Ion-beam modification of carbon textile Busofit T-040

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Abstract. The results of the study of ion-beam modification of the carbon fiber surface of
Busofit T-040 carbon textile using a 30 keV argon ion beam separated and unseparated by
mass have been presented. Scanning electron microscopy showed a significant ion-induced
change in the morphology from the smooth fiber surface to a developed surface with the
nanowalls of submicron height. Ion irradiation has led to significant changes in the
Raman spectra, showing the formation of a graphite-like surface layer.

1. Introduction

Plasma and ion-beam processing are effective methods of modifying carbon materials leading to a
change in morphology and an increase in the specific surface area. The studies of the effect of ion
irradiation on carbon fiber which are actual for practical applications show a significant difference in
ion-induced morphology of the carbon fibers based on polyacrylonitrile (PAN) and viscose ones [1]. A
comparative experiment with high-fluence 30 keV argon ion irradiation showed that for a carbon fiber
based on a PAN fiber a formation of ion-induced submicron corrugated structure was specific,
whereas a similar impact on a viscose-based carbon fiber led to a porous spongy structure with thin
walls. In [1] the carbon fibers were part of carbon-carbon and carbon-ceramic composites.

The present work has been dedicated to ion-beam modification of viscose-based carbon fiber of
Busofit T-040 textile which is promising for use in the supercapacitors (SC) and lithium-ion batteries
(LIB) structures [2, 3]. Accordingly [2], Busofit T-040 has a high specific capacity per unit surface
area of 3.4 F/cm², and this characteristic is combined with a sufficiently high capacity per unit mass of
145 F/g. Close to the rectangular shape of the volt-farad cyclic curves indicates the absence of faradaic
redox reactions as well as the high degree of reversibility of electrode processes occurring in charging
and discharging of the SC. Various methods of the surface modifying of electrode structures are used
to increase the specific capacitance and energy characteristics of SC. In particular, thin films of
transition metals and their oxides [3, 4] as well as conductive polymers (polyaniline, polypyrrole,
polythiophenes) [2, 5] are used.

2. Experimental

The samples of carbon textile Busofit T-040 produced by “Svetlogorsk-Khimvolokno” (Svetlogorsk,
Belarus) were used for ion-beam modification. Irradiation with 30 keV argon ions was carried out at
normal incidence on the textile surface using the mass-monochromator of the Skobeltsyn Institute of Nuclear Physics of Moscow State University [6]. The separated by mass ion current flux was 0.4 mA/cm² with the beam cross section of 0.3 cm², an irradiation fluence was of ~$10^{19}$ ion/cm². The target temperature was of 200 °C and controlled by a chromel-alumel thermocouple. According to the review [7], this temperature exceeds the temperature of the dynamic annealing of radiation damage that lead to the amorphization of the surface of carbon based materials such as graphites, glassy carbons, carbon fibers of carbon-carbon and carbon-ceramic composites.

The diameter of a homogeneous non-separated ion beam was more than 50 mm. The ion current to the target was 5–10 mA at an accelerating voltage of 30 kV. Targets from the textile Busofit T-040 were installed in aluminum 30×35 mm frame on the path of the non-separated beam. The irradiation was carried out along the normal to the plane of the frame. The target during the irradiation was heated to a temperature of at least of 200 °C. The use of a non-separated wide-aperture ion beam increases the productivity of ion treatment by two orders of magnitude in comparison with the separated beam. The morphology of the surface of the fibers before and after irradiation was analyzed with a Lyra 3 TESCAN scanning electron microscope. Structural studies were carried out on a Horiba Yvon T64000 by Raman spectroscopy with laser excitation wavelength of 514 nm and beam power of 0.1 mW.

3. Results and discussion
Figure 1 shows SEM images of carbon fibers of Busofit T-040 textile before and after irradiation of mass-separated and non-separated of 30 keV argon ion beams.

![Figure 1. SEM-images of carbon fiber of Busofit T-040 textile before (a) and after irradiation by mass-separated (b) and non-separated (c), (d) of 30 keV argon ion beam.](image-url)
Before irradiation open pores of up to 0.5 μm in size are observed on a relatively smooth fiber surface. Ion-beam treatment leads to a significant change in the surface morphology. After irradiation with a mass-separated ion beam the surface has been covered with thin-walled ridges of submicron height close to the known nanowall structures [8], figure 1(b). Processing with a non-separated beam leads to the same morphology, figure 1(d), as well as to the structure of submicron whiskers with large surface density, figure 1(c). The founded ion-beam modification of the fiber surface of Busofit T-040 textile may be of interest for increasing the characteristics of the SC and LIB electrode structures, taking into account the results of application of nanowall structures for these purposes and necessity for development of the surface relief for thin-film structures [2, 4, 5].

Ion irradiation leads both to a significant development of the relief, and to an improvement in the crystal structure of the Busofit T-040 fiber surface. This is evidenced by the comparison of the Raman spectra before and after ion irradiation. It is known that Raman spectra of graphite-like materials contain two main peaks: the G peak (graphite peak) at the Raman shift $\Delta k = \lambda_L^{-1} - \lambda_R^{-1}$ close to 1580 cm$^{-1}$ and the D peak due to the lattice defects at $\Delta k \approx 1355$ cm$^{-1}$, see, for example [9]. The Raman spectra reflect the processes of thermal treatment of the hydrocellulose and polyacrylonitrile fibers when processing respectively to these fibers [10, 11].

Figure 2 shows that the maxima of the D- and G-bands (1353 and 1583 cm$^{-1}$) in the Raman spectra for irradiated fibers differ markedly from the positions of the maxima in the spectra for the non-irradiated fiber (1334 and 1598 cm$^{-1}$) and shifted toward frequencies specific for graphitized materials with D- and G-bands at ~1355 cm$^{-1}$ and ~1580 cm$^{-1}$. An analogous shift of the G-band can be seen from the evolution of Raman spectra with an increase in the temperature of carbon fiber heat treatment leading to a perfect textured graphite shell of PAN based carbon fiber [9]. It can also be seen from figure 2 that the band at ~1212 cm$^{-1}$ responsible for the presence of $sp^2$ carbon bonds becomes less expressed after ion irradiation.

![Figure 2. Raman spectra of carbon fiber of Busofit T-040 textile before and after irradiation with 30keV argon mass-separated ion beam.](image)

Thus, Raman spectroscopy shows that ion irradiation leads to a transformation of the initially supramolecular structure of the fiber into a graphite-like structure. This is also indicated by a multiple decrease in the layer Ohmic resistance of irradiated carbon textile. The latter is one of the important factors in the quality of SC and LIB electrode structures.

4. Conclusions
The study of ion-beam modification of the viscose-based carbon fiber surface of Busofit T-040 carbon textile with 30 keV separated and non-separated by mass argon ions showed the possibility of a significant ion-induced change in the morphology of the fiber surface from a practically smooth to developed surface of nanowalls and whiskers of submicron height. Changes in the Raman spectra indicate the formation of a graphite-like surface layer.
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