactions between silicon and carbon at higher temperature.

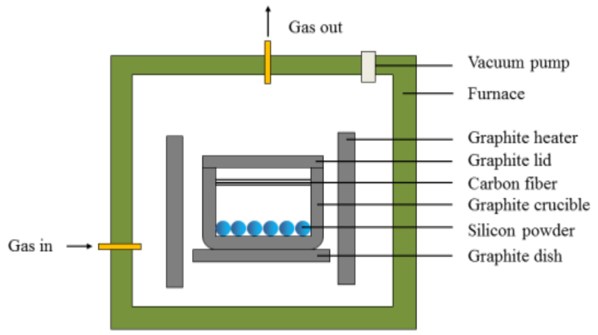

Fig.1 Schematic diagram of preparation equipment of SiC-coated carbon fiber

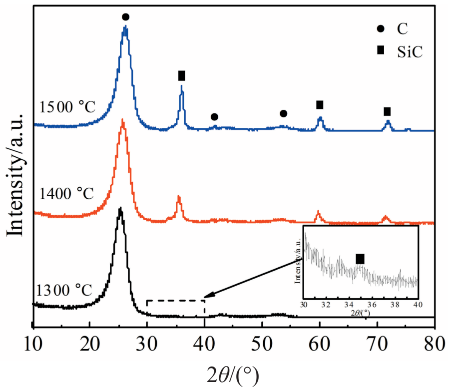

Fig.2 XRD patterns of APs at different temperatures

Fig. 3 shows SEM images of APs at different temperatures. When the reaction temperature is 1300 °C, a large number of randomly distributed SiC nanoparticles and discontinuous SiC coatings are formed on the surface of carbon fiber (Fig.3a and 3b). This is because the evaporation rate and diffusion rate of silicon vapor are low, causing that the heterogeneous nucleation of SiC can only occur at some active sites on the carbon fiber. In addition, numerous SiC nanowires grow from the surface of SiC coating. Since no catalyst is used in the experiments, the formation of the SiC nanowires can be explained by the vapor-solid (VS) growth mechanism, which has been extensively investigated by many researchers[16,17]. When the temperature increases to 1400 °C, the SiC coating can entirely cover the carbon fiber with the thickness of about 800 nm. However, the coating is loose and porous, separated by many gaps (Fig. 3c and 3d). This structure is similar to the Zone I structure in the structure zone model (SZM). The growth of this structure is believed to result from the low surface diffusion rate and the shadowing effect[18,19]. At 1500 °C, the SiC nanoparticles in the coating become faceted (Fig. 3e and 3f), which is driven by the anisotropic surface energies of involved facets at high temperature. These results reveal that the reaction temperature has a great influence on the morphologies and microstructures of SiC coating at atmospheric pressure.

2.2 Morphologies and microstructures of SiC-coated carbon fiber synthesized at low pressure

Fig. 4 shows the XRD patterns of LPs at different temperatures. Compared with those of APs, the diffraction peaks of 3C-SiC in the spectra of LPs are much sharper, presumably because the silicon is more likely to diffuse to the surface of carbon fiber when the reaction pressure is close to the saturated vapor pressure of silicon at the synthesis temperature. When the temperature is 1500 °C, the diffraction peak of graphite disappears, suggesting that the carbon fiber is completely converted into SiC.

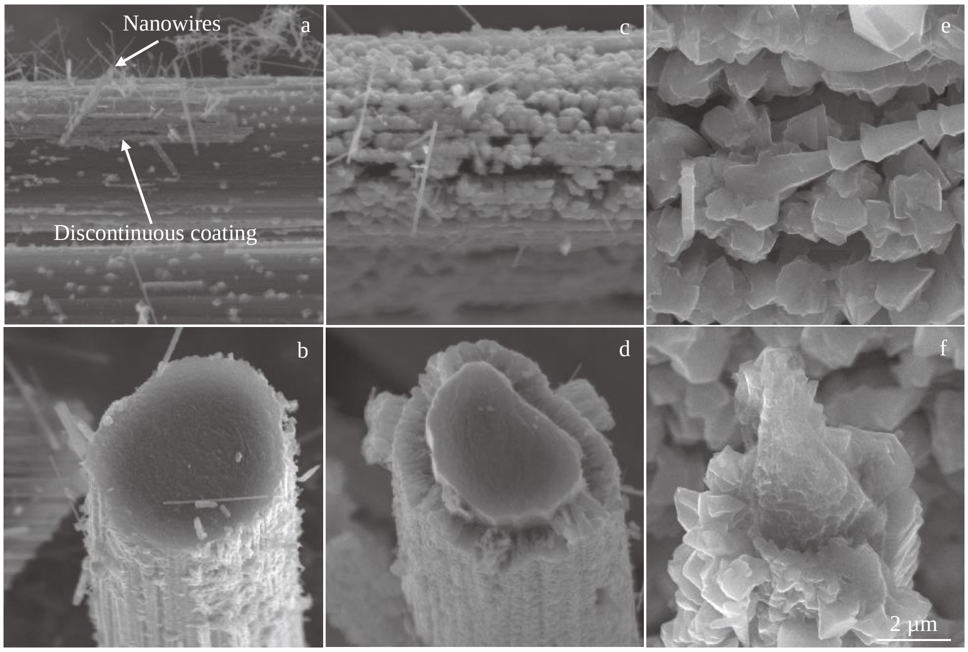

Fig.3 SEM images of APs at 1300 °C (a, b), 1400 °C (c, d), and 1500 °C (e, f)

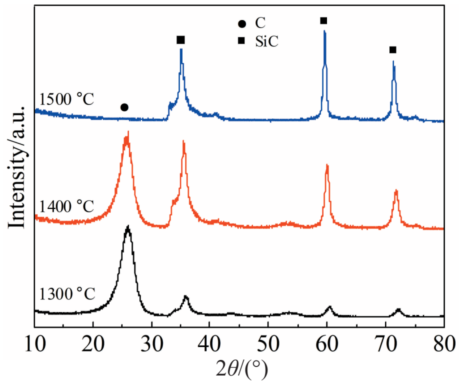

Fig.4 XRD patterns of LPs at different temperatures

Fig. 5 shows SEM images of LPs synthesized at different temperatures. A dense and uniform SiC coating without obvious cracks of defects is formed on the surface of carbon fiber at 1300 °C (Fig.5a and 5b). This coating structure can be represented as the Zone T structure in SZM. The formation mechanism can be explained as follows. As the surface diffusion rate of atoms is very high at low pressure, the SiC nuclei can effectively agglomerate together and form a uniform coating structure on the surface of carbon fiber. However, the reaction temperature is too low to allow the grain boundary migration, resulting in the small voids in the coating, as shown in the inset in Fig 5a. When the temperature reaches 1400 °C, the SiC nanoparticles in the coating become faceted (Fig. 5c and 5d). Furthermore, the small voids disappear. This structure is similar to the Zone II structure in SZM. Since the melting point of SiC (2700 °C) is much higher than the reaction temperature in the experiments, it is inferred that the coalescence of the SiC nanoparticles is promoted by the grain boundary migration during the grain growth. At 1500 °C, the SiC nanoparticles become larger, and the interfacial boundary between the carbon fiber substrate and the SiC coating vanishes (Fig.5e and 5f). Combined with the XRD results in Fig.4, it is concluded that the carbon fiber is completely converted into 3C-SiC. The results suggest that the SiC coating formed at low pressure is denser and more uniform than the one formed at atmospheric pressure.

2.3 Oxidation resistance of uncoated and SiC-coated carbon fiber

Fig.6 shows the mass loss curves of the uncoated and SiC-coated carbon fiber oxidized at 700 °C for 60 min in static air. After oxidation for 60 min, the mass loss ratio of uncoated carbon fiber is 65% of the original mass, while that of APs obtained at 1300, 1400, and 1500 °C is 45%, 18%, and 11% of the original mass, respectively, suggesting that the SiC coating can effectively prevent the carbon fiber from oxidation. In comparison, LPs obtained at 1300~1500 °C show even better oxidation resistance, and their mass loss ratio is 18%, 7%, and 2% at 1300, 1400, and 1500 °C, respectively.

To investigate the oxidation mechanism of SiC-coated carbon fiber, the morphologies of the carbon fiber after oxidation at 700 °C for 60 min were observed by SEM, as shown in Fig.7. It is observed that the uncoated carbon fiber become loose and porous after oxidation. This is because without any protection, the oxygen can directly reach the surface of carbon fiber and react with it to form CO and CO_2. APs obtained at 1400 °C are not severely damaged after oxidation, suggesting that the SiC coating can act as oxygen diffusion barriers during oxidation. However, the oxygen can

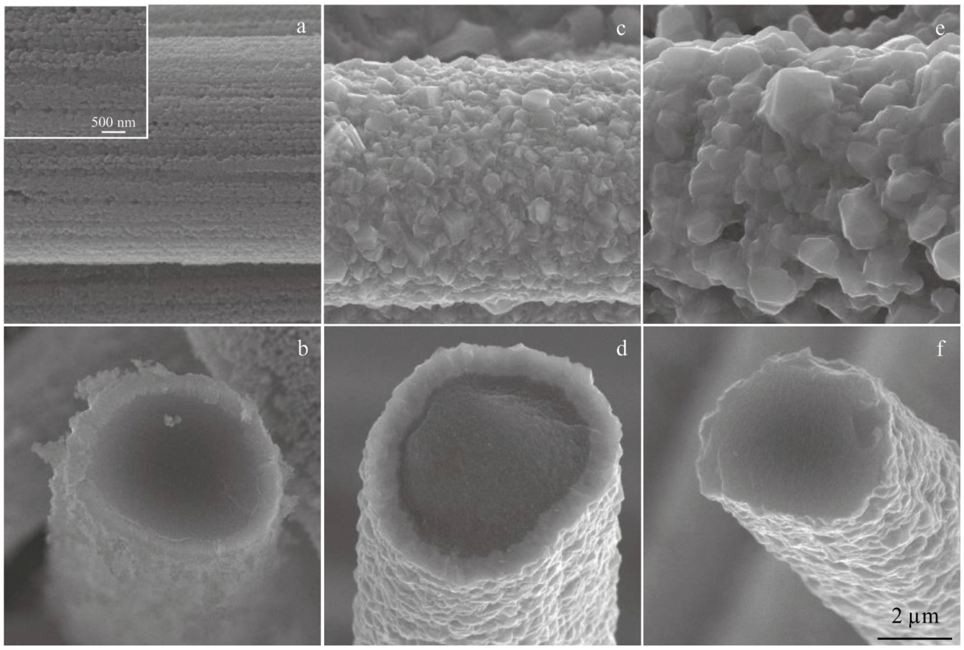

Fig.5 SEM images of LPs at 1300 °C (a, b), 1400 °C (c, d), and 1500 °C (e, f)

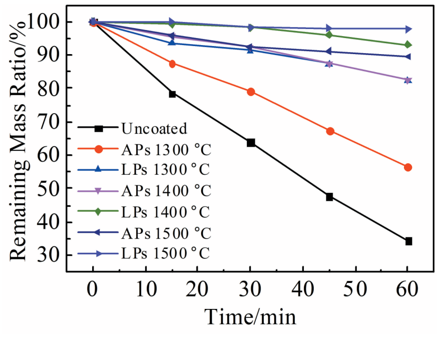

Fig.6 Mass loss curves of uncoated and SiC-coated carbon fiber after oxidation at 700 °C for 60 min

still diffuse to the surface of carbon fiber through the defects and voids of the SiC coating, which causes the mass loss of the carbon fiber. In comparison, LPs at 1400 °C have a dense and uniform structure, which can effectively inhibit the diffusion of oxygen from the coating surface to the inner carbon fiber. Therefore, the mass loss of LPs is much less than that of others. These results suggest that the dense and uniform SiC coating synthesized at low pressure shows better oxidation resistance than the porous SiC coating synthesized at atmospheric pressure.

2.4 Effect of reaction pressure on growth mechanism of SiC coating

Based on the experiment results, the growth mechanism of SiC coating on carbon fiber and the effect of reaction pressure on the microstructural evolution of SiC coating were established, as shown in Fig. 8. Firstly, the silicon powder is evaporated and becomes silicon vapor. Secondly, the silicon vapor reacts with carbon fiber to form SiC nuclei. Finally, the SiC nuclei grow into SiC coating.

At atmospheric pressure, the elastic collisions between the evaporated silicon and the inert argon cause the low kinetic energies of silicon atoms, and the shadowing effect is promoted when the silicon atoms arrive at the carbon fiber[20,21]. In this case, the SiC nuclei and the discontinuous SiC coating are likely to form on the surface of carbon fiber at low temperature due to the low surface diffusion rate. At elevated temperature, the SiC coating can completely cover the carbon fiber. However, the deposited atoms are insufficient to overcome the shadowing effect, thereby leaving obvious pores and gaps on the SiC coating. When the reaction pressure is reduced, the mean free path for collisions between silicon atoms and other gaseous atoms is increased[19]. This phenomenon leads to higher kinetic energies of silicon atoms impacting on the surface of carbon fiber substrate. Since the silicon atoms have high kinetic energies, the shadowing effect is reduced, thereby forming relatively dense microstructures. At higher temperature, grain boundary migration has a dominant influence on the final structure of the coating. The coalescence of SiC nuclei are promoted during the grain growth, and eventually a uniform and dense SiC coating is formed.

It is concluded that the reaction pressure has a great influence on the growth behavior of SiC coating. At atmospheric pressure, the kinetic energies of atoms are too low to overcome the shadowing effect, and thereby porous SiC coating is formed. By contrast, at low pressure, the deposited atoms have high surface diffusion rate on the surface of carbon fiber, which results in the densification of the SiC coating.

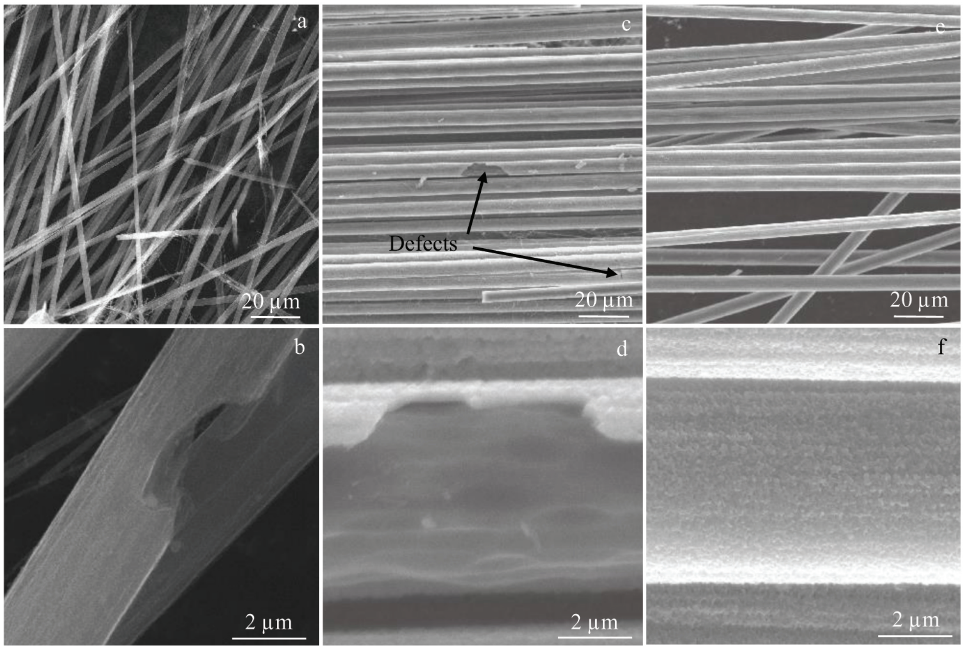

Fig.7 SEM images of carbon fiber after oxidation at 700 °C for 60 min: (a, b) uncoated carbon fiber, (c, d) APs obtained at 1400 °C, and (e, f) LPs obtained at 1400 °C

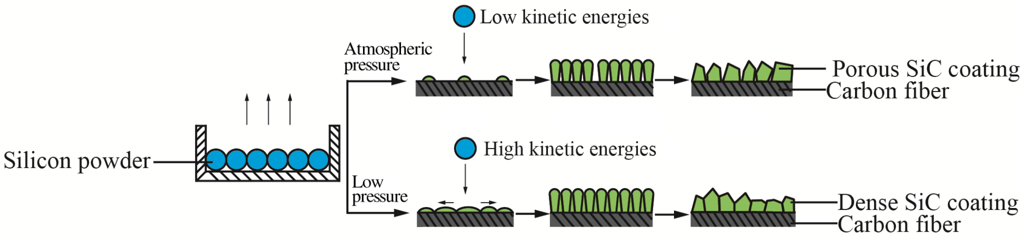

Fig.8 Growth mechanism of SiC coatings on carbon fiber at different pressures

3 Conclusions

1) The porous SiC coating with numerous SiC nanowires is formed at atmospheric pressure, while the dense and uniform SiC coating is formed at low pressure.

2) SiC-coated carbon fiber synthesized at low pressure shows better oxidation resistance than the one synthesized at atmospheric pressure does, because the dense SiC coating can effectively inhibit inward diffusion of oxygen.

3) The reaction pressure has a great influence on the growth behavior of SiC coating. The kinetic energies of atoms are too low to overcome the shadowing effect at atmospheric pressure, and thereby porous coating structure is formed. By contrast, the deposited atoms have high kinetic energies and high surface diffusion rate on the surface of carbon fiber treated at low pressure, resulting in the densification of SiC coating.

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反应压力对炭纤维表面SiC涂层制备及组织结构的影响

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摘　要：以硅粉为硅源，采用原位反应法在炭纤维表面制备了SiC涂层，并研究了反应压力对SiC涂层的制备、组织结构及抗氧化性能的影响。结果表明：常压下制备的涂层疏松多孔，表面有较多的SiC纳米线，而负压下制备的涂层致密均匀。静态氧化测试表明：与常压下制备的SiC涂层相比，负压下制备的SiC涂层抗氧化性能更好，主要是由于涂层致密均匀，能够更好地阻隔氧气的扩散。根据实验结果，探讨了反应压力对SiC涂层生长机理的影响。常压下，沉积粒子能量低，难以克服遮蔽效应，因此易形成疏松多孔的涂层；而负压下，沉积粒子能量高，表面扩散率高，易形成致密均匀的涂层。

关键词：反应压力；炭纤维；原位反应；SiC涂层；抗氧化性能

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