Modification of polyacrylonitrile carbon fibers by high-fluence ion irradiation

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Abstract. The Raman spectroscopy has been used to analyse ion-induced modifications of carbon PAN-fiber shell due to 10-30 keV Ar⁺ high fluence ion irradiation at normal and oblique incidence in the temperature range from RT to 400 °C. It has shown that formed in ion-induced processes of amorphization, recrystallization and crimping the modifications of PAN-fiber shell are characterized by the presence of the amorphous phase with the A peak in the Raman spectra and the increased intensity of the D peak relative to the G peak in comparison with non-irradiated fiber. Amorphous phase in the PAN-fiber shell is the highest in case of amorphization and the least at the crimping. The increased intensity of the D peak in the Raman spectra and the G peak shift towards higher frequencies during recrystallization and crimping indicates ion-induced nanostructuring of the PAN-fiber shell.

1. Introduction

Carbon-carbon and carbon-ceramic composite materials reinforced by carbon polyacrylonitrile (PAN) fibers are considered as priority structural materials for aerospace engineering. PAN-fibers have a core with turbostratic structure and structurally perfect textured shell. High-fluence ion irradiation leads to significant changes in surface morphology and crystalline structure of PAN-fiber shell and this procedure is considered as the modification method necessary for obtaining high-temperature strength and high heat resistance carbon-ceramic composites reinforced by the fibers with optimal adhesive interaction with composite matrix [1]. Ion irradiation of analyzed in this work carbon-carbon composite KUP-VM reinforced by VMN-4 PAN-fibers can lead to such processes as amorphization, recrystallization and development of the surface topography, in particular, the fiber crimping [2,3]. In the present work for the characterization corresponding to these processes of ion-induced modification of carbon PAN fiber surface and also its structure changes during heat treatment along with electron-microscopy, laser Raman spectroscopy has been applied.

2. Experimental

The heat treatment process has been studied for samples of carbon fibers from PAN-raw materials used for the production of carbon fiber KULON. The Raman spectra of KULON PAN-fiber have been
compared with the Raman spectra of PAN-fibers after carbonization at a temperature of 1000 °C and after graphitization at temperatures from 1450, 1550 and 1650 °C. The study of ion-beam modification has been performed for the carbon-carbon composite KUP-VM, reinforced carbon VMN-4 PAN-fibers. The samples of PAN-fibers have been analyzed using scanning electron microscope Quanta 600 and a Horiba JobinYvon T64000 Raman spectrometer at room temperature with the laser excitation wavelength $\lambda_L = 514.5$ nm. The ion irradiation of the samples of KUP-VM by 10, 25 and 30 keV Ar$^+$ ions at ion incidence angle $\theta = 0$ and $\theta = 70^\circ$ relative to the fiber axis have been carried out on the mass-monochromator of the Skobel’tsyn Research Institute of Nuclear Physics Moscow State University [4]. A special target holder with the water cooling was used for controlling the target temperature from RT to 400 °C during ion irradiation, which was measured by means of an alumel-chromel thermocouple with the junction attached to the irradiated side of the target away from the irradiated area. Ion irradiation was monitored via the periodic recording of the ion current and secondary electrons to determine the irradiation fluence and the ion-induced electron yield. Note that studied ion-induced processes are dependent on irradiation temperature and radiation damage level $\nu$ measured in the number of displacements per atom ($dpa$) as $\nu = \varphi \sigma_{\text{dam}}$ ($\sigma_{\text{dam}}$ is the cross section of defect formation, $\varphi$ is the incident-ion flux density; $t$ is the time of irradiation). At high fluences radiation damage level is determined by ion energy and, according to the evaluation [2], $\nu$ is ranging from 30 $dpa$ at the energy of the Ar$^+$ ions of 10 keV to 90 $dpa$ at 30 keV ion energy.

3. Results and discussion

It is known that Raman spectra of graphite-like materials contain two main peaks: the G peak (graphite peak) at the Raman shift $\Delta k = \lambda_{\text{G}}^{-1} - \lambda_{\text{R}}^{-1}$ close to 1580 cm$^{-1}$ and the D peak due to the lattice defects at $\Delta k \approx 1350$ cm$^{-1}$, see, for example [5]. The Raman spectra reflect the processes of thermal treatment of the hydrocellulose and polyacrylonitrile fibers when processing respectively to these fibers [6,7]. It also displays the evolution of the Raman spectra for PAN-fibers with increasing treatment temperature in Figure 1. The trend of growth of the relative intensity of the G peak is clearly visible with increasing the treatment temperature of PAN-fiber. The most perfect graphite fiber shell is formed at the final treatment temperature 3000 °C, see carbon fiber KULON spectra. The degree of shell perfection is characterized by the size of $L_a$ graphite microcrystallites in the basic plane. Thus, the larger the $L_a$ of the graphite microcrystallites, the smaller the relative intensity of the D peak [8]. Figure 1 also shows that the relative intensity of the D peak for the Raman spectrum of VMH-4 PAN carbon fibers embedded to composite KUP-VM is several times less than the $I_D/I_G$ for carbon fiber KULON that indicates a more perfect shell of the VMN-4 carbon fiber.

Radiation exposure can significantly change the structure of graphite-like materials up to amorphization. Ion-induced amorphous carbon in the Raman spectra is manifested as band at $\Delta k \approx 1500$ cm$^{-1}$ [5]. Radiation impact can also greatly reduce the size $L_a$ of the graphite crystallite. In this case the dependence of the intensities $I_D/I_G$ on $L_a$ in the Raman spectra will reverse if $L_a < 2$ nm namely, the greater $L_a$, then the greater relative intensity of the D peak [8]. The peculiarities of influence of radiation exposure on the Raman spectra of graphite-like materials are fully manifested in the present work for the carbon PAN-fibers.
Figure 1. Raman spectra of PAN-fibers corresponding to different thermal treatment temperatures and VMN-4 PAN-fiber embedded in composite KUP-VM.

The Raman spectra and SEM images for the samples of the KUP-VM after irradiation, leading to different ion-induced surface modification of fibres, such as amorphization, recrystallization and recrystallization with surface crimping, are presented in Figure 2. The most typical cases of these surface modifications chosen according to the data of [2, 3], are given. Amorphization leads to a qualitative change in the Raman spectra. Namely, two peaked structure of the spectrum is not resolved, see Figure 2a. Two peaked structure of the Raman spectra is observed at target irradiation temperature $T$ larger than the temperature of dynamic annealing of radiation damage 150 – 200 °C [2,3]. The examples are the Raman spectra, corresponding to the ion energy of 10 and 30 keV at the irradiation temperature $T = 400$ and 350 °C, respectively. Structural analysis shows that at 30 keV ion energy there occurs not only the recrystallization of the surface layer of a carbon fiber, like at the energy of 10 keV (figure 2b), but also crimping, see the SEM image in Figure 2c. To assess quantitative differences in the Raman spectra for different ion-induced modifications of PAN-fiber surface the decomposition of spectra into Gaussian components was carried. The decomposition for the irradiated samples in addition to the G and D peaks required the introduction of the A peak, taking into account radiation damage in the structure of short-range order upon amorphization of carbon materials.

The percentages of Gaussian components in the Raman spectra are shown in Table 1.
Figure 2. Raman spectra and SEM images of KUP-VM after ion irradiation.
Table 1. The percentages of Gaussian components in the Raman spectra of composite KUP-VM, reinforced by VMN-4 PAN fibers, before and after ion irradiation under various conditions.

| KUP-VM composite, reinforced by VMN-4 PAN fibers | D peak 1360 cm⁻¹, % | A peak ~1500 cm⁻¹, % | G peak 1580 cm⁻¹, % |
|-----------------------------------------------|---------------------|---------------------|---------------------|
| Before ion irradiation                        | 16                  | absent              | 84                  |
| Ion-induced amorphization                     | 56                  | 31                  | 13                  |
| 30 keV Ar⁺, T = 50 °C                         |                     |                     |                     |
| Ion-induced recrystallization                 | 44                  | 10                  | 46                  |
| 10 keV Ar⁺, T = 400 °C                        |                     |                     |                     |
| Ion-induced crimping                          | 49                  | 7                   | 44                  |
| 30 keV Ar⁺, T = 350 °C                        |                     |                     |                     |

It can be seen that the missing A peak in the Raman spectrum before irradiation, appears after irradiation, and it is the largest for ion-induced amorphization and several times less for recrystallized PAN-fiber shell. The processes of recrystallization including crimping are characterized by relatively small differences in the Raman spectra. Great relationship to \( \frac{I_D}{I_G} \approx 1 \) compared with \( \frac{I_D}{I_G} \approx 0.14 \) for non-irradiated fibers can be associated with a significant reduction of the graphite crystallites size \( L_a < 10 \) nm.

The Raman spectroscopy has shown that after ion irradiation at RT and 10 keV ion energy or at ion incidence angle 70° and 30 keV ion energy PAN-fiber amorphization in contrast to the normal incidence of 30 keV ions is not observed and the D and G peaks are separated. On the fiber surface there is ridge-like morphology, typical for oblique ion incidence on the surface of polycrystalline materials, see [9]. Taking into account the dependence of radiation damage level on ion energy and ion incidence angle [2] one may conclude about radiation damage threshold level of PAN-fiber amorphization. A similar conclusion was assumed in [2,3] by analyzing the temperature dependences of ion-induced electron emission yield at the normal ion incidence and different ion energies.

4. Conclusions
The Raman spectroscopy has been used to characterize the ion-induced modifications of carbon PAN-fiber shell due to 10-30 keV Ar⁺ high fluence ion irradiation at normal and oblique incidence in the temperature range from RT to 400 °C and also structure change during thermal treatment of PAN-fiber.

Formed in ion-induced processes of amorphization, recrystallization and crimping of PAN-fiber modifications are characterized by the presence of the amorphous phase with the A peak in the Raman spectra and the increased intensity of the D peak relative to the G peak in comparison with non-irradiated fiber.

At high-fluence ion irradiation the decrease of radiation damage level with ion energy decreasing or with ion incidence angle increasing suppresses amorphization, the structure of the carbon fiber shell is recrystallized, which manifests in the Raman spectra in the form of separated the D and G-peaks.

Amorphous phase in the Raman spectra till irradiation is practically missed and it is the highest during the PAN-fiber amorphization and the least at crimping.

The increased intensity of the D peak and the G peak shift towards higher frequencies during recrystallization and crimping in the Raman spectra indicate ion-induced nanostructuring of the PAN-fiber shell.

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