Thermal stability of the carbon fibers with SiO₂ coating

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Abstract. This paper presents the results of a study of silicon dioxide coating deposited on the surface of carbon fiber by the sol-gel method. The effect of the viscosity of the prepared sol-gel solution and the oxidizing properties at elevated temperatures obtained by SiO₂ coatings were studied. It was found that the kinematic viscosity of the sol-gel solution does not change for 72 hours. An increase in viscosity leads to the formation of colloidal particles, which degrades the quality of the coatings. Studies have shown that in the temperature range 600-800 °C, the quality of uncoated fibers degrade, but the SiO₂ coating well protects the fiber surface and significantly slows down the rate of destruction.

1 Introduction

Recently, carbon fibers are one of the most promising materials for composite producing. The most widely used carbon fibers in carbon fibers reinforced polymer composites (CFRPC). The use of carbon fiber in a composite material with an aluminium matrix is a difficult due to the chemical interaction of the matrix and the fiber. As a result of the interaction, a brittle composition Al₄C₃ is formed, which negatively affects the properties of the entire composite. Prevention of the carbides formation is possible by creating special protective coatings on the surface of carbon fibers [1, 2].

Most works about protective coatings consider metal coatings obtained by the electrolytic method [3, 4]. Such coatings are in contact with the matrix to form intermetallic compounds, which reduce the mechanical properties of the composite [5]. Many researchers in their papers [6, 7] show that ceramic coatings, due to their high chemical resistance, can be used as a diffusion barrier between the matrix and fibers. In [8, 9], SiC and TiC barrier coatings were obtained by chemical vapor deposition (CVD). The complexity of this method lies in the need for surface preparation before coating, the presence of expensive precursors that can be toxic or explosive [10].

Compared to the methods mentioned above the most simple is sol-gel method, which does not require expensive and energy-intensive equipment, complex chemicals, high temperatures and pressures. Based on the sol-gel method, materials of complex chemical composition and structure, as well as with the necessary properties, can be

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obtained [11, 12]. A composite wire reinforced with Al_2O_3 -coated carbon fiber was obtained in [11]. The authors showed that the aluminium oxide coating increases the strength of the composite. Using this method, coatings based on SiO_2 , TiO_2 , and ZrO_2 are obtained [13-15]. However, questions of selection the optimal application mode and the effect of various parameters of the sol-gel process on the formation and properties of coatings remain poorly understood. This study evaluated the effect of the viscosity of a sol-gel solution on the formation of SiO_2 coatings and the behavior of coated carbon fibers when heated in an air atmosphere.

2 Materials and method

As an initial material, the carbon fibers from a PAN precursor of the brand UMT49-12K-EP (manufactured by the UMATEX group) were used, the average diameter of one filament is $5.5 \mu\text{m}$. The surface of the carbon fiber in the initial state is shown in fig. 1 a. In the initial state, the surface of the fiber is mostly smooth, subtle longitudinal bands are observed. The polymer size was removed from the surface of the fibers by exposure to acetone for 2 h [16] in order to provide adhesion between the fiber and the barrier oxide coating. After removal of the polymer layer, longitudinal strips on the surface become more noticeable as a result of an increase in the step height associated with the strip (fig. 1 b).

Fig. 1. The surface of the carbon fiber: a) initial state; b) after removing the polymer size (stripes are shown by arrows).

The silicon coating was applied by immersing the fibers in a sol-gel solution, which was prepared according to the following procedure [17]: an aqueous ethanol solution acidified with 1 M HCl solution was slowly added dropwise to a mixture of solutions (tetraethoxysilane (TEOS), ethanol). The solution was stirred for 30 minutes. Carbon fibers were immersed in the obtained sol-gel solution and soaked for 15 seconds. Then, the coated fibers were dried in air for 30 minutes and then subjected to heat treatment at a temperature of 500°C (the heating rate to a given temperature was $2.5^\circ\text{C}/\text{min}$).

The processes occurring in sol-gel solution were evaluated by measuring the kinematic viscosity at room temperature using a capillary viscometer. Kinematic viscosity was calculated by the formula:

$$\nu = \frac{g}{9,807} \cdot \tau \cdot K, \quad (1)$$

where ν is the kinematic viscosity of the solution, mm^2/s ; $K = 0.01060 \text{ mm}^2/\text{s}^2$, viscometer constant; τ is the time of expiration of the solution through the capillary, s; g - acceleration of gravity at the measurement site in m/s^2 .

To evaluate the protective properties of the sol-gel coating the carbon fibers were subjected to isothermal aging at temperatures of 500–800 °C in an air atmosphere. During the exposure, the mass of fibers on the balance was measured (Mettler Toledo XP26). The surface of the carbon fibers was investigated by the scanning electron microscope (SEM JEOL JSM 6490-LV).

3 Results and discussion

To determine the lifetime of the solution used and the optimal mode of deposition of SiO_2 coatings, the viscosity of the sol-gel solution was studied. Dependence of the kinematic viscosity on the sol exposure time is shown in fig. 2. This dependence can be divided into three parts. In section I, the first 72 hours, the viscosity does not change significantly, the sol is in a stable state. Viscosity values vary within 3.6 ... 3.69 mm^2/s . In the second section, the sol ripens (nucleation), as a result of hydrolysis and polycondensation reactions, which is accompanied by an increase in viscosity. Viscosity increases to 4 mm^2/s . In the third section, there is a sharp increase in viscosity to 5.5 mm^2/s , which indicates the onset of gel formation of the sol.

Fig. 2. Dependence of the kinematic viscosity on the exposure time of the sol-gel solution at room temperature.

In order to evaluate the interaction between SiO_2 coating and carbon fiber, coatings were applied at various viscosity values. The surface of the coated carbon fibers is shown in fig. 3. Electron microscopy studies have shown that the coating is generally applied uniformly with a stable sol-gel solution, but there are uncoated areas (fig. 3 a). During the ripening period of the sol, spherical or lamellar particles appear on the surface of the carbon fibers, as evidence of occurring hydrolysis and polycondensation reactions (fig. 3 b). The particles accumulate on the surface, thereby leading to delamination SiO_2 coatings (fig. 3 c). Thus, with a viscosity value of 5.5 mm^2/s , the deposition of SiO_2 coating is impractical. As a result of the research, SiO_2 coatings should be applied to the surface of the carbon fiber at a viscosity of 3.6 ... 3.69 mm^2/s or within 72 hours of storage of the sol.

Fig. 3. Coated carbon fibers a) at a viscosity of $3.6 \text{ mm}^2/\text{s}$; b) at a viscosity of $5.5 \text{ mm}^2/\text{s}$; c) delamination of the coating (shown by arrows).

For evaluation of protective properties of the coatings at a viscosity of $3.6 \text{ mm}^2/\text{s}$ the samples were subjected to isothermal exposure in the temperature range of $500 \dots 800 \text{ }^\circ\text{C}$. The dynamics of changes in the carbon fiber mass during annealing is shown in fig. 4. Heat treatment at a temperature of $500 \text{ }^\circ\text{C}$ is the final step in the formation of the SiO_2 coating. Significant changes in the mass of carbon fiber without coating and with coating were not observed. As can be seen, the graph shows that uncoated carbon fibers (dotted line) burn out much faster in comparison to SiO_2 coated fibers (solid line). The mass of carbon fiber with SiO_2 coating during the annealing decreases monotonically, after 6 hours of annealing, the mass of the coated fiber is 69 % of the original, when, as for uncoated fibers, it is 33 %. At a temperature of $600 \text{ }^\circ\text{C}$, SiO_2 coating protects the carbon fiber from burning out [14] during 6 hours of annealing. An increase in temperature to $700 \text{ }^\circ\text{C}$ contributes to an increase in the rate of burnout of the fiber by about 3 times. Uncoated carbon fibers completely burn out after 30 minutes of annealing; SiO_2 coating protects the fiber for 90 minutes of annealing (mass of retained fibers is 13 %). Increasing

the temperature to 800 °C the uncoated fibers burn out within 2 minutes, SiO₂ coating retains the fiber for 60 minutes (~ 13 %). In the temperature range of 600–800 °C SiO₂ coating shows sufficient oxidation resistance.

Fig. 4. Dependence of fiber mass from annealing time at temperature: ♦ – 500 °C; ● – 600 °C; ▲ – 700 °C; ■ – 800 °C.

In the process of isothermal exposure of samples in the temperature range 600–800 °C, destruction of the carbon fiber is observed. The carbon surface during annealing is shown in Fig. 5. On the surface of uncoated fibers destruction is observed in the form of ulcers the average size of which is 2.7 μm (fig. 5 a). For coated fibers, no degradation in the form of ulcers is observed (fig. 5 b). To a temperature of 600 °C SiO₂ coating well protect the carbon fibers. An increase in temperature to 700 and 800 °C leads to a sharp decrease in the mass of uncoated carbon fibers. A decrease in the mass of coated carbon fibers may be due to etching of the SiO₂ coating during annealing. In general, the SiO₂ coating slows down the destruction process, while protecting the fiber structure.

Fig. 5. The surface of carbon fibers after 30 minutes of annealing at a temperature of 700 °C: a) without coating (ulcers are shown by arrows); b) with SiO₂ coating.

4 Conclusion

The results of the studies show that the optimal time for using the sol-gel solution for coating does not exceed 72 hours. A further increase in viscosity leads to the formation of colloidal particles, which significantly affects the quality of the coatings.

The isothermal exposure of carbon fibers after coating shows that at 600 °C the coating well protects the fibers. At a temperature of 700 °C and 800 °C it leads to a sharp deterioration in the quality of carbon fibers, but the barrier oxide coating significantly slows down the rate of destruction.

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References

1. M. Lee, Y. Choi, K. Sugio, K. Matsugi, G.Sasaki, *Composites Science and Technology*, **97** (2014)
2. K. Xia, C. Lu, Y. Yang, *Applied Surface Science*, **265** (2013)
3. S. Abraham, B. C. Pal, K. G. Satyanarayana, V. K. Vaidyan, *J. Mater. Sci.* **27** (1992)
4. T. Suzuki, H. Umehara, R. Hayashi, S. Watanabe, *J. Mater. Res.* **8** (1993)
5. S.T. Mileiko, *Metal and Ceramic Based Composites* (Elsevier, Amsterdam, 1997)
6. A. Olszówka-Myalska, A. Botor-Probierz, *IOP Conf. Series: Materials Science and Engineering*, **7** (2010)
7. R. Gadiou, S. Serverin, P. Gibot, C. Vix-Guterl, *Journal of the European Ceramic Society*, **28** (2008)
8. G. Hackl, H. Gerhard, N. Popovska, *Thin Solid Films* **513** (2006)
9. K. Yu, H. L. Li, B. L. Shanga, *J. Mater. Sci.* **29** (1994)
10. T. Piquero, H. Vincent, C. Vincent, J. Bouix, *Carbon* **33** (1995)
11. Q. Zeng, *Journal of Applied Polymer Science*, **70** (1998)
12. P. Y. Chu, D. E Clark, *Spectroscopy Letters*, **25** (1992)
13. P. Gibot, C. Vix-Guterl, *Journal of the European Ceramic Society*, **27** (2007)
14. R. F. Gallyamova, S. N. Galyshev, F.F. Musin, A.G. Badamshin, V.A. Dokichev, *Solid state phenomena*, **284** (2018)
15. R. F. Gallyamova, S. N. Galyshev, A. G. Badamshin, F. F. Musin, V. A. Dokichev, *AIP Conference Proceedings*, **2053** (2018)
16. GOST R ISO 10548 – 2012, *Carbon fiber. Methods for determining the content of the sizing* (Standartinform, Moscow, 2015)
17. C. Vix-Gutesrl, P. Ehrburger, *Carbon*, **35** (1997)