

INFLUENCE OF OXIDIZING MEDIA ON THE PROPERTIES OF CARBON-BASED FIBROUS MATERIALS WITH PROTECTIVE COATINGS

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A study has been made of the influence of oxidizing media (an air medium and a steam–helium mixture) in heating on the structure and thermooxidation stability of carbon-based fibrous materials with alumina, silica, and silicon-carbide coatings applied to the surface of the fibers. It has been established that determining factors in production of protective films are the adhesive interaction of the reagents with the fiber surface and the regime of their heat treatment. It has been shown that the protective films formed increase the thermooxidation stability of carbon-based fibrous materials 1.5–2 times.

Carbon-based fibrous materials are widely used for production of carbon-filled plastics and carbon–carbon composites [1]. Strong carbon threads, ropes, cords, and cloths are used to create flexible high-temperature heat-insulating materials. However, the stability of carbon-based fibrous materials is insufficiently high in heating in air [2]. Increase in the stability of carbon-based fibrous materials in an oxidizing medium can be ensured by creating protective films of glassy or amorphous structure on the surface of the materials. Protective nitride, oxide, or carbide films are deposited on carbon-based fibrous materials from a gas phase, as a rule; however this technology is distinguished by its complex implementation and makes the production of the material more expensive [3, 4].

The present report seeks to simplify the method of deposition of protective coatings on carbon-based fibrous materials and to evaluate the influence of oxidizing media on the properties of the materials produced.

For the experiment we have selected commercial carbon cloths with a heat-treatment temperature of 900 to 2200°C (UUT-2, Ural T-15, and Ural T-22) and unwoven carbon-based materials (felts) and a rope differing in the texture of the material and the degree of perfection of the fiber surface. Unlike graphite and diamond, the crystal structure of carbon-based fibrous materials is characterized by a two-dimensional order. This structure is based on the basis hexagonal planes which are similar to graphite planes but do not have strictly fixed distances between crystallite layers; such a structure is called turbostratic [5]. As the film-forming reagents we used aqueous solutions of silicosol, alumosol, sodium diethyl silicate, and silicone oligomers by which the carbon-based fibrous materials were impregnated. Then we heat-treated the cloths in an inert atmosphere at prescribed temperatures (Table 1).

The stability of the coated elastic composite materials in heating to 1000°C in air in the dynamic regime was determined by the thermogravimetric method with an MOM Paulik–Paulik–Erdei thermograph. Furthermore, we evaluated the mass loss by the samples of the materials after isothermal annealings carried out in an air atmosphere at temperatures of 700, 800, and 900°C. We studied the kinetics of oxidation of carbon-based materials by steam, placing the samples in the cup of a quartz spiral in a reaction vessel that was introduced into the isothermal zone of heating of a tube furnace. The system was blown with pure helium; a mixture (preheated in a separate furnace to 900°C) of helium and steam in a 1:2 ratio was fed to the reaction vessel after the attainment of a prescribed temperature. Changes in the position of the mark on the quartz spiral were recorded with a KM-6 cathetometer. In each experiment, in addition to the mass loss by the samples, we determined their thermal conductivity and tensile strength before and after the tests and investigated the structure of the coatings on the carbon-based fibrous materials.

In the process of impregnation of the carbon-based materials, the reagents wetted the fiber surface and penetrated into the pores and the capillaries between the fibers. The solvents were removed in subsequent drying, and polymer or hydroxide layers (depending on the reagent used) were formed on the fiber surface; these layers became

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TABLE 1. Starting Materials and Treating Reagents

Sample No.	Carbon-based material (CBM)	Temperature of production of a CBM, °C	Reagents for treatment of a CBM	Temperature of treatment after impregnation, °C
1	Cord cloth	500	Silicosol (4%)	1500
2	»	500	Silicone oligomer (KO-075)	1500
3	»	900	Alumosol (6%)	900
4	Ural T-15 cloth	1500	Silicone oligomer (KO-075)	1200
5	»	1500	Silicosol (15%)	1100
6	Ural T-22 cloth containing 2.5% SiO ₂	2200	Sodium diethyl siliconate	1100
7	Unwoven material containing 10% SiO ₂	1500	Silicone oligomer (KO-815)	1000
8	Unwoven material containing 4% Al ₂ O ₃	2200	Alumosol (4.5%)	1400
9	UUT-2 cloth	900	Alumosol (15%)	1200
10	Rope containing 5% Al ₂ O ₃	1100	Sodium diethyl siliconate	1800

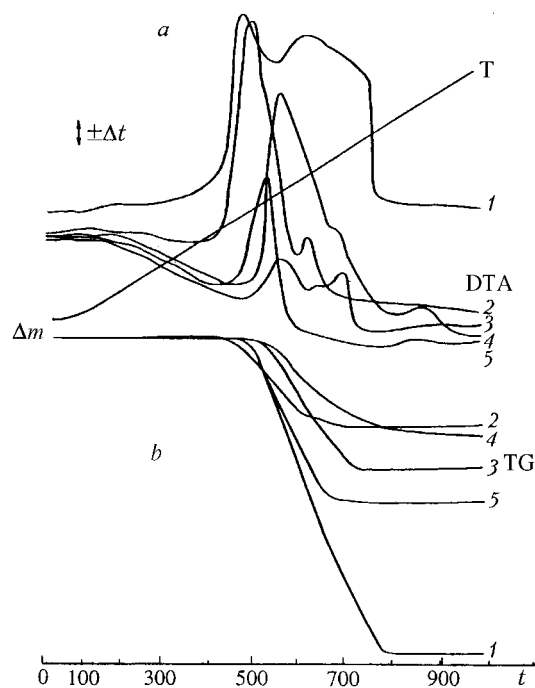


Fig. 1. Derivatograms (a) and thermograms (b) of the process of oxidation in air of carbon-based fibrous materials: 1) without a coating; 2) with a silica coating produced after the treatment with silicosol; 3) dimethyl-dichlorosilane; 4) vinyl-trichlorosilane; 5) tetraethoxysilane (T, temperature curve; DTA, differential curves of temperature analysis; TG, thermogravimetric curves of mass loss by the samples; t , temperature, °C; Δm , change in the mass, mg).

alumina or silica layers in the process of heat treatment in the temperature range 600–1000°C [6]. The structure of the protective coatings on the carbon fibers was x-ray amorphous except for the films produced with the use of sodium diethyl siliconate with a catalyst of tetrabutoxytitanium polymerization. The latter caused partial crystallization of silica in the α -tridymite phase in the process of heat treatment of the samples at 900°C. In the temperature range 1200–1400°C, the siliceous coatings interacted with the carbon fibers forming oxycarbide or silicon carbide on their surface. In heating to 600°C, the coatings on the alumosol fibers became those of amorphously structured metal

TABLE 2. Properties of Carbon-Based Materials before and after the Tests

Sample No.	Breaking load (on the base) before the tests, N	Thermal conductivity, W/(m ² ·K)	Mass loss after the tests, g/(m ² ·sec)				Breaking load (on the base) after the tests in a steam–helium atmosphere, N
			in air at temperatures, °C			in a steam–helium atmosphere at 900°C	
			700	800	900		
1	808	0.146	0.041	0.062	0.093	0.008	775
2	925	0.128	0.050	0.071	0.085	0.009	873
3	1195	0.168	0.049	0.071	0.106	0.010	1123
4	1530	0.135	0.077	0.088	0.075	0.095	1450
5	1367	0.159	0.047	0.058	0.092	0.006	1355
6	1786	0.197	0.037	0.049	0.085	0.003	1765
7	152	0.062	0.050	0.071	0.104	0.009	127
8	165	0.090	0.075	0.095	0.110	0.085	137
9	1200	0.143	0.033	0.068	0.100	0.007	1100
10	170	0.160	0.064	0.087	0.112	0.011	152
UUT-2	1006	0.147	0.160	0.250	0.538	0.021	451
Ural T-15	1235	0.167	0.145	0.193	0.443	0.020	565
Ural T-22	1500	0.210	0.090	0.160	0.238	0.019	614

Note. Numbers of samples in the tables coincide.

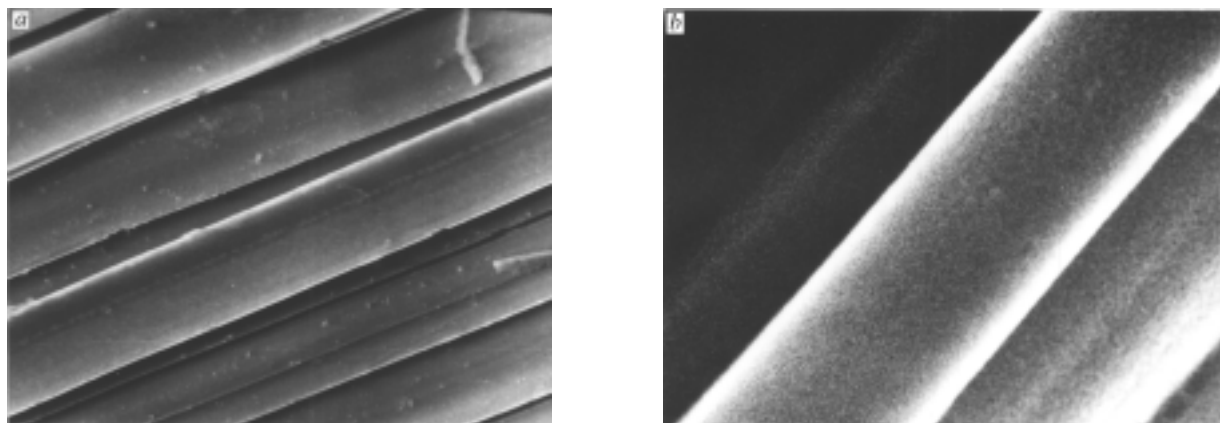


Fig. 2. Microstructure of the fibers of Ural T-15 carbon cloth with a silicosol coating before (a) and after the test in a steam–helium atmosphere at 900°C

oxide, which crystallized in the γ phase at 900°C, and as the heat-treatment temperature increased to 1200°C, Al₂O₃ acquired the structure of α corundum.

The analysis of the results obtained has shown that in all cases the elastic carbon compositions with coatings were more stable to the action of the oxidizing atmosphere than the initial commercial materials (Fig. 1). The rupture strength of the samples of the coated compositions, tested for 2 h at 900°C in a steam–helium-mixture flow, decreased by 1–8% in the cloths and by 16–17% in the unwoven felts, whereas in the unprotected carbon-based materials it decreased more than twice (Table 2). A direct dependence of the stability of the carbon-based materials on the heat-treatment temperature and the density of protective coatings was clearly tracked. The density was determined by the adhesive interaction of the fiber surface with the reagents and by the conditions of subsequent heat treatment, as a result of which a protective layer of highly dispersed particles of alumina, silica, or silicon carbide was formed.

The x-ray phase and electron-microscopic investigations of the coatings of silicosol, almosol, and silicone oligomers have shown that they had an x-ray amorphous structure after the action of the gas atmosphere of helium and steam, whereas the carbon of the fibrous materials retained its initial turbostratic structure. In the case of deposition of

sodium diethyl siliconate on the carbon fibers of the coatings, the protective SiO₂ layer formed after the action of the steam–helium jet had the structure of α cristobalite (sample 6), which caused a partial flexibility loss by the material but increased its rigidity and strength. Figure 2 gives microphotographs of the surface of the fibers of Ural T-15 cloth with a coating of highly dispersed silicon-carbide particles (sample 4). The investigation has confirmed that the coating did not fail after the tests in the steam–helium mixture. The best indices of strength after testing in an oxidizing atmosphere were exhibited by the samples of carbon cloths heat-treated in the temperature range 1500–2200°C and coated with silica (which became silicon carbide after the heat treatment) (samples 4–6) and the fibers with a protective alumina film (samples 3 and 9). After the analogous tests of the samples of unprotected commercial carbon-based fibrous materials (UUT-2, Ural T-15, and Ural T-22), their strength amounted to 40.9–45% of the initial value; it amounted to 83.0–91.0% in the unwoven materials and the rope with coatings (samples 7, 8, and 10) and to 91.7–99.0% in the cord cloths with protective coatings.

Thus, the investigation of the thermooxidation stability of elastic carbon-based fibrous materials with deposited coatings of alumina, silica, and silicon carbide has shown that the protective coatings formed (consisting of highly dispersed grains) and their x-ray amorphous structure contribute to the retention of elasticity by carbon-based materials and increase their chemical stability in oxidizing media 1.5–2 times.

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