Ion-plasma modification of the surface of light fiber materials

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Abstract. The results of experimental study of the irradiation under 30 keV Ar⁺ with the temperature ~250 °C of viscose based carbon cloth TGN-2MK and SU-2500 glassy carbon are presented. According to the scanning electron microscopy and Raman spectroscopy, modified layer of TGN-2MK obtained by ion irradiation is similar of modified layer of the glassy carbon in the structure and morphology. The formation of nanoscale wall in both cases occurs during graphitization under conditions of dynamic annealing of radiation damage.

1. Introduction
The development of composite materials with a combination of low mass and a high level of physical and mechanical properties has a significant interest for the aerospace industry. A promising approach in this direction is the development of metal matrix and polymer systems reinforced with fibers [1]. From the perspective of improving the mass performance of such composites with a simultaneous increase in the value of their consumer characteristics, it seems reasonable to use the fibers of light and ultra-light materials, which directly relate to the carbon and magnesium-based alloys.

There is a direct correlation between the adhesion force in the reinforcement additive – matrix system and the total surface of the reinforcement additive: the higher the specific surface, the stronger the bonds. The metal and carbon fibers obtained by different methods are usually characterized by a relatively smooth surface, which requires additional modification to increase the specific surface area. The formation of a modified surface of metal and carbon fibers is also beneficial for catalytic and electrophysical properties [2, 3].

There are various approaches to solving the problem of the surface morphology changing of fiber materials to increase their adhesive strength with the composite matrix, including oxidation and structurization at the nanoscale size. In this range, ion-plasma and ion-beam processing methods are particularly promising as the most effective ways to modify and structure the surface of materials, resulting in the formation of micro- and nanoscale morphological elements [4–6]. In particular, one of the results of such exposure is an increase in specific surface area, which is important for many applications of fiber materials. Thus, after plasma electrolyte treatment of light magnesium alloy
fibers, their specific surface increased by more than two orders of magnitude [4]. The impact of accelerated ion beams also leads to similar results. Thus, the ion-induced corrugation of the carbon fiber surface based on polyacrylonitrile (PAN) also increased the specific surface area by more than a hundred times [6]. At the same time, the ion-induced morphology of the carbon fibers surface from PAN and viscose may differ drastically. It follows, for example, from comparison of SEM of irradiated carbon fiber of "Busofit" textile based on viscose, which shows formation of nanoscale structure [7] and carbon fiber VMN-4 from PAN [5]. The difference can be explained by the different nanostructure of these carbon fibers, which generally contain a textured graphite-like shell and a core similar to a glassy carbon [8]. The present work is devoted to comparison of ion-beam modification of thearbon fibers based on viscose and glassy carbon.

2. Experimental
In the experiment we used samples of TGN-2MK carbon fiber cloth based on viscose with the final temperature of heat treatment 2400 °C, and SU-2500 glassy carbon with the final temperature of heat treatment of 2500 °C. Irradiation was carried out with 30 keV Ar⁺ ions at normal incidence to the axis of the fibers on a mass-monochromator of the Scobeltsyn Institute of Nuclear Physics, Moscow State University [9], by the method similar to [5, 6]. The temperature of the targets was ~250 °C and above the temperature of dynamic annealing of radiation damage in the carbon materials. The ion current density was 0.2–0.4 mA/cm² with a beam cross section of 0.3 cm² and the irradiation fluence was ~3·10¹⁸ cm⁻². Before and after irradiation the surface of materials was studied using the scanning electron microscope (SEM) LEO1430-vp and Raman spectroscopy on Horiba Yvon T64000 with the laser excitation wavelength 514.5 nm.

3. Results and discussion
Figure 1 shows SEM images of TGN-2M carbon fiber and SU-2500 glassy carbon after 30 keV Ar⁺ irradiation. In both cases, the formation of the nanocellular structures with nanoscale walls 150–300 nm thick are observed. Typical for glassy carbon association of nanowalls into the nodes [10] for carbon fiber is practically not observed. The formation of such surface patterns can be associated with the radiation-induced shrinkage of porous fibers and glassy carbon and the formation of stationary pore profiles with steep walls at physical sputtering.

(a) TGN-2MK

(b) SU-2500

![SEM images](image-url)

**Figure 1.** SEM images after 30 keV Ar⁺ ion irradiation of carbon fiber based on viscose (a) and SU-2500 glassy carbon (b) at temperatures of irradiation 250 °C.
The microstructure of modified layer has been studied by Raman spectroscopy. Raman spectra of non-irradiated and 30 keV Ar⁺ ion irradiated viscose based carbon fiber cloth TGN-2MK and SU-2500 at temperature 250 °C are presented in figure 2.

Figure 2. Raman spectra of non-irradiated and 30 keV Ar⁺ ion irradiated at temperature ~250 °C viscose based carbon fiber cloth TGN-2MK (a) and glassy carbon SU-2500 (b).

The Raman spectra of non-irradiated samples contain two main peaks in the first order: the G peak (graphite peak) at Raman shift ~1590 cm⁻¹ and the D peak due to imperfection of the crystal structure at ~1345 cm⁻¹. Ion irradiation for both types of the material leads to an increase in G-peak intensity compared to D-peak. Such Raman spectra are characteristic of the graphites with a significant level of radiation damage [11]. Thus, the dynamic annealing of radiation damage occurring at a temperature of 250 °C leads to ion-induced graphitization of fibrillar carbon fiber and globular glassy carbon.

4. Conclusions
The comparison of surface morphology and Raman spectra for viscose based carbon fiber cloth TGN-2MK and glassy carbon SU-2500 after high fluence 30 keV Ar⁺ irradiated at temperature ~250 °C was carried out.

SEM images of the carbon fibers and glassy carbon show the similarity of ion-induced surface morphology. In both cases, the formation of the nanocellular structures with nanoscale walls 150–300 nm thick are observed.

In Raman spectra, there is an increase in G-peak intensity compared to D-peak for both types of material, which can be connected with ion-induced graphitization of fibrillar carbon fiber and globular glassy carbon.

Acknowledgments
The reported study was funded by RFBR and NSFC according to the research project №20-58-53023/20.

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