Metallic coating technologies for carbon fabrics and methods for assessing their quality

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Abstract. The results of experimental analyses of the properties of carbon tapes (and filaments) after the application of metal coatings on them are presented. Various methods have been investigated for pre-cleaning the surface of carbon tapes and fabrics before applying a metallic coating thereon. A magnetron sputtering method was used to apply the metallic coating. An algorithm has been developed that allows determining the method of pre-cleaning carbon tape before its metallization. An adhesive test method was used as a criterion, allowing to determine the adhesion strength of the metallic coating to the carbon tape. An algorithm has been developed that allows determining the modes of applying metallic coatings on a carbon tape. Modes of applying metallic coatings on carbon tapes have been developed.

Keywords: carbon tape, elementary thread, metal coating, sputtering modes.

Introduction
Carbon fabrics, tapes and fibers are widely used as reinforcing materials in the manufacture of rocket and space technology products, aircraft industry, automotive industry and many other industries, due to their high specific characteristics, unique thermal and operational properties [1, 2]. In recent years, new binders have been created that allow creation of carbon plastics with higher mechanical properties, including increased strength for interlayer shear [3,4], new theoretical [5-7] and experimental methods for evaluating their properties [8-10].

To impart functional properties to CFRPs, technologies are used to apply thin metallic coatings to the surface of carbon fabrics [11, 12]. The main purpose of metallization is to change the microstructure and physicochemical properties of the surface of carbon fabrics, which allows to regulate their reactivity, wear resistance, thermal and electrophysical properties, biocompatibility, etc. [13].

Metallization occurs as a result of chemical (or electrochemical) reactions from aqueous solutions. A typical technological process of metallization of fabrics consists of the operations of degreasing the surface, etching, sensitization, activation and direct deposition of the coating. The thickness of metal coatings using electrochemical metallization can vary from tenths of a micrometer to several micrometers [14]. If instead of the electrochemical method, a chemical method is used, then it is possible to obtain coatings from units of nanometers to several microns [15]. Another method of metallization of fabrics is sputtering technology, in which the metal is initially converted into a gaseous or liquid state, and then transferred to the surface of the fabric, where it turns into a solid material, forming a metal coating.

The main methods of sputtering are: vacuum, plasma and gas plasma [15, 16]. During vacuum
sputtering, the material is heated in any inert medium, it passes into a gaseous state and then condenses on the surface of the fabric. When using this technology, coatings of any composition can be applied. When using plasma or gas-plasma sputtering, an electric arc arises between a pair of electrodes. An inert gas is injected into its combustion zone that can ionize to form a plasma. The powder of the applied metal enters the plasma jet, which melts and transfers to the substrate, which is fabric. The method of magnetron sputtering is widespread, and its modern modification - reactive magnetron sputtering. Using modern sputtering plants, coatings of various thickness and composition can be obtained. Before applying metallic coatings on the surface of metal fabrics, it is necessary to carry out their preliminary cleaning, the main purpose of which is to remove various types of contaminants from the surface, which according to a number of specialists [14] will increase the adhesive strength of adhesion of the metal coating to the fabric. The purpose of this paper is to develop a technology for activating the surface of a carbon tape and a technology for applying a metal coating on its surface.

**Objects and Methodology**

The research objects are carbon fabric ТВЧ 2/2 312-10 and carbon tape LUP and FibArm Tape-230/300, on which metal coatings of stainless steel 12X18H10T and titanium were applied by way of magnetron sputtering. We used three methods of activating the surface of the carbon tape:

1) processing with xenon lamp INP7 / 120;
2) processing on a special unit, plasma activation of the YIIM-500;
3) processing directly in the chamber of the magnetron sputtering unit.

For each of these three activation methods, the magnitude of the discharge current, the pressure, and the duration of the treatment were varied as treatment modes. The processing of all samples of carbon tape was performed from two sides.

The duration of treatment in the air plasma ranged from 10 seconds to 3 minutes. The pressure was from 10 to 100 MPa. The total complexity of processing (along with the process of installing the sample and creating a vacuum) was 15 minutes.

When using the “Betta-One-2” unit, only the duration of exposure was varied from 1 to 10 min, which corresponded to doses of 1 min - 240 mJ / cm²; 3 min - 720 mJ / cm², etc.

As the main criterion for the quality of the pretreatment, the strength characteristic of the filament after processing carbon fabrics and ribbons was used, the value of which should not be lower than for the initial one.

To carry out mechanical tests, the reinforcing filler was divided into filaments, which were tested on a Favimat + Textechno tensile testing machine. A feature of this equipment was its high accuracy and the possibility, along with the magnitude of the breaking stress under tension, elongation and modulus, also to determine the diameter of the filaments and the linear density. Only those samples that had no external damage to the carbon reinforcing fillers were subjected to mechanical testing. The thickness of the coating was determined directly on the filament using an atomic force microscope of the brand SOLVER47PRO.
The deposition of thin films of metallic coatings of titanium and stainless on samples of carbon tapes was carried out in a laboratory magnetron sputtering unit MIR-2. The diameter of all targets was 130 mm, the size of the chamber made it possible to process samples of carbon tapes 210 × 297 mm in size. The quality of the adhesion of the metallic coating to the carbon tape was assessed by adhesive tape test (ASTMD3359).

Results and discussion
The algorithm for choosing a technique for treating carbon fabric before applying a metal coating thereon is shown in Fig.1. Table 1 shows the average values of the breaking stress (σ) and the diameter of the filaments for all used processing modes.

Fig.1. Algorithm for selecting carbon tape activation modes before plating
Table 1. Properties of filaments before and after processing the ТВЧ 2/2 312-10 carbon fabric

| Item No. | Modes of processing | Destructive stress, \( \sigma \) (MPa) | Diameter of the elementary thread (\( \mu \)) |
|----------|---------------------|--------------------------------------|----------------------------------|
| 1        | Original            | 1850                                 | 5.98                             |
| 2        | “Betta-One-2” unit, lamp irradiation for 10 min | 1750                                 | 5.96                             |
| 3        | 5 min               | 1800                                 | 5.97                             |
| 4        | 3 min               | 1850                                 | 5.97                             |
| 5        | 1 min               | 1850                                 | 5.97                             |
| 6        | YTIM-500 unit, irradiation in the air plasma 5 min | 1400                                 | 5.24                             |
| 7        | 4 min               | 1600                                 | 5.33                             |
| 8        | 3 min               | 1750                                 | 5.95                             |
| 9        | 1 min               | 1750                                 | 6.01                             |
| 10       | 30 sec              | 1800                                 | 5.95                             |
| 11       | 10 sec              | 1800                                 | 5.97                             |
| 12       | Bulat-6 unit, processing in argon 5 min | 950                                  | 4.82                             |
| 13       | 3 min               | 1200                                 | 5.22                             |
| 14       | 1 min               | 1400                                 | 5.89                             |

An analysis of the results showed that processing on Bulat-6 units for more than 1 minute and on the YTIM-500 units for more than 3 minutes results in a significant decrease in the strength of the filament and a decrease in its diameter. However, the fact of a change in the strength characteristics indicates a relationship between the type and duration of treatment and the properties of the carbon tape. Surface treatment of carbon fabric ТВЧ 2/2 312-10 using “Bette-One-2” unit does not change the mechanical characteristics of the filament, which is an indirect confirmation that this type of treatment is not at all effective, because it has no effect on the surface of the carbon fabric.

Following the results of the analyses, for the activation of carbon fabric surface, the best results were shown by modes No. 8-11 (using the YTIM-500 unit) and mode 14 (using the Bulat unit), which were used in further work to prepare the surface of all the used adhesive tapes before applying of metallic coatings on them.

Using the activation mode found, metal coatings were applied to carbon tapes. Sputtering was performed under the following modes: Plasma gas pressure (Ar) 1.3x10-3-1.8x10-3tor, discharge current 2-4 A, sputtering time 2-3 min. Argon was used as a plasma gas. The algorithm for determining the metallization modes is shown in Fig. 2.
Fig. 2. Algorithm for determining the modes of metallization
The pressure range of the plasma gas (argon) was determined from the following considerations: at pressures below 1.3x10^-3 tor, the plasma around the target cathode becomes unstable, which adversely affects the quality of the coatings. When argon pressures are higher than 1.8x10^-3 tor, the deposited metal films become loose, which significantly impairs their adhesion and the quality of metal coatings. As a result of the tests, it was found that the discharge current should not be higher than 2-4 amperes, since at a lower current, the adhesion of the coating to the substrate is deteriorated (assessed by the method of adhesive tape test), and the deposition rate also decreases, the value of which is directly proportional to the discharge current. An increase in current leads to overheating of the substrate, which leads to its deterioration or to a significant increase in gas evolution, which significantly degrades the quality of coatings. Spray time varied in the range of 2-3 minutes. Reducing the sputtering time led to the formation of a non-continuous metal film, and with increasing duration, the thickness of the coatings increased.

The total duration of metallization of one sample from one side on the unit MIR-2 was 2.5 hours. Most of the time (2 hours) was required on the creation of a vacuum, not more than 1 minute, was spent on the flow of argon, the duration of deposition depended on the mode and ranged from 5 seconds to 5 minutes.

The results of the adhesive tape test are given in table 2. The test was performed using a graphite plate, the surface of which was prepared in various ways before titanium was sprayed onto it, as well as directly on carbon tapes LUP and FibArm Tape-230300 and carbon fabric ТВЧ 2/2 312-10

| Surface preparation technology and type of coating | % removed area of the total coverage area |
|---------------------------------------------------|------------------------------------------|
| Graphite plate, titanium coating                   |                                          |
| Without prior preparation                         | 30-35                                    |
| Cleaning in the unit ЮПМ-500 –1 min               | 5-10                                     |
| Cleaning in the unit ЮПМ-500 –2 min               | 3-5                                      |
| Cleaning in the unit ЮПМ-500 –10 min              | < 1                                      |

| Graphite plate, stainless steel coating            |                                          |
| Without prior preparation                         | 10-20                                    |
| Cleaning in the unit ЮПМ-500 –2 min               | 1-3                                      |

| Carbon fabric ТВЧ 2/2 312-10                      |                                          |
| Without prior preparation, coating of titanium    | 70-90                                    |
| Cleaning in the unit ЮПМ-500 –3 min, coating of titanium | 10-20                                    |
| Without prior preparation, coating of stainless steel | 30-50                                    |
| Cleaning in the unit ЮПМ-500 –3 min, coating of stainless steel | 10-20                                    |

| Carbon tape LUP                                   |                                          |
| Without prior preparation, coating of titanium    | 60-80                                    |
| Cleaning in the unit ЮПМ-500 –3 min, coating of titanium | 15-20                                    |
| Without prior preparation, coating of stainless steel | 40-60                                    |
Cleaning in the unit УПМ-500 −3 min, coating of
stainless steel

| Carbon tape FibArm Tape-230 | 300 |

Cleaning in the unit УПМ-500 −3 min, coating of
titanium

| Without prior preparation, coating of |
| 70-80 |

Cleaning in the unit УПМ-500 −3 min, coating of
titanium

| Without prior preparation, coating of |
| 60-75 |

Cleaning in the unit УПМ-500 −3 min, coating of
stainless steel

| 10-30 |

The results of the adhesion test using the adhesive tape test showed that the adhesive strength of the stainless steel coating is somewhat higher than for titanium. Comparison of two carbon tapes with each other showed that the adhesion strength of metal coatings with carbon tape of LUP is higher than with Fibra tape, but lower than with carbon fiber fabric 2/2 312-10. For all investigated coatings and carbon fabrics and tapes, surface activation before metallization

Conclusions

An algorithm and a pretreatment mode for carbon tape before metallization, as well as an algorithm and modes for applying metallic coatings, have been developed. As a result of the research it was found that to activate the surface of the carbon tape, it is advisable to process them on the УПМ-500 unit (irradiation in air plasma) for 1-3 minutes immediately before applying metal coatings.

When working out the coating modes on the installation of a magnetron sputtering MIR, it was found that the discharge current should not be higher - 4 amperes, and the sputtering time should not exceed 2-3 minutes. When the current decreases below 2 amps, the adhesion strength of the metal coating to the carbon tape deteriorates, and the deposition rate also decreases, the magnitude of which is directly proportional to the discharge current. An increase in current leads to overheating of the substrate and to a decrease in the uniformity of the metallic coating. A decrease in the duration of the deposition of coatings below 2 min of sputtering led to the formation of a non-continuous metal film, and with an increase in the duration, the thickness of the coatings increased.

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