Irradiation effects in carbon fibers after N^+-ion irradiation

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Abstract

Surface treatment of high modulus carbon fibers by pulsed N^+-ion beams has been carried out, and changes in morphology and structure of the carbon fibers (d_{002} and L_a parameters) have been investigated by using scanning electron microscopy, RBS and X-ray diffraction.

1. Introduction

Carbon fibers are widely used as a reinforcement in different matrices (for example, epoxy resins, polysulfone, polycarbonate). The adhesive strength between carbon fibers and matrices depends strongly on the fiber–matrix interface. A lot of methods have been used to change the physical and chemical properties of the fiber surface, such as oxidation ("dry" oxidation in air, oxygen, ozone [1]), "wet" chemical oxidation, plasma treatment in various gases [2] and so on.

A relatively new approach to surface modification of carbon fibers is ion irradiation in the "low energy irradiation" regime, involving 0–40 keV ions, and ion current densities of 0–10 mA/cm^2. After ion irradiation the topography and parameters of carbon fiber structure may be changed.

Ion implantation of carbon fibers with the purpose of direct modification of their properties is an area of prospective interest for scientific research and for practical applications. Irradiation of carbon fibers by nonmetal (carbon, nitrogen, oxygen) and metal ions can change the structure of the fibers and change the relative concentration of chemical elements in the near-surface layer of the fiber; thereby, the physical–chemical properties of the carbon fibers will be changed.

In the present work, topography of the surface and structure of the carbon fibers after N^+-ion irradiation were investigated.

2. Experimental

Carbon fibers produced from polyacrylonitrile (PAN) precursor were used in our experiments (Figs. 1–3). The fibers were supported on beryllium substrates, and irradiated by pulsed N^+-ion beams (energy = 30 keV, current density during a pulse 3–9 mA/cm^2, pulse length ~ 1 ms). The ion source showed stable operation with pulse repetition rates of up to 50 s^{-1} [3]. The structure parameter of the carbon fibers (d_{002} — the distance between planes of the crystalline lattice), and L_a, a parameter that characterizes the evolution of apparent size of the crystallites along the a-axis, were analyzed by X-ray diffraction. Spectra were recorded over 2θ interval, using a diffractometer DRON-3 with CuK_α radiation after filtration, without any rotation of the specimen. The topography of the fiber surface was investigated by scanning electron microscopy.

The chemical composition of the carbon fibers was measured by RBS (Rutherford backscattering spectrometry), using ^{4}He ions accelerated to 1.6 MeV with a Van de Graaff accelerator. The vacuum in the target chamber was usually better than

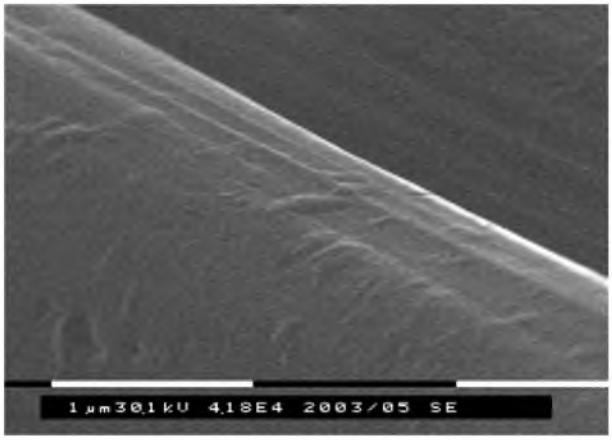

Fig. 1. Surface of unirradiated carbon fiber (SEM scale bar length = 1 µm).

8×10^{-5} mbar, and it dropped during the ion irradiation to 3×10^{-5} mbar.

Fig. 4 shows the RBS spectrum (solid line) recorded for carbon fibers that had been irradiated by nitrogen ions. Distinct sharp profiles corresponding to different elements are evident: oxygen (E_R=0.6 MeV), nitrogen (E_R=0.54 MeV), carbon (E_R=0.4 MeV). The dashed line shows the shape of the RBS spectrum simulated by the computer program "BS". The simulated spectrum was generated by numerical integration using the stopping powers given by Ziegler and Baglin [4].

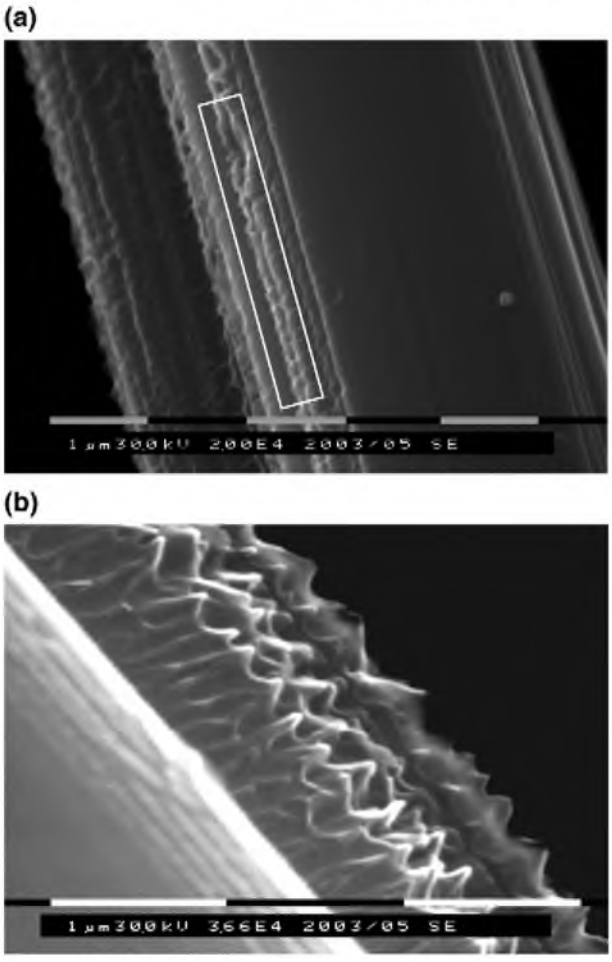

Fig. 2. Surface of irradiated carbon fiber: (a) 10^{17} cm^{-2} and (b) 10^{18} cm^{-2} (SEM scale bar length = 1 mm).

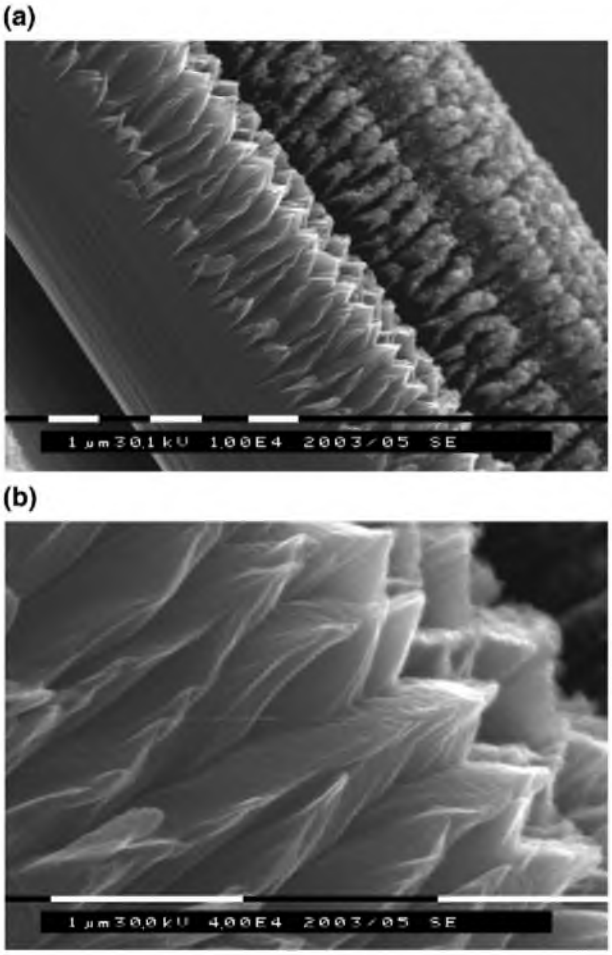

Fig. 3. Surface of irradiated carbon fiber, 10^{19} cm^{-2} (SEM scale bar length = 1 µm).

3. Results and discussion

Evident changes of topography of the surface of carbon fibers take place after ion irradiation (1×10^{18} N^+ cm^{-2}). The

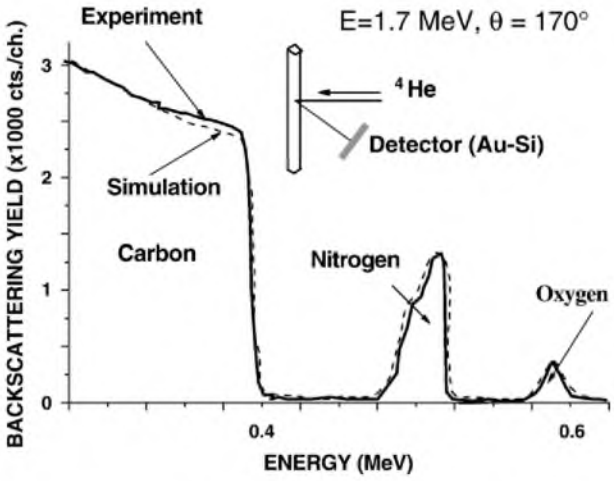

Fig. 4. RBS spectra from carbon fibers following N^+-ion irradiation.

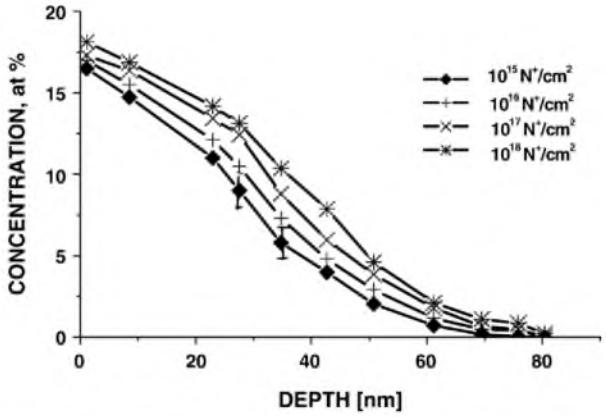

Fig. 5. The nitrogen profiles after N^+-ion irradiation of carbon fibers at fluences up to 10^{18} cm^{-2}, derived from RBS spectra. The *y*-axis shows the atomic concentration of nitrogen, calculated as a percentage of the total nitrogen and carbon (but excluding the observed oxygen), as a function of depth in the sample.

wavy surface of carbon fibers became particularly evident after N^+ irradiation at fluences of 5×10^{17} cm^{-2} and more (Fig. 2a, outlined area). The surface became ribbed, with the ribs being oriented along the axis of the fiber. The roughness of the fiber surface increased, and the height at the center of the profile peak was 0.05–0.15 μm (Fig. 2b).

During the growth of ion irradiation fluence to 10^{19} cm^{-2} the topography of the fiber surface changed, and the roughness of the surface reached 0.4–0.5 μm. Such roughness as formed on the surface fibers is probably connected mainly with ion sputtering, and to a lesser degree with chemical interactions of nitrogen and carbon (Fig. 3a,b).

The RBS depth profiles for N in the ion irradiated carbon fibers are presented in Fig. 5. The *y*-axis shows the atomic concentration of nitrogen, as a percentage of the total nitrogen and carbon (but excluding the observed oxygen), as a function of depth in the sample.

According to these RBS profiles, the thickness of the ion implanted surface layer formed by high fluence irradiation is 80 nm. Besides the elements C and N, oxygen impurities (>2 vol.%) were observed in the irradiated surface layers,

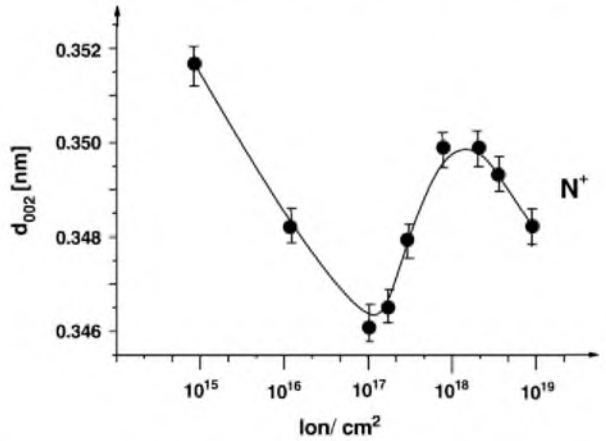

Fig. 6. Evolution of interplanar distance d_{002} of carbon fibers after N^+-ion irradiation.

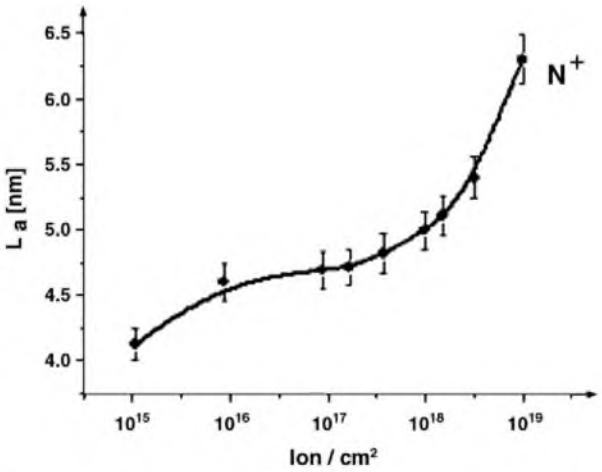

Fig. 7. Evolution of apparent sizes of carbon fibers along the *a*-axis, L_a, as a function of N^+ fluence.

presumably arising from the residual atmosphere in the vacuum system. Oxygen was presumably absorbed on the fiber surface during ion irradiation and then was intermixed by the ion beam.

X-ray results showed the following: in the fluence range 10^{15}–10^{17} cm^{-2}, the interplanar distance d_{002} was decreased, with the minimum d_{002} being observed at a fluence of 10^{17} cm^{-2}. In the fluence range 10^{17}–10^{19} cm^{-2}, d_{002} increased, possibly because of large quantities of interstitial atoms in the carbon fiber and simultaneous destruction of the structure of the carbon fiber (Fig. 6). The parameter L_a increased by 15–20% with changing fluence of N^+ from 10^{15} to 10^{19} cm^{-2} (Fig. 7).

4. Conclusion

After N^+-ion irradiation, the morphology of the surface of carbon fiber and its diameter are changed by both ion sputtering (mostly), and ion implantation, and also maybe by chemical reaction between carbon fiber and nitrogen atoms, especially in the fluence range 10^{17}–10^{19} cm^{-2}.

The structure parameters of the carbon fiber (d_{002} and L_a) are changed too, after ion irradiation.

The next step of our research will be to study defects in the bulk structure of carbon fibers, because the mechanism of property changes of carbon fibers during ion irradiation is still not fully understood.

Acknowledgments

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