The Effect of Irradiation with Nitrogen Ions on the Properties of Pyrolytic Graphite

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Abstract—The effect of irradiation with nitrogen ions ($E = 30$ keV, $J = 10^{16}$–10^{18} cm^{-2}) on the elemental composition, surface topography, and structure of the near-surface layer of pyrolytic graphite are investigated.

1. INTRODUCTION

One of most promising methods for increasing the adhesive strength of various types of coatings is treating them with charged particles (electrons, ions, plasma flows). In most cases this operation can be carried out along with coating application in a vacuum.

In the present work, the effect of treating the graphite surface (pyrographite was used as the substrate material) with beams of nitrogen ions on the elemental composition, structure of the near-surface layer, and surface topography of graphite before and after the ion-beam treatment are investigated.

2. EXPERIMENTAL

The irradiation of graphite with nitrogen ions was carried out using a hollow-cathode plasma ion source constructed at the Institute of Electrophysics, Ural Division, Russian Academy of Sciences (Yekaterinburg) [1]; it operated in either a pulsed-periodic mode or a continuous mode of beam generation. The former (pulse duration 1ms, pulsed current density 3mA/cm^{-2}) was used in the case of small radiation doses, and the latter (pulsed current density 0.3 mA/cm^2) in the case of high radiation doses. The accelerating potential of the ion source was 30 kV. The process was carried out in a vacuum chamber. Prior to starting the irradiation treatment, the residual gas pressure was no higher than 3×10^{-5} mmHg, and during the process the pressure varied in a range of $(3–5) \times 10^{-4}$ mmHg. The beam of nitrogen ions contained approximately equal amounts of atomic and molecular single-charged ions. The ion radiation dose (J) varied from 10^{15} to 5×10^{18} cm^2.

The surface topography of graphite was investigated on a Quanta 200 3D ion electron microscope.

The nitrogen distribution in the near-surface layer of pyrographite was determined using the method of Rezerford back scattering (RBS) of α-particles (energy $E_0 = 1.7$ MeV) scattered to an angle of $\theta = 170°$. The concentration profile of elements was obtained from the RBS energy spectra using a SIMRA mathematical modeling program with the degree of fitting of $\chi^2 \geq 1$.

The crystallite size (L_c) and interplanar spacing (d_{002}) of graphite were found using a DRON-2 X-ray diffractometer with filtrered copper radiation.

3. RESULTS AND DISCUSSION

Using the RBS method, the dependences of the concentration of implanted nitrogen ions on their penetration depth into the near-surface layer of graphite were obtained (Fig. 1). As the irradiation dose increases, the nitrogen concentration also increases, and the penetration depth of ions at the maximum value $J = 5 \times 10^{18}$ cm^2 is 80 nm.

The interplanar spacings (d_{002}), heights of crystallites, and internal microstresses that appear in the near-surface layer of pyrographite were determined by X-ray diffractometry. It was found that, in the case of small doses (Fig. 2), the ion irradiation almost did not affect the value of d_{002}.

As J increases to 10^{17} cm^2, the interplanar distance changes, which is accompanied by the appearance of two lines on Fig. 2 associated with peak splitting in the X-ray diffraction pattern. This splitting is apparently caused by the formation of two interference planes,

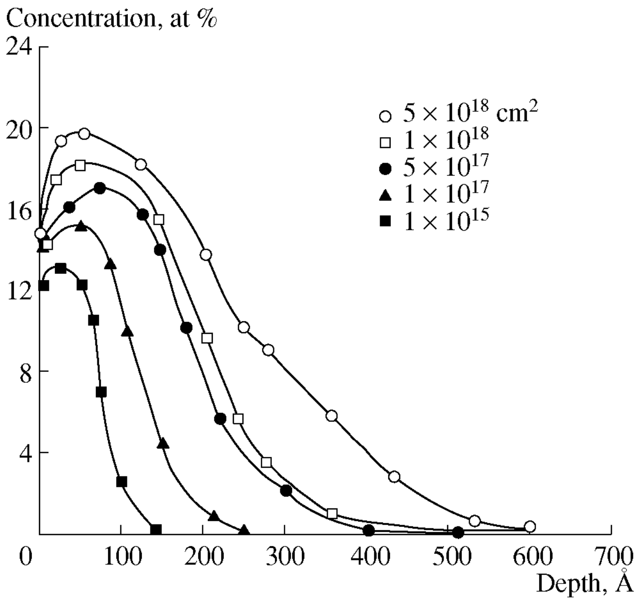

Fig. 1. Effect of irradiation dose on the penetration depth of nitrogen ions into graphite.

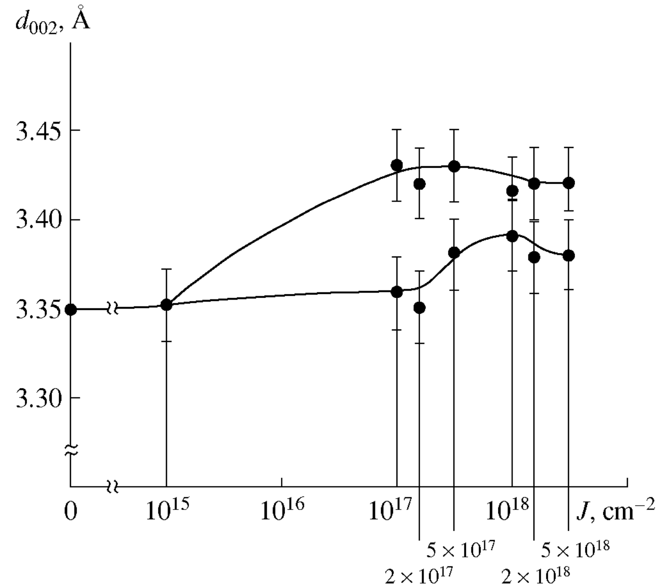

Fig. 2. Dependence of interplanar spacing in the near-surface layer of pyrographite on the irradiation dose of nitrogen ions.

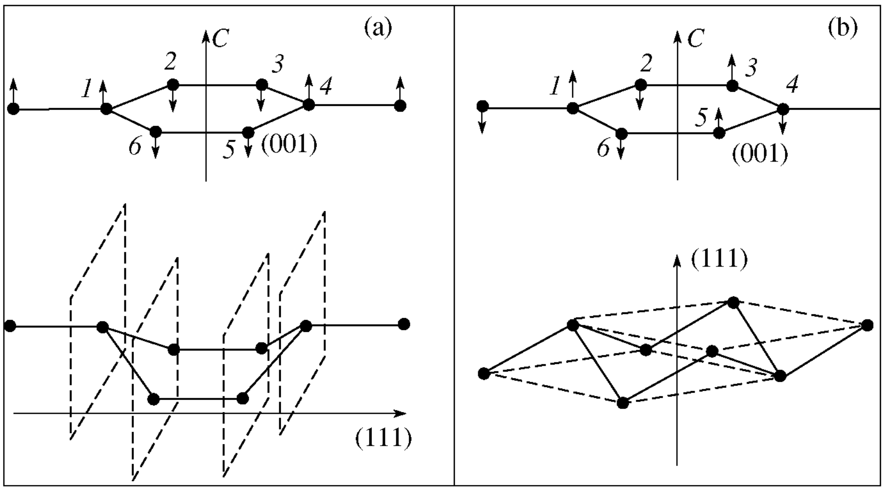

Fig. 3. Atomic shift under corrugation of graphite planes. a and b are the ways of splitting the graphite planes. Initial planes with directions and shifts under the shear deformation are at the top, and the configuration after the shift is at the bottom.

which is most probably conditioned by the displacement of atoms from their equilibriumsites, leading to the distortion of crystal lattice. We can suggest that ion implantation into the layered structure of pyrographite also promotes the formation of local displacements of basal planes (Fig. 3).

As a result, two different values of parameter d_{002} which correspond to the new (shifted) and old (unshifted) basal planes may appear. The appearance of these two planes can be explained by the shift of atoms from their initial sites under the effect of the ion beam (Fig. 3). A similar interpretation was suggested by the authors of [2], who investigated the effect of copper atoms on the graphite structure.

The described differences between two interference planes were observed up to $J = 5 \times 10^{17}$ cm^{-2}. As the irradiation dose decreases, they disappear, and an average value ($d_{002} \approx 3.42$ Å) corresponding to the amorphous structure of pyrographite appears. We can assume that the further increase in J to above 5×10^{18} cm^{-2} will lead to the transformation of the split peak in the X-ray diffraction pattern to the single one.

At low irradiation doses, the size of ordered regions remains virtually invariable (Fig. 4). As J increases to

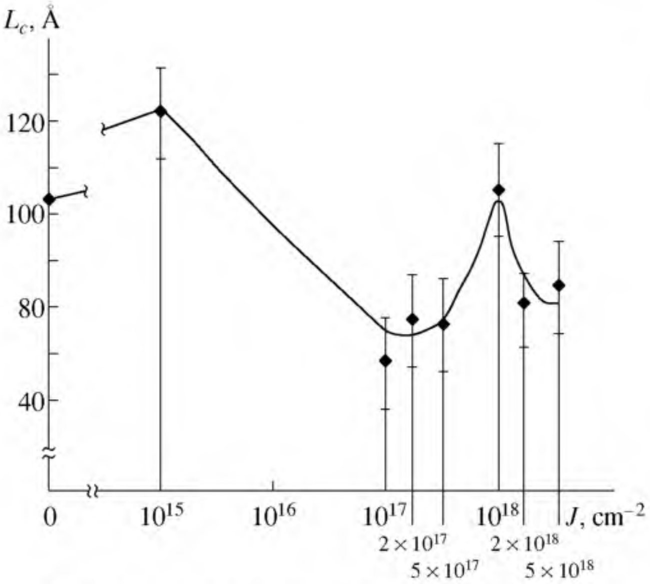

Fig. 4. Dependence of crystallite height in the near-surface layer of pyrographite on the irradiation dose of nitrogen ions.

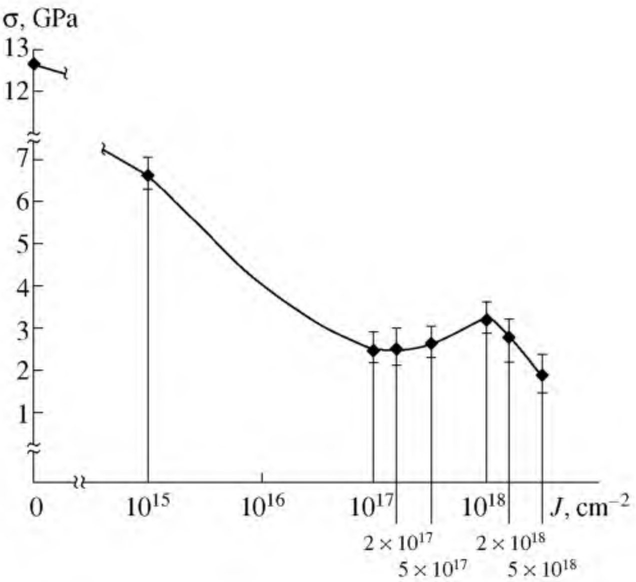

Fig. 5. Dependence of microstrains in the near-surface layer of pyrographite on the irradiation dose of nitrogen ions.

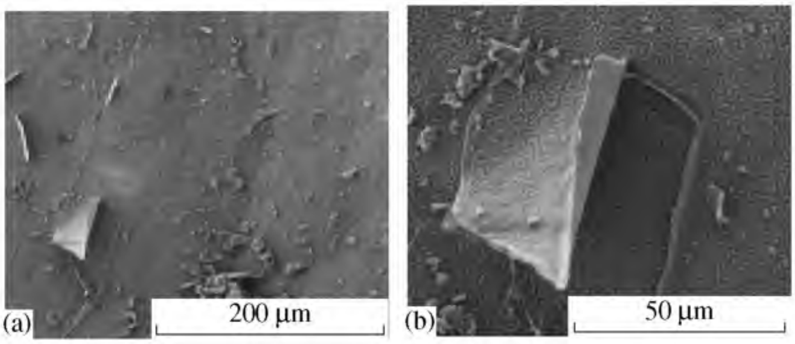

Fig. 6. Pyrographite surface after irradiation with nitrogen ions. $J = 10^{18}$ cm^{-2}; magnification (a) 800 and (b) 3000.

10^{17} cm^{-2}, the crystallite size decreases to $L_c = 70$ Å due to the break of chemical bonds of the hexagon and local shifts of basal planes with respect to one another. This is also indicated by peak splitting in the X-ray diffraction pattern and by the change of interplanar spacing (Fig. 2). In the range $J = (1–5) \times 10^{17}$ cm^{-2}, the value of L_c remains almost at the same level. An increase in the dose of the irradiating ions to 10^{18} cm^{-2} leads to an increase in L_c in the size of crystallites of untreated pyrographite (~100 Å). This is accompanied by the disappearance of strong differences between interplanar spacings, which corresponds to a decrease in the degree of misorientation of the pyrographite structure. At the largest dose of nitrogen ions ($2–5 \times 10^{18}$ cm^{-2}), the pyrographite structure is misoriented (the value of L_c decreases) and transforms into the amorphous state again.

Using the X-ray structural analysis, the internal microstresses appearing in the pyrographite after ion irradiation were determined (Fig. 5). Their level decreases as J decreases, probably because of the destruction of crystallites and changes of interplanar spacings in pyrographite. At $J = 10^{18}$ cm^{-2}, the insignificant repeated accumulation of microstresses is observed, which is probably associated with the improvement of the pyrographite structure (see Figs. 2, 4). At the largest doses ($J = (2–5) \times 10^{18}$ cm^{-2}), the relaxation of microstresses caused by misorientation and amorphization of the near-surface layer takes place again.

As a result of ion irradiation, a significant transformation of the surface topography is also observed. As the value of J increases, the accumulated internal stresses in the near-surface layer of pyrographite lead to the scaling (Fig. 6) and even partial distortion of upper layers.

The thickness of the near-surface layer with the modified structure reaches 2.0–2.1 μm (Fig. 7), which

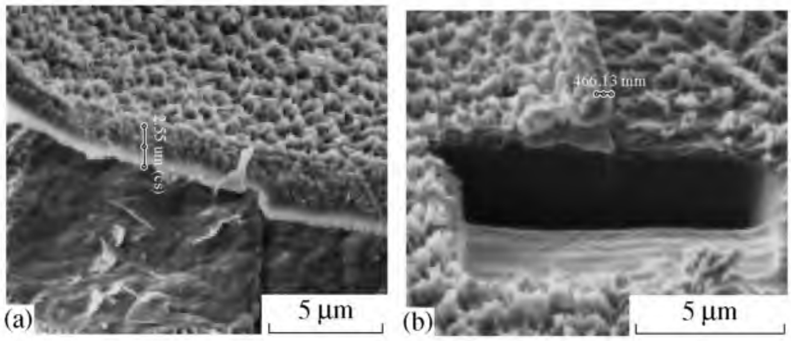

Fig. 7. Thickness of the near-surface layer of pyrographite modified by nitrogen ions. $J = 10^{18}$ cm^{-2}; magnification (a) 16000 and (b) 8000.

is associated with the sputtering of the pyrographite surface and its intense etching by the ion beam.

CONCLUSIONS

The surface topography, penetration depth of nitrogen ions, and structure of the near-surface layer of pyrographite subjected to irradiation with low-energy nitrogen ions are investigated. The penetration depth of nitrogen ions depends on the irradiation dose and does not exceed 80 nm at $J = 5 \times 10^{18}$ cm^{-2}. A method that can change the interplanar spacing and height of the package of layers in pyrographite is suggested.

REFERENCES

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