Surface corrugation of carbon fiber via high-fluence nitrogen ion irradiation

N N Andrianova¹, A M Borisov¹, A V Makunin², E S Mashkova², M A Ovchinnikov¹,² and F F Umarov³

¹ Moscow Aviation Institute (National Research University), Volokolamskoe sh. 4, 125993 Moscow, Russia
² Skobel’tsyn Institute of Nuclear Physics, Moscow State University, Leninskie gory 1(2), 119991, Moscow, Russia
³ Kazakh-British Technical University, 050000, Almaty, Tole bi str., 59, Kazakhstan

E-mail: anatoly_borisov@mail.ru

Abstract. SEM and laser goniophotometry were used to study a corrugation of VMN-4 carbon fiber shell of KUP-VM composite after high-fluence 30 keV N²⁺ ion irradiation at temperatures range from 100 to 600 °C. It has been found that the angles of an inclination of corrugated structure increase with temperature so that at temperature ~270 °C reach maximum values ~40°, staying at this level at subsequent temperature elevation up to 600 °C. Spatial period of corrugations alternation is about 1 µm for temperatures range 100–200 °C and 0.6 µm for higher temperatures. Qualitative difference of nitrogen from noble gas temperature dependences of a corrugation is connected with a nitrogen chemical activity and creation of C–N bonds due to implantation.

1. Introduction

The interest in research on carbon–carbon composites reinforced with carbon fibers based on polyacrylonitrile (PAN) is due to their use as structural materials for nuclear reactors, plasma equipment and aerospace technique [1]. Carbon fibers based on PAN-fibers consist of a core with turbostratic structure and structurally perfect, textured shell formed by graphite layers oriented along the surface of the fiber, so that the c-axis is directed along the radius of the fiber. Radiation impact on carbon materials leads to strong temperature dependences of various physical and mechanical properties see for example, [1–3]. Thus, high-fluence ion irradiation of composite materials based on carbon fibers can lead to both structural changes and significant morphological changes of carbon fiber surface [3–6]. Here with, depending on temperature T of irradiation and the level of the radiation damage determined by the number of displacements per atom (dpa), amorphization and recrystallization processes are possible, as well as the development of specific surface morphology in a form of corrugation. The detailed study of the influence of temperature on the ion-induced corrugation of a carbon fiber in of one-dimensional composite KUP-VM using scanning electron microscopy, laser goniophotometry and Raman spectroscopy is devoted to the work [6]. It has been found, that the formation of corrugated submicron structures upon 30 keV noble gas (Ne⁺ and Ar⁺) ion-induced irradiation at temperatures from 100 to 600 °C shows feature at temperatures of 400–500 °C. Namely, the temperature dependences of the corrugated faces' angles of inclination and fraction of corrugated structure on the fiber surface show minima deeper for argon ions, besides that
the range of corrugated faces' angles of inclination fall into the twinning angles during plastic deformation of the graphite crystallites of carbon fiber surface. This made it possible to relate the phenomenon of ion-induced corrugation with anisotropic radiation-induced plastic processes of forming of carbon materials taking into account the sputtering of the surface by ion bombardment. Studies of the structure and morphology of carbon fibers of the KUP-VM composite after 30 keV \( \text{N}_2^+ \) irradiation were carried out in [7, 8] to a temperature 300 °C. It has been shown that the temperature dependence of the ion-electron emission yield \( \gamma(T) \) for KUP-VM illustrates, in contrast to cases of irradiation with ions of noble gases, a complex two-step character, and high-fluence ion irradiation by itself leads to a loss of anisotropy of the structure of the surface layer of the composite KUP-VM – either to its amorphization at room temperature or to isotropic recrystallization at a temperature above \( T \approx 175 \text{ °C} \) of the high-temperature jump on the \( \gamma(T) \) dependence.

Present work continues the studies of ion-induced corrugation regularities of carbon fibers based of PAN-fibers for 30 keV \( \text{N}_2^+ \) ion irradiation at temperatures range from 100 to 600 °C including features of structural and dimensional changes of graphites under radiation impact.

2. Experimental
The experimental procedure was similar to that used in [7, 8]. Samples of one-dimensional composite KUP-VM reinforced by PAN-based carbon fibers VMN-4 were analyzed before and after irradiation using scanning electron microscopy (SEM) with a Lyra 3 Tescan microscope and laser gonio photometry (LGPh). Samples were irradiated with 30 keV \( \text{N}_2^+ \) ions at normal incidence using the mass-monochromator of the Skobeltsyn Institute of Nuclear Physics of Moscow State University [9]. The irradiated targets were rectangular plates with dimensions of 15×40×2 mm. Reinforcing carbon fibers were parallel to the long side of the plates. The temperature of the target was varied from 100 to 600 °C. The temperature was controlled using a chromel–alumel thermocouple with its junction fixed on the irradiated side of the target outside the irradiation zone. The ion current density was 0.2–0.4 mA/cm², irradiation fluencies – 6·10¹⁸ ion/cm². The ion irradiation was monitored by registering the current of ions and electrons to determine the irradiation fluence and ion-electron emission yield.

3. Results and discussion
After high-fluence irradiation with nitrogen ions at temperatures of the irradiated target of 100–600 °C, quasiperiodic sequence of symmetrical prismatic structures (corrugations) with ribs perpendicular to the axis of the fiber is appeared on fiber surface. Figure 1 shows examples of typical SEM images, the distributions of local angles of inclination of \( \gamma(\beta) \) microfaces obtained by LGPh, as well as the scheme and designations of the parameters of the corrugated structure. The period \( L \) of the corrugations was determined from the SEM images, the angles of inclination of the corrugated faces \( \beta_1 \) and \( \beta_2 \) respectively, from the \( \gamma(\beta) \) distributions.

An analysis of the obtained data shows that the temperature dependence of the local angle of inclination of the corrugations \( \beta(T) \) is nonmonotonic. In the temperature range from 100 to 275 °C, the angle of inclination \( \beta \) increases with the irradiation temperature reaches the maximum values \( \beta > 40° \) and with a further temperature increase up 600 °C remains at this level, see figure 2(a). Differences in the role of the irradiation temperature in the ranges (100–275 °C) and (275–600 °C) can also be seen in figure 1 when comparing the SEM images of the corrugated structures and the \( \gamma(\beta) \) distributions for temperatures from these intervals. In particular, for the temperature range (100–275 °C) in SEM images the corrugated structure at the fiber periphery is more distinctly visible than at the vertex part of the fiber. Differences in the irradiation temperature ranges also appear for periods of the corrugated structure, amounting to 1 and 0.6 \( \mu \text{m} \) in the intervals (100–275 °C) and (275–600 °C), respectively, figure 2(b).

Observed at irradiation temperatures from 275 to 600 °C the corrugation faces’ angles of inclination 40–45° are close to the twinning angles \( \beta_{\text{d1}} = 48°18' \) and \( \beta_{\text{d2}} = 35°12' \) of plastic deformation of the graphite crystallites of the carbon fiber shell. We note that the same ion-induced corrugations faces’ angles of inclination were observed also in the case of irradiation by noble gas ions [6].
However, in contrast to irradiation with nitrogen ions the $\beta(T)$ dependence for noble gas ions exhibited a minimum at 400–500 °C.

$T = 100$ °C

$T = 230$ °C

$T = 275$ °C

$T = 600$ °C

**Figure 1.** Scheme of the corrugated structure, SEM patterns of carbon fibers (a), (b), (c), (d) and the distributions of local angles of inclination of $f(\beta)$ microfaces of surface relief (e), (f), (g), (h) after high fluence 30 keV $N_2^+$ ion irradiation of composite KUP-VM at different temperatures.
The obtained regularities together with the previously established ones make it possible to relate the phenomenon of ion-induced corrugation in the case of irradiation with nitrogen ions not only with the anisotropic radiation-induced plastic forming processes of carbon materials taking into account surface sputtering, but also with the formation of C-N bonds in the modified layer.

![Temperature dependences of angle of inclination β(T) (a) and period L (b) of the corrugated structure after 30 keV N$_2^+$ ion irradiation of KUP-VM composite. β$_{11}$ = 48°18’ and β$_{22}$ = 35°12’ – are the angles of twinning in graphite.](image)

It can be assumed that the chemical activity of nitrogen imposes additional conditions on the recrystallization of graphite and, respectively, on the dimensional changes of the modified layer. According to the Rutherford backscattering analysis, the content of implanted nitrogen in the modified layer is: for $T < T_a - 16 \%$, for $T > T_a - 11 \%$ [8]. Such concentration of nitrogen atoms after ion irradiation leads to the inevitable formation of a large number of C-N bonds [10]. X-ray photoelectron spectroscopy data show that the fraction of implanted nitrogen involved in the formation of C-N bonds can reach 92 \% [11]. It was shown theoretically [12] that at a concentration of embedded nitrogen atoms in graphite-like materials below 20 \% at. nitrogen atoms occupy vacancies in graphene planes with preservation of planar structure. In general, irradiation with nitrogen ions leads to a decrease in the defectiveness of the modifiable layer due to chemical bonds formed between nitrogen ions and carbon atoms [13], which is reflected in the development of corrugation at lower irradiation temperatures in comparison with the corrugation with noble gas ions.

4. Conclusions
The regularities of ion-induced corrugation of a shell of polyacrylonitrile carbon fiber VMN-4 of one-dimensional composite KUP-VM under high-fluence irradiation with 30 keV N$_2^+$ ions in the temperature range from 100 to 600 °C were investigated using the methods of scanning electron microscopy and laser goniophotometry. The formation of corrugated submicron structures under ion-beam irradiation on the projected range (~40 nm) begins at a temperature $T \sim 100 \, ^\circ C$. With increasing temperature the angles of inclination of the corrugation faces increase monotonically and at temperatures $T > 275 \, ^\circ C$ reach the maximum values $\beta_1 = \beta_2 > 40°$. The period of the corrugated structure are 1 and 0.6 μm in the irradiation temperature ranges (100–275 °C) and (275–600 °C), respectively. The manifestation of the corrugation effect at temperatures of 100–275 °C can be related to anisotropic ion-induced plastic processes in a modified layer containing C-N bonds.

Acknowledgement
This work was supported by the Russian Ministry of Education and Science by an agreement to provide subsidies №14.577.21.0275 from 26.09.2017.

References
[1] Virgil’ev Yu S and Kalyagina I P 2004 *Inorganic Materials. Suppl. I* 1 S33–49
[2] Burchell T D 1997 MRS Bulletin 22(4) 29–35
[3] Blackstone R 1977 Journal of Nuclear Materials 65 72–8
[4] Andrianova N N, Borisov A M, Mashkova E S, Parilis E S and Virgiliev Yu S 2013 Horizons in World Physics 280 171 (New-York: Nova Science Publishing)
[5] Andrianova N N, Borisov A M, Virgil’ev Yu S, Mashkova E S and Petrov D V 2014 J. Surf. Invest.: X-ray, Synchrotron Neutron Tech. 6(3) 513–8
[6] Andrianova N N, Anikin V A, Borisov A M, Kazakov V A, Mashkova E S, Ovchinnikov M A and Savushkina S V 2018 Bull. Russ. Acad. Sci. Phys. 82(2) 122–6
[7] Andrianova N N, Borisov A M, Virgil’ev Yu S, Mashkova E S, Nemov A S, Pitirimova E A and Timofeev M A 2008 J. Surf. Invest.: X-ray, Synchrotron Neutron Tech. 2(3) 376–9
[8] Andrianova N N, Borisov A M, Mashkova E S and Virgiliev Yu S 2009 Nuclear Instruments and Methods in Physics Research B 267 2778–81
[9] Mashkova E S and Molchanov V A 1985 Medium-energy ion reflection from solids (North Holland, Amsterdam)
[10] Bogomolova L D, Borisov A M, Kurnaev V A and Mashkova E S 2003 Nuclear Instruments and Methods in Physics Research B 212 164–8
[11] Gouzman I, Brener R and Hoffman A 1999 Journal of Vacuum Science & Technology A 17 411–20
[12] Dos Santos M C and Alvarez F 1998 Physical Review B 58 13918–24
[13] Gouzman I, Brener R, Cytermann C and Hoffman A 1994 Surface And Interface Analysis 22 524–7