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A Novel Electrolytic Plasma Spraying Preparation SiO_2/SiC Coating on Carbon Fiber Fabric

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Abstract: A good quality of SiO_2/SiC coating was successfully fabricated on carbon fiber fabric by a novel electrolytic plasma spraying method, where $Na_2SiO_3 \cdot 9H_2O$ aqueous solution was used as an electrolyte. In this study, we discussed the effect of spraying distance on the coating. The microstructure and composition coating were characterized by scanning electron microscopy with energy-dispersive spectroscopy and XPS, respectively. An effective coating can be easily prepared within several tens of seconds through this approach by adjusting the spraying distance. Results show that the sample oxidation resistance temperature was up to 1000 °C while the spraying distance was 15 mm, and tensile strength increased by 73 MPa after heat treatment at 900 °C for 20 min. The study provides additional insights into the feasibility of modification of carbon fiber fabric. Meanwhile, this method can be expected to extend to the fabrication of other oxide coatings or the modification of the surfaces of other complicated and/or large-scale easily oxidized materials.

Keywords: plasma electrolysis spraying; carbon fiber fabric; SiO_2/SiC coating; oxidation resistance; tensile strength

1. Introduction

With the continuing development of the aerospace, automotive manufacturing, and building materials fields, carbon fiber has become a material of interest for its many excellent properties. First, it can reduce the whole quality of the part. Second, its strength is two times higher than that of steel and alloy. Third, it can be used in chemical and petroleum equipment because of its good wear and corrosion resistance [1,2]. Therefore, the industrial and structural properties of carbon fiber and carbon fiber fabrics lend themselves to a wide range of applications [3,4]. Unfortunately, the main drawback of carbon fiber is the poor oxidation resistance in an oxygen-containing atmosphere above 500 °C, which limits its applications in a high-temperature oxidizing environment [5–7]. Therefore, it is of great importance to create dense and crack-free oxide films to protect carbon materials from oxidation.

SiO_2/SiC ceramic coatings are widely applied because of their excellent mechanical properties at high temperature, high melting point, and relatively good oxidation resistance in an oxygen-rich atmosphere [8–10]. To date, numerous techniques such as chemical vapor deposition (CVD), electrochemical deposition, gas phase oxidation, and plasma treatment have been developed to prepare coatings [11–15]. However, most modification techniques are accompanied by simultaneous decreases in the tensile strength of carbon fiber [16]. After carefully reviewing the limitations of each technology, we have decided that the plasma electrolysis method shows the most promise.

The non-electrode plasma electrolysis method has been developed by improving the electrolytic cathode in our laboratory [17–21]. We use an auxiliary electrode as the cathode to generate the plasma arc, and the fiber-deposited ceramic nanocoating passed through the cathodic plasma arc zone. This can continuously prepare coatings on fibers. However, complicated and/or large-scale working parts cannot be applied. The thermal spray technique is widely used because of its flexible and convenient operation and it not being restricted by the shape and size of the workpiece. The process of thermal spraying coating is to heat the metal, reduce the molten or semi-molten particles to a powder using a heat source, and then spray them onto the surface of the substrate at a certain speed by the flame itself or compressed air, so that a functional coating is deposited on the surface [22]. Unfortunately, most materials have poor heat resistance so cannot deposit a coating without substrate degradation. Liu et al. [23–26] have reported on polymeric matrix degradation due to impingement of hot particles via plasma spray. The melt temperature is above 1000 °C. Based on the above two methods, our previous work developed a novel electrolytic plasma spraying on complicated and/or large-scale, low-melting point and/or easily oxidized materials.

The electrolytic plasma spraying uses an auxiliary electrode as the cathode to produce the plasma arc and plasma stream ejecting from the nozzle by hydraulic pressure. Not only can this handle complex shape parts, but it is also low-cost and easy to operate. The objectives of this work are to demonstrate the feasibility of electrolytic plasma spraying onto carbon fiber fabric and investigate the impact of the spray distance on the coating oxidation resistance. The effect of spray distance on the morphology and composition of the coating was also studied. This new method is a simple, economical, and controllable route to obtain continuous coatings. The main purpose of this paper was to study the feasibility of the novel method and device, and discuss the effect of spray distance on the coating when the spraying time was 30 s.

2. Materials and Methods

2.1. Preparation of SiO_2/SiC Coating

Figure 1a shows the apparatus of the novel electrolytic plasma spraying process. The commercialized carbon fiber fabric was used as the substrate, which is placed under the nozzle. The device uses a copper rod as the cathode and graphite as the anode. The electrolyte was 30 g/L $Na_2SiO_3 \cdot 9H_2O$ aqueous solution. First, adjust the distance between the nozzle and the substrate. Control the temperature and intensity of plasma arc reaction to the substrate surface by adjusting the spraying distance. Second, open the circulating pump switch circulating electrolyte and discharge the electrolyte from the nozzle. Finally, apply a voltage between the cathode and the anode to generate a plasma arc, and eject the plasma stream from the nozzle by hydraulic pressure. The DC power between the anode and the cathode is 120–145 V. Figure 1b shows the cathodic plasma flow during the experiment. It can be seen from the photo that the plasma arc and electrolytes are spewing out uniformly from the nozzle. The device can move along the XYZ directions in order to facilitate the processing of 3D samples.

2.2. Characterization of SiO_2/SiC Coating

The surface morphologies and composition of the SiO_2/SiC nanocoating were investigated using a scanning electron microscopy (SEM, Hitach, Tokyo, Japan) with an energy-dispersive spectroscopy (EDS) detector Hitach, Tokyo, Japan). The chemical compositions as well as the chemical binding states were characterized by X-ray photoelectron spectroscopy (XPS, Ulvac-Phi, Tokyo, Japan). Thermogravimetry (TG) and differential thermal gravimetry (DTG) were performed to characterize the thermal properties. The samples were heated from room temperature up to 1300 °C at a 10 °C/min heating rate in air. The tensile strength of the heat-treated bare carbon fiber braid and the SiO_2/SiC coating sample were measured. The sample was loaded at a speed of 2 mm/min until fracture.

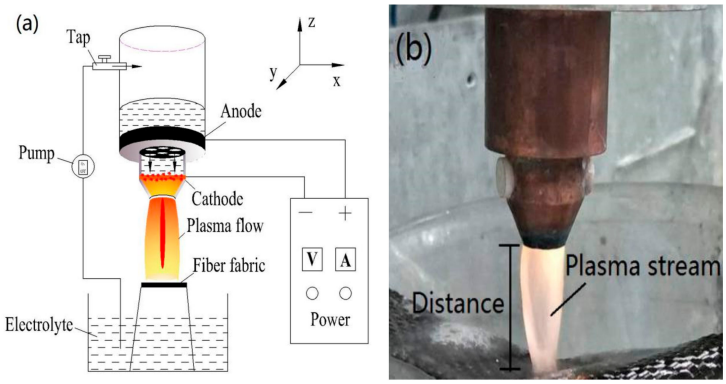

Figure 1. (**a**) Schematic diagram of the electrolytic plasma spraying; (**b**) Photo of the cathodic plasma flow taken during the experiment.

3. Results and Discussion

3.1. Microstructure Characterization

In order to visualize the changes in surface morphology of the carbon fiber fabric before and after treatment, the surface of the fibers' fabric were imaged under a scanning electron microscope (SEM). At the same time, we observed the effect of spraying distance on surface topography. Figure 2a shows a SEM image of the bare carbon fiber fabric, which displayed a relatively smooth surface and longitudinal ridges and striations along the fibers' axis. Figure 2b,c shows SEM images of SiO_2/SiC coating on carbon fiber fabric after a deposition of 30 s from spraying distances of 15 and 25 mm, respectively. It can be seen from Figure 2b that no microcracks or pores can be observed at the surface of coating, and the interfacial gaps are almost non-existent between the coating and the substrate, indicating that an intact coating has been achieved. The coating uniformly fills the carbon fiber longitudinal ridges and striations, but there is a local agglomeration phenomenon, which may be caused by small fluctuations in current during spraying. More importantly, no spallation phenomenon was found at the two interfaces of the coating and substrate, confirming excellent interfacial bonding among the carbon fiber fabric and coating. However, Figure 2c indicates the poor coating and substrate interfacial bonding strength. There was exfoliation of the coating and the carbon fiber fabric was fluffing. This is because the temperature of the plasma arc reaching the surface of the fiber fabric was not high enough to make the reaction continuous because the spraying distance is too long, and so there was damage to the carbon fiber fabric. This affects the interfacial bonding strength and overall mechanical properties of the composite. Figure 2d,e shows the EDS analysis of the coated carbon fiber fabric after a deposition of 30 s from spraying distances of 15 mm and 25 mm, respectively. The EDS analysis revealed C, O, and Si element peaks, and the Si content was 8.51 wt % and 1.82 wt %, respectively. Consistent with the above results, if the substrate is too far from the nozzle, the temperature of the plasma reaching the substrate is not sufficient for continuous physical-chemical reactions. Therefore, the silicon content is only 1.82 wt %. At the same time, the plasma arc will also damage the substrate.

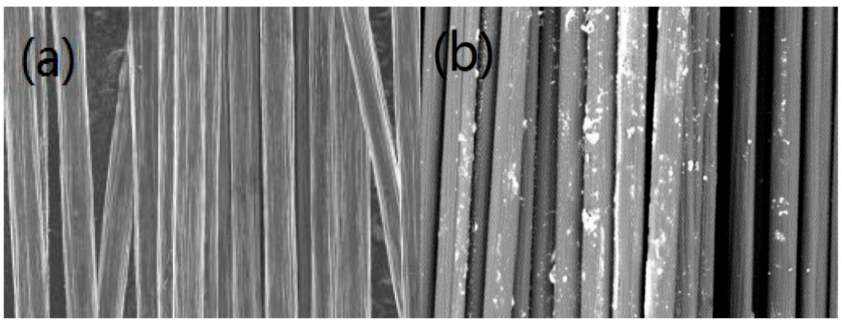

Figure 2. *Cont.*

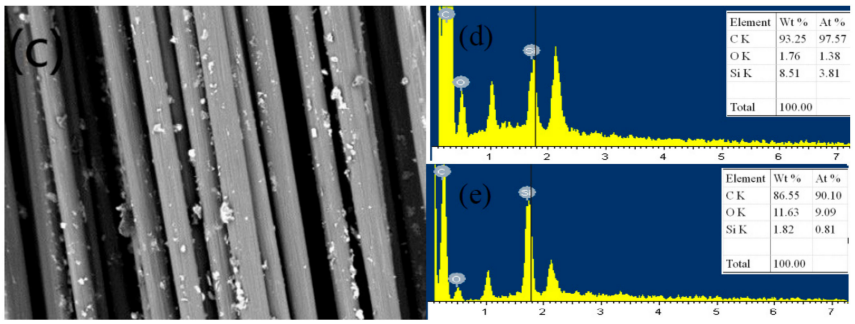

Figure 2. (**a**) SEM image of the bare, (**b**) SEM image of deposition time of 30 s and spraying distance of 15 mm and (**d**) EDS analysis, (**c**) SEM image of deposition time of 30 s and spraying distance of 25 mm and (**e**) EDS analysis.

3.2. XPS Analysis

The surface chemical composition of coating was investigated by XPS. Figure 3 shows the XPS spectra of the uncoated sample and coated sample. The elemental concentrations demonstrate clearly that C1s and O1s are the main surface constituents on both uncoated and coated sample surfaces. A negligible amount of nitrogen is found on bare surfaces, possibly deriving from the incomplete carbonization of the carbon fiber fabric precursor. The increase of O1s intensity also confirms the high content of oxygen on the surface of the treated sample. The Si2p element peaks can be observed on the coated sample, indicating that silicon is formed on the surface after plasma electrolytic spraying treatment. Figure 4a,b shows the Si2p and C1s spectra with a deposition time of 30 s and a spraying distance of 15 mm, and the deposition time of 30 s and spraying distance of 25 mm is shown in Figure 4c,d. From the C1s spectrum shown in Figure 4a,c, the peak is further curve-fitted with two components, attributed to C-C (284.5 eV) and C-O (285.8 eV), respectively. Fitting Si2p spectra shows two binding energy peaks of Si-C (101.6 eV) and Si-O (102.3 eV), indicating that SiC/SiO_2 coatings may exist on the surface of the carbon fiber fabric.

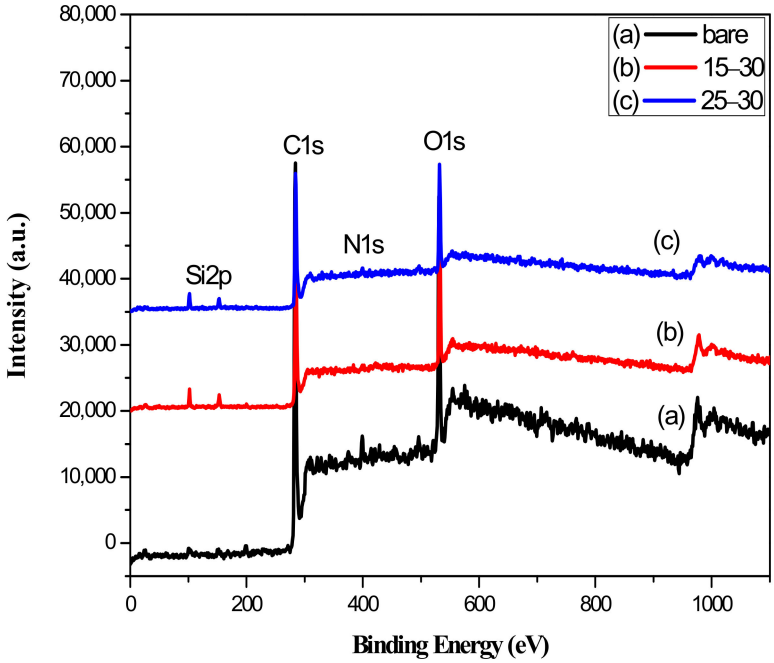

Figure 3. XPS spectra of uncoated sample and coated samples: (**a**) bare; (**b**) deposition time 30 s and spraying distance 15 mm; (**c**) deposition time 30 s and spraying distance 25 mm.

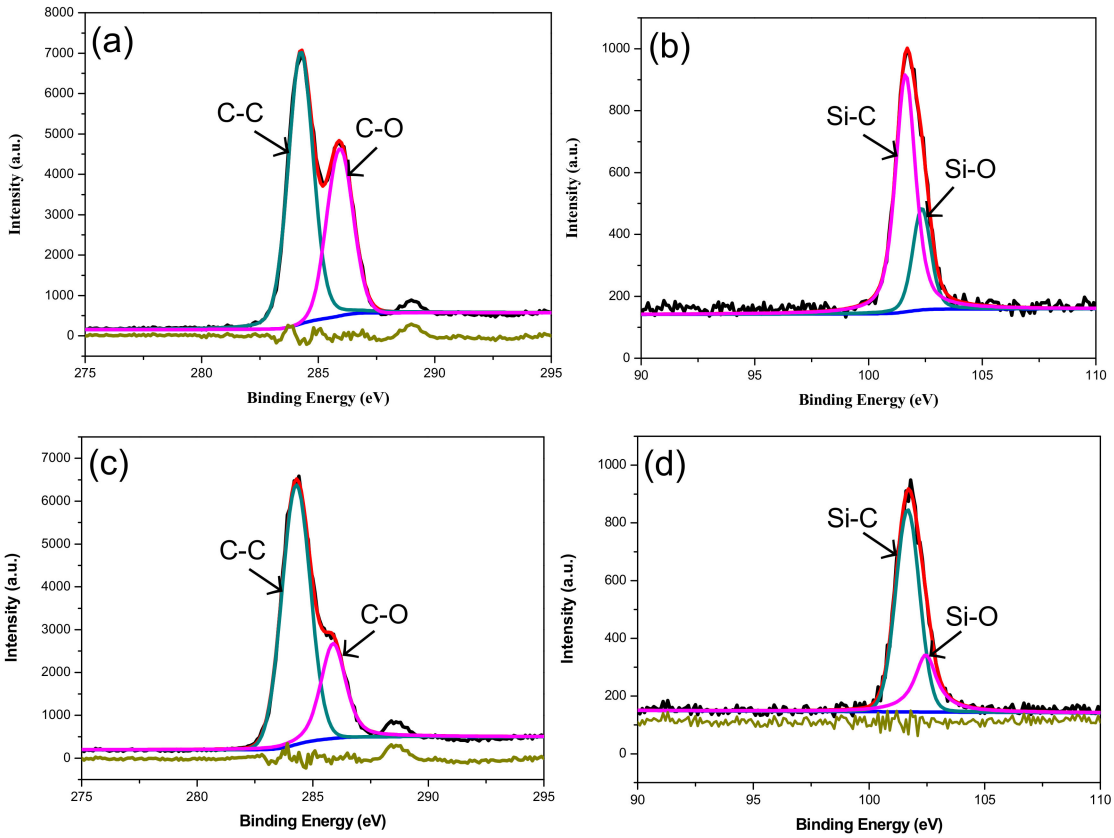

Figure 4. XPS spectra Si2p and C1s XPS spectra of deposition time 30 s and spraying distance 15 mm (**a**,**b**); deposition time 30 s and spraying distance 25 mm (**c**,**d**).

3.3. Oxidation Resistance

TG and DTG were performed under air in order to investigate the oxidation stability as well as the mass change of the uncoated and coated sample, as illustrated in Figure 5a,b. The TG curves in Figure 5a revealed that the mass loss of each sample changed slightly at an oxidation temperature about 600 °C. As the temperature rises, mass loss started to appear, but the weight loss rates are different from each other, as can be seen from the slope. The mass loss values of TG are summarized in Table 1. The sample with a spraying distance of 25 mm is almost completely weightless at 800 °C, but the bare sample mass loss is 59%. It has poorer oxidation resistance than the untreated samples. This may be caused by the plasma arc reaching the surface of the fiber at a relatively low temperature because the spray distance is too long. This causes the strength of the carbon fiber fabric to decrease. This is consistent with the results of SEM. Exfoliation of the carbon fiber surface and poor adhesion of the coating lead to a decrease in the oxidation resistance. The bare sample is almost completely weightless at 900 °C, but the weight loss rate of the sample with a spray distance of 15 mm is 75%. Obviously, the SiC/SiO_2 coating can effectively protect the carbon fiber and increase the safe application temperature by 100 °C when the sample deposition time is 30 s and the spraying distance is 25 mm. The DTG curves show that the maximum mass loss rate of the bare sample is at 785 °C, but for the No. 3 sample it is at 766 °C. This is consistent with the above results. The maximum mass loss rate of the No. 2 sample is at 872 °C and the weight loss rate is very slow. The SiC/SiO_2 coating hindered the oxidation of the carbon fiber fabric and also postponed the maximum mass loss rate.

Figure 6 shows the tensile strength of the heat-treated bare and SiO_2/SiC-coated samples at a deposition time of 30 s and a spraying distance of 15 mm. The sample oxidation was at 900 °C for 20 min. The heat-treated bare sample tensile strength was 77 MPa; however, the SiO_2/SiC-coated carbon fiber fabric tensile strength was up to 150 MPa. The results show that the tensile strength of carbon fiber fabric is greatly improved by the SiO_2/SiC coating.

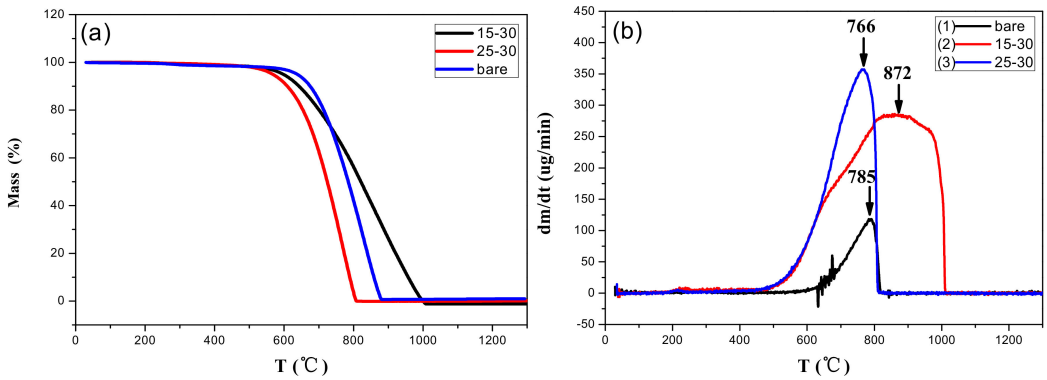

Figure 5. The TG (**a**) and DTG (**b**) curves of uncoated (1) and coated sample, deposition time 30 s and spraying distance 15 mm (2) and deposition time 30 s and spraying distance 25 mm (3).

Table 1. Mass loss at different temperature stages in air (according to TG data).

Sample	Time (s)	Distance (mm)	Mass Loss (wt %)			
			700 °C	800 °C	900 °C	1000 °C
No. 1	–	–	16	59	99	–
No. 2	30	15	21	45	75	99
No. 3	30	25	41	97	–	–

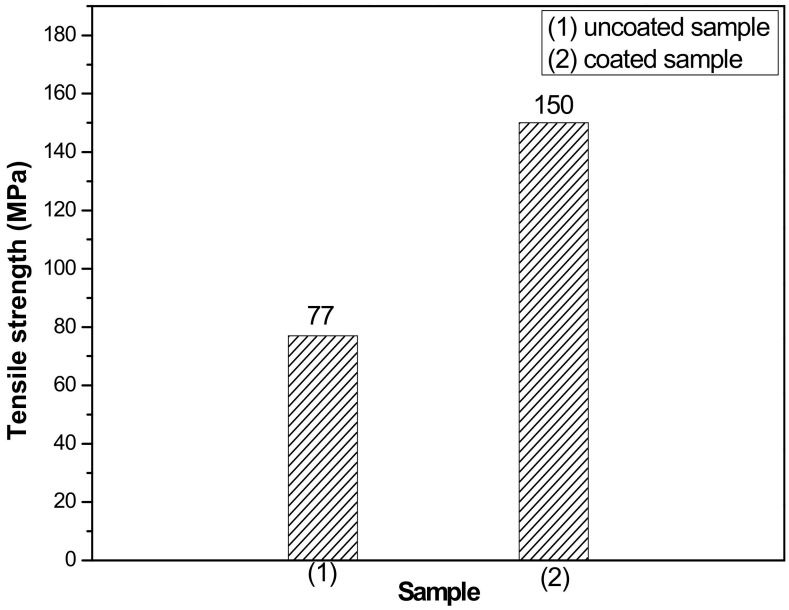

Figure 6. Tensile strength for heat-treated bare and the SiO_2/SiC-coated sample at deposition time 30 s and spraying distance 15 mm.

4. Conclusions

Using a novel electrolytic plasma spraying method, we successfully prepared a SiO_2/SiC coating on carbon fiber fabric with improved mechanical properties and oxidation resistance. In this study, 30 g/L $Na_2SiO_3 \cdot 9H_2O$ aqueous solution was used as the electrolyte. We studied the effect of spraying distance on microstructure and oxidation stability. The results of our study indicated that the coated sample at a deposition time of 30 s and a spraying distance of 25 mm had poor interfacial bonding strength, and the surface of the carbon fiber fabric had fluffing. This leads to poor high-temperature oxidation resistance. However, the coated sample at a deposition time of 30 s and a spraying distance

of 15 mm exhibited outstanding oxidation resistance and thermomechanical properties. Its oxidation resistance has increased the temperature by 100 °C, and the tensile strength for the heat-treated sample has increased by 73 MPa. Therefore, the SiO_2/SiC coating, which has a good oxidation resistance protection effect, could effectively protect CF and maintain its mechanical enhancement.

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Conflicts of Interest: The authors declare no conflict of interest.

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