Effect of carbon fiber nanostructure on surface morphology under high-fluence ion irradiation

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Abstract. The results of experimental study of the surface nano- and microstructuring of polyacrylonitrile (PAN) based carbon fiber VMN-4 and viscose based carbon cloth TGN-2MK under 30 keV Ar⁺ irradiation are presented. Scanning electron microscopy shows a strong difference in evolution of ion-induced morphology for these two carbon fiber types. At sufficiently high fluences, a corrugated morphology is formed on the PAN based carbon fiber, while a network of nanowalls is formed on the viscose based carbon fiber. The found differences are associated with a significant effect of the structure of the surface layer of carbon fiber on ion-induced dimensional changes.

1. Introduction

Ion-beam methods are used to form micro- and nanosize elements on the surface of carbon materials [1–3]. High-fluence ion irradiation of carbon fibers depending on irradiation temperature leads to the amorphization, recrystallization and formation of surface topography, including the fiber surface corrugation [2]. The present work considers the processes of formation and evolution of surface topography under ion irradiation in conditions of the dynamic annealing of radiation damage at elevated temperatures of polyacrylonitrile (PAN) and viscose based carbon fibers with significantly different nanostructure of the fiber surface [4].

The graphitized viscose based carbon fibers are characterized by almost complete absence of oriented layers on the surface. This significantly separates them from PAN based carbon fibers, whose layered shell contains large crystallites with a dominant orientation of the crystallographic axis c along the fiber radius [5]. For the graphite materials, the dynamic annealing of radiation damage begins from 150 to 200 °C depending on the ion species [3]. Under these conditions, changes in the topography of the fiber surface are associated with the anisotropic radiation-induced plastic processes of dimensional changes in carbon materials [5], including twinning and sputtering of the carbon fibers during the ion irradiation [6].
2. Experimental
The targets were VMN-4 carbon fibers thread based on the PAN fibers and a TGN-2MK carbon fiber cloth based on viscose carbon fibers. 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 [7]. The temperature of the targets was ≥ 200 °C. The experimental technique was similar to that used in. The ion current density was 0.2–0.4 mA/cm² with a beam cross section of 0.3 cm². The irradiation fluence reached the order of magnitude of 10¹⁹ cm⁻² in the epicenter of the irradiated zone and exponentially decreased at the periphery. Structural and morphological investigations of the carbon fibers before and after irradiation were carried out using scanning electron microscopy (SEM) with a Lyra 3 Tescan microscope and Raman spectroscopy with Horiba Yvon T64000.

3. Results and discussion
The analysis of SEM-images (figure 1) shows that irradiation of the carbon fibers based on PAN and viscose leads to the different types of ion-induced morphology depending on the irradiation fluence, i.e. at the given ion energy and irradiation temperature the threshold character of micro- and nanostructuring of the surface is observed as a result of structural difference in the types of carbon fiber prepggs.

![Figure 1](image_url)

**Figure 1.** Varieties of ion-induced morphology on carbon fibers from PAN (VMN-4) and viscose (TGN-2MK).

At the fluence of irradiation ≤ 10¹⁸ cm⁻² on the surface of carbon fiber from PAN nanosize conical elements are formed on the original longitudinal texture ridges that parallel to an axis of the fiber. The irradiation of carbon fiber from viscose at fluence ≤ 10¹⁸ cm⁻² leads to the randomly directed nanosize ridge structures on the whole surface. At the increase of the irradiation fluence on the carbon fiber from PAN, the conical elements increase in size, unite and transforming through the growth of ribs perpendicular to the fiber axis into submicron corrugations with the angles corresponding to the angles of graphite twinning, which is typical for high fluence irradiation [1, 2, 6, 8, 9]. For the carbon fibers from viscose, the increase in irradiation fluence leads to the sputtering of ridge structures and formation of mesh topography with the nanoscale walls.
A detailed study of the topography of PAN based carbon fibers with an increase in the irradiation fluence is described in [9]. It is noted that for the processes of formation of a nanoscale topography on the surface is required a much lower threshold of radiation damage than for corrugation. At the same time, the centers of growth are most often intergranular boundaries with the nanosize structure. The same situation is probably applicable to the viscose based carbon fiber shell, the only difference being that the growth centers are located randomly. It is known that for PAN based carbon fibers hexagonal planes are oriented at a small angle to the fiber axis, while for viscose carbon fibers crystallites are oriented at large angles [5, 10], which provides favorable conditions for the pores formation under ion irradiation, see SEM for TGN-2MK at fluence $\leq 10^{18}$ ion/cm$^2$ in figure 1. For the carbon materials, the pores formation is associated with the loose packing of crystallites [4]. It is connected with the distortions of carbon layers periphery, i.e. with the decrease of ordering to the crystallite periphery.

Taking into account the difference in nanostructures on the surface, one can trace the difference in the structure of the viscose fiber shell and its core when the irradiation fluence increases. The heterogeneity of the fiber structure and on the other hand the general low level of perfection of the viscose fiber structure in comparison with PAN carbon fibers cause the presence of two types of ion-induced nanoscale topography. One can see, the network of nanowalls is formed on the fiber surface, when shell with nanoscale ridge structures have been sputtered at sufficiently large irradiation fluences.

SEM images of carbon fiber from viscose show the similarity of its nanoscale morphology and glassy carbon surface morphology after high fluence irradiation [3]. In both cases, the formation of the nanocellular structures with nanoscale walls 150–300 nm thick are observed, cf. figure 1 with figure 6b in [3]. It is known that the ion-induced shrinkage with compaction of surface layer is observed for the irradiation of glassy carbons [11]. It is possible to assume, that at ion fluences $\geq 3 \cdot 10^{18}$ cm$^{-2}$ because of the ion-induced shrinkage and sputtering the formation of nanocellular structure with nanosized walls takes place.

The analogy with the nanostructure of glassy carbons is also confirmed by the fact that the Raman spectra of non-irradiated carbon fibers from viscose (see figure 2) have similarity with those of non-irradiated low-temperature glassy carbon, cf. with figure 3 in [12].

The Raman spectrum of Ar$^+$ ion irradiated viscose based carbon fiber shows the presence of the dynamically annealed graphite structure, which has a correlation with the processes of dynamic annealing on glassy carbons [12].
4. Conclusions
The modification of the surface of graphitized carbon fibers from PAN and viscose by 30 keV Ar$^+$ irradiation at the temperature of at 200 °C has been experimentally studied. Scanning electron microscopy shows a strong difference of ion-induced morphology with irradiation fluences for these two types carbon fibers.

For the PAN based carbon fibers, the changing of the surface morphology with the irradiation fluence involves a sequential transformation of the nanosized ion-induced structure into a submicron corrugation.

For the viscose based carbon fiber two stages of formation of nanoscale morphology are observed. The change in the type of ion-induced surface morphology may be connected with the less perfect structure both of the fiber shell and core. After shell sputtering at sufficiently large irradiation fluences, a network of nanowalls is formed on the fiber surface.

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