Surface nanostructure evolution in carbon fiber under ion-induced corrugation

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Abstract. The results of experimental study of the morphology evolution of carbon fiber VMN-4 based on PAN fiber depending on 30 keV Ar⁺ irradiation with exponential fluence decrease from center to periphery of ion beam spot on the target are presented and discussed. Scanning electron microscopy show a strong influence of ion fluence on the morphology, expressed by the transformation of nanoscale conical elements in a submicron corrugated structure.

1. Introduction
Ion beam treatment is an effective method for modifying the surface of carbon materials, leading to the formation of micro and nanoscale elements on the surface [1, 2]. Thus, high-fluence ion irradiation of carbon fibers based on PAN, depending on the irradiation temperature $T$ and the level of the radiation damage determined by the number $\nu$ of displacements per atom ($dpa$), leads to the processes of amorphization, recrystallization, and development of surface topography in the form of corrugation [2]. The formation of prismatic elements (corrugations) on the surface of the carbon fiber occurs at $T > T_a$, where the temperature of the dynamic annealing of radiation damage $T_a$ in graphite materials is 150–200°C, depending on the type of ion [1]. The phenomenon of corrugation of the surface is associated with anisotropic radiation-induced plastic forming processes of carbon materials [3, 4]. In similar studies of periodic structures under ion irradiation, the dependences of the evolution of the structure on the irradiation fluence are important for the theoretical approaches [5, 6].

The aim of the present work is focusing on the initial stage of the formation of the corrugated structure and its evolution with a change in the irradiation fluence.

2. Experimental
The targets were rectangular plates of the one-dimensional KUP-VM composite, reinforced with VMN-4 carbon fibers based on the PAN fibers, $5\times40\times2$ mm in size, and a VMN-4 carbon fiber thread. Irradiation was carried out with 30 keV Ar⁺ ions at normal incidence to the axis of the fiber on a mass-monochromator of the Scobeltsyn Institute of Nuclear Physics, Moscow State University [7]. The temperature of the target ranged from 100 to 600°C. The experimental technique was similar to that used in [3,4]. The ion current density was 0.2–0.4 mA/cm² with a beam cross section of 0.3 cm², and
the irradiation fluences were $10^{18} - 10^{19}$ cm$^{-2}$. Investigations of carbon fiber before and after irradiation were carried out using scanning electron microscopy (SEM) with a Lyra 3 Tescan microscope.

3. Results and discussion
The surface morphology in the form of a sequence of prismatic elements with a triangular base - corrugations, without significant distortion of a single corrugation, is shown in figure 1 for VMN-4 carbon fiber irradiated with 30 keV Ar$^+$ ions. Such morphology is distinctive for irradiation with fluences of $10^{18} - 10^{19}$ cm$^{-2}$.

![Figure 1. SEM-image at the epicenter of irradiation for VMN-4 carbon fiber irradiated with 30 keV Ar$^+$ with fluence $3 \cdot 10^{18}$ cm$^{-2}$.](image)

SEM-images show that at low irradiation fluence, not only the geometrical parameters of the corrugated structure change but also the pattern of ion-induced deformation of the surface changes. Irradiation with lower fluences, both due to a decrease in the exposure time, figure 2a, and due to a decrease in the ion current density at the periphery of the irradiation zone, figure 2b, leads to a segmentation of the corrugated structure, the corrugations cease to be perpendicular to the fiber axis, the prismatic elements are reduced to nanometer sizes.

![Figure 2. SEM-image of carbon fiber VMN-4 (as part of KUP-VM composite) at the epicenter of 30 keV Ar$^+$ irradiation with fluence $1 \cdot 10^{18}$ cm$^{-2}$ (a) at the periphery of the irradiation zone for carbon fiber VMN-4 with 30 keV Ar$^+$ irradiation with fluence $3 \cdot 10^{18}$ cm$^{-2}$ (b).](image)
Comparison of SEM images shown in figure 2 shows the similarity of the morphology and size of the ion-induced structure of the fiber surface, which allows us to trace the evolution of corrugation with a change in the irradiation fluence by studying the morphology in the near and far peripheral irradiation zone with an exponential decrease in the ion current density.

The change in the surface morphology of the VMN-4 fiber from the epicenter to the periphery of the irradiation zone is shown in figure 3. One can see, that ion irradiation, at first, leads to the deformation of nanoscale traces of mechanical treatment, which has been appeared during production and placed parallel to fiber axis, to the form of the conical structures. Increase of irradiation fluence results in appearance of comb-shaped structures with the ribs perpendicular to the fiber axis. At the same time the ribs between conical structures on nanoscale traces decrease in sizes. At irradiation fluence > $1 \times 10^{18}$ cm$^{-2}$ comb-shaped structures agglomerate and transform into submicron corrugations. Further increase of an irradiation fluence leads to a disappearance of nanoscale traces of mechanical treatment, an enlargement of corrugations and less segmentation of quasiperiodic corrugated structures.

![Image](image.png)

**Figure 3.** The evolution of corrugation on the carbon fiber surface.

The same evolution of ion-induced deformation of fiber surface is seen for mutual masking of fiber in carbon fiber thread. The decrease of the incident particle fluence for masked areas takes place sharply and allows one to trace evolution in a much narrower area using one SEM image, figure 4.

The fundamental cause of ion-induced deformation in graphite is a shrinkage of the graphite crystallites in basal plane and their growth in the plane perpendicular to basal plane. This process leads to mechanical strains together with a relaxation in the form of plastic deformation for highly-textured carbon fiber shell. At high irradiation fluences the threshold level of radiation damage is characteristic for the ion-induced corrugation resulted by plastic deformation of twinning [8]. This also confirms by evolution of carbon fiber morphology described above. The comb-shaped structure preceding the corrugation, with a combs perpendicular to fiber axis appears only at relatively high fluences > $1 \times 10^{18}$ cm$^{-2}$.

The deformation of the nanoscale traces of mechanical treatment parallel to the fiber axes in the form of conical structures is observed on the long range periphery at low irradiation fluences. One may suppose, that it is connected with dominance of nanostructure fraction in this part of carbon fiber surface, with relatively low content of microcrystallites, which irradiation has been caused the
corrugation. The similar effect has been observed for irradiation of mosaic highly oriented pyrolytic graphite [9], where at lower levels of radiation damage the nanoscale topography was grown on the boundary of microcrystallites, in the form of closed polyhedrals.

Figure 4. SEM-image of carbon fiber VMN-4 irradiated with 30 keV Ar$^+$ with fluence $3 \cdot 10^{18}$ cm$^{-2}$ at boundary region of masking.

4. Conclusions
The studies of morphological changes in carbon fiber surface of VMN-4 based on PAN-fiber under irradiation with 30 keV Ar$^+$ ions in the cases of increase of the irradiation fluence are presented.

The ion irradiation at fluences $\leq 1 \cdot 10^{18}$ cm$^{-2}$ leads to conical deformation of the nanoscale traces of mechanical treatment parallel to the fiber axes. The increase in irradiation fluence leads to comb-shaped structures, their coagulation and transition from longitudinal nanostructure to submicron one with the transverse corrugations.

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