Sol-gel synthesis of oxide protective coatings of carbon fibers to increase heat resistance in aggressive oxidizing environments

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Abstract. Ceramic coatings of the Al₂O₃/SiO₂ composition by the sol-gel method on carbon fibers were obtained in order to prevent oxidation and destruction of the fiber at temperatures above 450°C. Various combinations and ratios of aluminum and silicon oxides were used. The results of scanning electron microscopy and X-ray diffraction showed a change in the topographic properties of carbon fiber during the deposition of coatings thereon. Thermal analysis showed that oxidative stability improved significantly due to coverage, increased to 1100°C.

1. Introduction
To create new ceramic materials with enhanced properties and characteristics, the development of ceramic-matrix composites (CMC) using various fibers as a reinforcing component seems to be the most relevant. The use of various fibers as a reinforcing component can significantly improve the final properties of the composite material, namely, to increase the impact strength, reduce brittleness, and preserve the carrying capacity. However, the mere use of fibers as a component of CMC does not yet guarantee automatic improvement of the properties of the material being developed. Undoubtedly, the use of fibers leads to an increase in the strength and rigidity of the CMC, since in the direction of the fiber axis in the reinforced materials, the ability to absorb loads increases by an order of magnitude compared with unreinforced material of the same chemical composition. However, in the case when the determining factors for the effectiveness of the application is a complex of material properties — for example, its high thermal resistance and thermal strength combined with low density — there is a need to apply special processing methods for fibrous materials to optimize their properties relative to the conditions of manufacturing processes or subsequent operation of the final product.

The most difficult problem when creating a CMC with a reinforcing component in the form of fibers is the choice of fiber. The most applicable are carbon fibers oxidized with air oxygen at temperatures above 450°C, which is a limitation for their use in a wide temperature range [1-11]. To solve this problem, it was proposed to apply thin ceramic coatings on carbon fiber, which will be resistant to oxidation, as well as a binder between the matrix and fiber materials. For carbon fiber as a coating material, it was decided to choose alumina and silicon oxide at the first stage, since these compounds have good heat resistance and are also fairly simple to produce. The sol-gel method
was chosen as the method of preparation, since it is simple, affordable and does not require expensive equipment [12-17]

2. Materials and methods
In this paper, a carbon fiber grade URAL H-400Э was used. The mass fraction of the coupling agent on the fiber (synthetic rubber) is 0.8%. Technical ethyl alcohol, acetone and distilled water were used to prepare the carbon fiber for synthesis. Removal of the coupling agent was carried out as follows. The coupling agent was originally removed from the surface of the carbon fiber using a mixture of acetone and ethanol in a volume ratio of 1:1, followed by purification in distilled water using ultrasound. Then, for additional purification, the fiber samples were annealed in a furnace in air at a temperature of 240°C.

The following initial reagents were used in the paper: aluminum nitrate Al(NO3)3 9H2O, ammonia aqueous concentrated NH3 H2O, tetraethoxysilane (C2H5O)4Si, technical ethyl alcohol C2H5OH, hydrochloric acid HCl.

2.1. Preparation of sols of aluminum hydroxide and silicon oxide
To prepare an aluminum hydroxide sol, a concentrated solution of ammonia in water (NH4OH) was added to the aqueous solution of aluminum nitrate (Al(NO3)3) while stirring the solution on a magnetic stirrer with a speed of 120 rpm and a temperature of 50°C until a gel-like precipitate formed aluminum hydroxide (Al(OH)3). Further, the solution with the precipitate continued to stir for 20-25 minutes until the complete transition of the precipitate to the sol.

The method of preparation of the silica sol was as follows: The required amount of tetroethoxysilane was mixed with ethyl alcohol. Then, with stirring on a magnetic stirrer with a speed of 120 rpm, hydrochloric acid solution was added. When this occurred, the mixture was heated to a temperature of 50°C. The stability of the solution and its suitability for the formation of films was determined by the change in viscosity.

2.2. Carbon Coating Preparation
For the synthesis of coatings on the surface of the fiber, the fiber was passed through a bath containing a sol at a speed of 10 cm/min.

After passing through the sol bath, the fiber was subjected to 3-step heat treatment. Stage 1 included drying the fiber at a temperature of about 22-24°C until the fiber completely dried. At the 2nd stage, the fiber passed through the first furnace and dried at the temperature of from 80°C to 150°C in an oxidizing atmosphere for 30 minutes. At the 3rd stage, the fiber passed through the second furnace, where it was annealed. The annealing of the fiber was carried out in a furnace, the temperature of the annealing was regulated in the range of 400°C to 570°C in an oxidizing atmosphere for 20-60 minutes.

Temperature selection is associated with the transition of coating materials to the required phases.

3. Results and discussion
The microstructure, elemental composition of the samples and the composition of individual phases were determined by scanning electron microscopy (SEM) and electron microprobe analysis (EMPA) using a FEI Quanta 200 scanning electron microscope with a thermal emission cathode and an energy dispersive Si (Li) EDAX detector for microanalysis.

Using a scanning electron microscope, surface images of coated carbon fiber samples were obtained. According to the images, an analysis of the surface morphology of these samples was carried out. Figure 1 depicts images of the surface of a carbon fiber with a single-layer (a) and four-layer (b) Al2O3 coating.
As can be seen from the images, a single-layer coating of aluminum oxide forms a thin, fairly uniform coating. Separate areas of inhomogeneities can be associated with the roughness of the fiber itself or residual coupling on the fiber. Four-layer coating forms an uneven cracked coating. Many separate agglomerates are formed. This may be due to the fact that the initial irregularities of the fiber formed points of growth, on which agglomerates were subsequently formed upon repeated application of coatings.

Figure 2 shows images of the surface of a carbon fiber with a single-layer (a) and four-layer (b) SiO2 coating.

These images show that the single-layer coating is a homogeneous structure, without pores and defects, consisting of small elongated crystals. On the surface of the carbon fiber there are agglomerates, which may be due to the uneven surface of the fiber itself, residual dressing or other contaminants. Four-layer coating forms an uneven coating with a large number of cracks. Coating morphology is heterogeneous. A large number of cracks in the coating may be due to the stress in the layer caused by the thickness of the coating.

Thermal analysis of the samples was carried out in a muffle furnace in an atmosphere of air. According to the results of thermal analysis, graphs of the dependence of the mass loss on temperature were plotted.

Fig. 3 shows a plot of mass loss (%) versus temperature in the range from 500 to 1100°C for 5 samples of carbon fiber with alumina obtained from Al(OH)3 sol.
In analyzing the data obtained, we can conclude about the behavior of the fiber with and without coating at elevated temperatures. At a temperature of 500°C, the weight loss is <5% for all coated fibers. Loss of fiber mass at the same temperature of 11%. As the temperature increases, the mass loss for all samples increases. However, for samples without coating and with a 4-layer coating, the temperature curve is described by an exponential relationship. In the case of a 1,2,3-layer coating, the dependence can be approximated by a linear function. The best indicators of oxidative resistance of the fiber with a 3-layer coating. This may be due to the fact that the coating has sufficient thickness and density, and oxygen practically does not penetrate to the surface of the carbon fiber. With an increase in the thickness of the coating, a large number of defects form and the coating cracks; these defects are a source of oxygen penetration to the fiber surface. The mass loss in this case is comparable to the mass loss of the uncoated fiber. Fig. 4 depicts a plot of mass loss (%) versus temperature in the range from 500 to 1100°C for 5 carbon fiber samples with silicon oxide obtained from SiO2 sol.

For samples with silicon oxide at a temperature of 500°C, the mass loss is <5% for samples with a 1,2,3-layer coating. The loss of fiber mass without coating and with a 4-layer coating at the same temperature is 12%. With increasing temperature, fiber with 2- and 3-layer coatings shows the best properties. However, at a temperature of 1100°C, the oxidation of a fiber with a 2-layer coating occurs more strongly than with a 3-layer coating. The temperature dependence of
the sample with a 3-layer coating on this temperature range is linear, the remaining dependencies tend to be exponential.

4. Conclusion

Test samples were obtained and analyzed by scanning electron microscopy and thermal analysis. Thin coatings exhibit optimal properties, with the best temperature resistance shown by coatings consisting of 2 and 3 layers. Multilayer coatings have a large number of defects, which causes the destruction of the fibers at increased temperatures. Also, multilayer coatings adversely affect the mechanical properties of the fibers, the fiber becomes less flexible, difficult to weave. Analysis of the morphology of the coating also shows the advantage of thin, single and several layer coatings over multilayer coatings. According to the images obtained using SEM, multilayer coatings have increased defects, uneven surface and a large number of cracks.

References
[1] Kablov E, Grashchenkov D 2010 Advanced high-temperature ceramic composite materials Russian Chem. Mag. 5
[2] Dham T, Bahl O 1995 Oxidation Protection of Carbon Composites Carbon 33 349–59
[3] Jian H, ZengXie F 2003 Mullite-Al2O3-SiC oxidation protective coating for carbon/carbon composites Carbon 41 2825–9
[4] Tkachenko L., Shaulov A. 2012 Protective heat-resistant coatings of carbon materials Inorg. Mat. 48 261–71
[5] Baosheng X, Changqing H 2015 Preparation of a multi-composition coating for oxidation protection of modified carbon-bonded carbon fiber composites by a rapid sintering method Surf. and Coat. Tehny 270 109–16
[6] Lei Z, Jianfeng H 2018 A novel design of oxidation protective β-Y2Si2O7 nanowire toughened Y2SiO4/Y2O3-Al2O3-SiO2 glass ceramic coating for SiC coated carbon/carbon composite Corros. Scienc. 135 233-42
[7] Zang Y 2009 AntiOxidation Behavior of Alumina Coating on Carbon Fibre by Sol–Gel Adv. Mater. Res. 79 819-22
[8] Landry C, Barron A 1995 MOCVD of Alumina–Silica Oxidation Resistant Coatings on Carbon Fibers Carbon 33 381–7
[9] Mohammad A, Heike H 2016 Thermal and oxidation resistant barrier on carbon fiber with Si–Ti based pre-ceramic coatings for high temperature application Text. Res. J. 3 212-6
[10] Baklanova N.I., Zima T.M., Titov A.T. 2006 Protective coatings for carbon fibers Inorg. Mat. 42
[11] Baklanova N, Zima T, Nimushina T, Kosheev S 2004 The Formation of Refractory Oxide Coatings on NicalonTM Fiber by Sol–Gel Process J. Eur. Ceram. Soc. 24 3139–48
[12] Fatemeh M, Hasmaliza M, Luqman C 2011 Preparation of nano-scale α-Al2O3 powder by the sol-gel method Silikaty 55 378–83
[13] Qiang F, Chuan-Bao C, He-Sun Z 1999 Preparation of alumina films from a new sol–gel route Thin Sol. Film 48 99-102
[14] Naoufal B 2000 New Sol–Gel Route for the Preparation of Pure Alumina at 950°C Ceram. Soc. 83 2324-6
[15] Hu B, Yao M 2014 Preparation of Al2O3 dense films using sol derived from Al(NO3)3·9H2O Mat. tech.: Adv. perf. mat. 29 47-51
[16] Qiu X, Han K 2010 Sol–gel prepared Al2O3 coatings for the application as tritium permeation barrier Fus. engine. and design 85 1068–72
[17] NilguKn O, John P, Yong-Jin Y, Antoni P 1999 Optical properties of sol-gel deposited Al2O3 Sol. Ener. Mat.and Sol. Cells 59 355–66