Preparation of the Anti-Oxidation SiO$_2$ Coating on Carbon Fibers by Modified Sol-Gel Method

X Wang$^1$, Z X Huang$^1$, G Y Yang$^{1,a}$ and J Q Song$^1$

$^1$ Department of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China.
$^a$ yangguangyuan@whut.edu.cn; Tel. +86-135-9779-7555.

Abstract: Carbon fibers have been widely used in various fields due to excellent physical and chemical properties. However, the presence of oxygen limits the use of carbon fibers in high temperature applications. In this paper, a modified sol-gel method for the preparation of SiO$_2$ coating was proposed. Through the preparation of the emulsion, the SiO$_2$ sol added with the amino-functional silane was uniformly mixed. The results showed that the optimal ratio of SiO$_2$ sol was ethanol: distilled water: tetraethyl orthosilicate = 3 :1:5. After the preparation of the emulsion, the coating thickness was greatly increased and the performance was excellent. The initial oxidation temperature of carbon fiber was increased from 400℃ to 600℃ by preparing SiO$_2$ coating. The coating obtained by emulsifying treatment could reduce the weight loss rate of carbon fiber cloth at 1450℃ from 83.72% to 28.67%.

1. Introduction
Carbon fibres (CF) have been widely used in aerospace, sports, and industrial fields due to excellent physical and chemical properties such as high specific modulus, high strength, low coefficient of expansion, and good flexibility. Traditional ultra-high temperature protection materials contain refractory metal, ceramic composites, etc$^1$. They were either too heavy, or the mechanical properties were not very good. CF reinforced composites have great potential to replace them because of lightweight, high-strength and flexibility$^2$. However, the carbon fibers have poor oxidation resistance even at temperatures as low as 400℃, which results in limitations of the application of carbon fibers in the high temperature field under oxygen atmosphere. Therefore, it is necessary to improve the oxidation resistance of carbon fibers to extend their applications.

Ceramic coatings such as carbides, nitrides, and oxides have been proved to be effective ways to improve the high-temperature oxidation resistance of carbon fibers$^{3,4}$. The most common techniques for preparing ceramic coatings are chemical vapor deposition (CVD), precursor osmosis pyrolysis (PIP), and sol-gel (SG)$^5$. In contrast, the reactants are uniformly mixed from the molecular point of view when the gel is formed, and it is easy to add the desired element to the system by using sol-gel methods to prepare the coating. At the same time, the reaction is easier and the synthesis temperature is lower. There are a lot of micropores after the gelation, which generates a lot of gas and shrinks during drying$^{6,7,8}$.

The main research content of this paper was carbon fiber high-temperature anti-oxidation SiO$_2$ coating. In order to improve the mechanical strength of the modified carbon fiber composite material, an amino functional silane KH550 was added during the conventional sol preparation process. The conventional sol-gel method was modified by the prepared emulsion so that the sol was sufficiently mixed and the coating was coated on the carbon fiber.
2. Experiments

2.1. Experimental Principle

The sol is a dispersion system in which solid particles (colloidal particles) are uniformly dispersed in a medium. In this test, sol was prepared by solution of organic alcohol salt water, which was the most widely used method in sol-gel technology. Specifically, the organic alkoxide was dissolved in a solvent to undergo hydrolysis or alcoholysis reaction, and the reaction products were aggregated into particles of tens of nanometers to about ten nanometers and formed sol. The formation of sols was as follows.

a. Hydrolysis: organic alkoxide reacted with water:

\[
(MOR)_n + xH_2O \rightarrow M(OH)_x(OR)_{n-x} + xROH
\]  

(2.1)

M—Si; R—organic group (-C4H9).

The hydrolysis reaction of ethyl orthosilicate can be regarded as a bimolecular nucleophilic substitution reaction. The reaction history was:

b. Polycondensation: Once the hydroxide was formed, polycondensation occurred and was divided into:

Dehydration condensation: \(-M-OH+OH-M- \rightarrow -M-O-M- + H_2O\)  

(2.2)

Loss of alcohol condensation: \(-M-OR+OH-M- \rightarrow -M-O-M- + ROH\)  

(2.3)

The sol particles generated by the reaction had various sizes and structures. The ceramic films prepared by the alkoxide solution mainly include SiO2, TiO2, PbTiO3, and BaTiO3.

2.2. Carbon fiber pretreatment

A layer of organic protective glue was attached to the surface of the untreated carbon fiber. If it was not pretreated, a weak interface would be formed on the surface of the fiber. After the heat treatment at 400°C, nitric acid treatment, washing and drying, the organic adhesive layer on the carbon fiber surface was removed. The previously smooth surface became rough, and the increased micropores and grooves increased the contact area between the fiber and the coating. It facilitates the combination and thickening of the coating. The production of carboxylic acid, hydroxyl and lactone functional groups helped to increase the bonding strength[9].

2.3. Preparation of Sol and Emulsion

In the experiment, anhydrous ethanol, distilled water, and tetraethyl orthosilicate were mixed at a ratio of 2:12:3 and 3:1:5 in order to prepare a SiO2 sol. An equal amount of KH550 and hydrochloric acid were separately added to the two mixed solutions. In order to uniformly mix the substances and enhance the degree of application of the sol to the carbon fibers, an appropriate amount of dimethyl silicone oil was added to the above solution. Tween 80 was added as an emulsifier and the homogenizer was used to prepare the emulsion.

2.4. Coating Preparation

After the sol has been demulsified, carbon fibers were treated by a dipping method. The carbon fibers were immersed in the solution for 30 minutes and then the carbon fibers were uniformly extracted at a rate of 10 mm/min. Repeat several times to increase the coating thickness. Finally, the sample was placed in a high-temperature tube furnace to prepare a SiO2 coating, and a four-stage heat treatment
was performed under the protection of an inert gas with a gas flow size of approximately 19 ml/min.

3. Results and Analysis

3.1. The choice of the ratio of the sol

![Figure 1. Infrared spectrum of SiO₂ coating.](image)

The resulting coating was subjected to a smart Fourier transform infrared analysis. In the figure 1, a strong and wide absorption band can be observed at 1103 cm⁻¹. By consulting the literature, it is known that Si-O-Si is an anti-symmetrical stretching vibration. The peaks observed at 799 cm⁻¹ and 468 cm⁻¹ are respectively the symmetrical stretching vibration peaks and bending vibration peaks of the Si-O bond. Here it can be demonstrated that there is SiO₂ formation in the carbon fiber surface coating.

![Figure 2. TG analysis of SiO₂ coating prepared from different sol ratios.](image)

![Figure 3. XRD analysis of SiO₂ coating prepared by different ratios.](image)

Figure 2 shows the thermogravimetric analysis of carbon fiber products protected by anti-oxidation SiO₂ coatings which was prepared from different sol ratios. It can clearly be seen in the figure that the coatings prepared by the two ratios have a certain degree of improvement in the thermal properties of the carbon fibers. Among them, when the ratio of anhydrous ethanol, distilled water, and tetraethyl orthosilicate is 3:1:5, the thermal performance is greatly improved when compared with 2:12:3. The initial oxidation temperature increased, and the mass loss also dropped from the original 83.72% to 28.67%. Obviously, anhydrous ethanol: distilled water: tetraethyl orthosilicate = 3:1:5 have better
thermal properties and better protection of carbon fiber fabrics. The main reason for the analysis is that the excessive water content during the preparation of the sol at the ratio of 2:12:3 caused the reaction to take a long time. Not fully reacted during the stirring process, and thus the carbon fiber coating had a poor effect. The sol-gel produced with a ratio of 3:1:5 formed a relatively complete coating on the surface of the carbon fiber, which prevented the infiltration of oxygen to a certain extent and better protected the carbon fiber.

The X-ray diffraction spectra of the SiO$_2$ coatings prepared at different ratios are shown in the figure 3. It can be observed in the figure that there are obvious SiO$_2$ diffraction peaks in the two measured spectra, and their corresponding diffraction angles are almost the same as 25.65° and 25.84°. Among them, the ratio of 2:12:3 results in a stronger SiO$_2$ coating peak and relatively higher crystallinity. At the same time, the peak is sharper, the width at half height is narrower, and the crystal grains are larger. The reason for the analysis may be due to the lower water content at the ratio of 3:1:5 so that the reaction proceeds faster, and the coating obtained is not stable enough. The resulting crystallinity is lower when the coating is formed, and the crystal grains are also relatively small.

3.2. Effect of Emulsion Preparation on Coating Properties

In order to study the influence of the emulsion on the coating properties, the unprocessed gel was coated on the carbon fiber in one layer, three layers, and compared with the carbon fiber coated after emulsification

The effect of different coating frequency on the thermal properties of the SiO$_2$ coating is shown in figure 4. As can be seen from the figure, the weight loss rates of the three samples were 57.24%, 55.72%, and 28.67%, respectively. Obviously, the emulsified SiO$_2$ coated sample has the lowest weight loss rate at high temperature. The initial oxidation temperature of the coated sample also increased, and the emulsified sample have the highest initial oxidation temperature. The analysis may be due to the fact that the thickness of the SiO$_2$ coating formed on the surface of the carbon fiber is insufficient when the sol is coated with a single layer or a few layers so that the oxygen erosion cannot be completely blocked. After the emulsification treatment, the thickness of the coating increases, and the protective effect has been significantly improved.

X-ray diffraction analysis was performed on the test sample, and the results are shown in figure 5. The figure shows that there are obvious SiO$_2$ diffraction peaks in the three sample spectra, and their corresponding diffraction angles are similar. Among them, the sample with only one coating was found to have the strongest diffraction peak and relatively the highest degree of crystallinity. Followed by the emulsified sample, the three-layer sample tested shows the lowest crystallinity. The reason for the analysis may be that the coating produced by one coating is thinner and more conducive to the reaction, and the heating is uniform and the crystallinity is relatively high. It is inferred that the degree of crystallinity in the coating is closely related to the preparation process, and the gel-time drying temperature will have a certain impact on it.

The microstructure of the surface of the carbon fiber coating obtained under different experimental
conditions is observed, as shown in figure 6.

![Figure 6. Effect of Emulsion Preparation on SEM of Coatings.](image)

(a) One coat.  
(b) Three coats.  
(c) After emulsification.

As can be seen in the figure, there was no coating adhesion to be observed on the surface of the sample that had not been emulsified. After the emulsification treatment, there was a clear coating on the surface of the fiber. It shows that the emulsification treatment significantly changes the thickness of the carbon fiber coating, and the overall performance can be qualitatively improved by preparing the emulsion.

4. Conclusions

In this paper, the sol-gel method was adopted. Tetraethyl orthosilicate was used as the main raw material, ethyl alcohol absolute was used as the solvent, and the pH was adjusted by hydrochloric acid. In order to uniformly mix the solution to which KH550 was added, emulsification treatment was performed. Coating the pretreated carbon fiber with the above sol. The nitrogen gas is used as a protective gas for heat treatment in a tube furnace to obtain a carbon fiber sample having a high-temperature oxidation resistant coating of SiO\textsubscript{2}. This article discussed the formation mechanism of the coating. Then studied the effects of different ratios of sols on the coating and whether emulsification treatment will affect the final coating formation. The conclusions were as follows:

1. SiO\textsubscript{2} was formed in the coating after the reaction of the sol prepared by the two ratios, which played a certain protective effect on the carbon fiber. When anhydrous ethanol: distilled water: tetraethyl orthosilicate was mixed in a ratio of 3:1:5, the resulting coating was best protected against
carbon fiber by decomposition of the SiO\textsubscript{2} sol. This coating had the best heat treatment properties, and relatively low crystallinity.

(2) SiO\textsubscript{2} was generated in the samples prepared regardless of whether or not the emulsion was prepared. The emulsified coating made the sample at the high temperature loss rate of only 28.67% at 1450°C, which had the best protective effect on carbon fiber.

References
[1] Fahrenholtz W G and Hilmas G E 2017 Scr. Mater. 129 94-9
[2] Yang G Y, Huang Z X, Wang X and Wang B 2018 MDPI. Materials 11(3)
[3] Yong X, Cao L, Huang J, Kong W, Su J, Li C, Ouyang H, Zhou L and Liu J 2017 Surf. Coat. Technol. 311 63-9
[4] Kern F and Gadow R 2002 Surf. Coat. Technol 151-2 418-23
[5] Szczurek A, Barcikowski M, Leluk K, Babiarczuk B, Kaleta J and Krzak J 2017 Materials 10 990
[6] Wang J, Lin W, Yan X, Wu X, Wu F and Yang Y 2016 Mater. Des. 89 928-32
[7] Xiang Y, Li X, Du A, Wu S, Shen J and Zhou B 2017 Coat. Technol. Res. 14 447-54
[8] Xia K, Lu C and Yang Y 2013 Appl. Surf. Sci. 265 603-9
[9] Vautard F, Fioux P, Vidal L, Dentzer J, Schultz J, Nardin M and Defoort B 2013 Surf. Interface Anal. 45 722-41
[10] Bohye K, Kapseung Y, Heegweon W and Suyeun K 2011 Journal of Nanoscience and Nanotechnology 11(8)
[11] Ratnayake S, Silva N, Kaupuge T, Weerasekera T, Senarathyapa M, Karunaratne V and Amaratunga G 2018 Materials Science & Engineering B 229