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Enhancing interfacial adhesion at the carbon nanotube/titanium interface using ion beam irradiation

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The effect of increasing interfacial adhesion at the interface between a layer of multi-walled carbon nanotubes and titanium foil as a result of irradiation with argon ions was discovered and interpreted. Scanning electron microscopy was used to characterize the layer of carbon nanotubes before and after irradiation. The core-level photoelectron spectra of carbon, oxygen and titanium atoms were analyzed using X-ray photoelectron spectroscopy. It is shown that the increase in adhesion at the „multi-walled carbon nanotubes/Ti“ interface is due to the chemical bonding of titanium atoms with oxygen atoms of oxygen-containing functional groups formed on the surface of carbon nanotubes as a result of its irradiation with an ion beam. It is important that in this case the formation of titanium carbides does not occur.

Keywords: carbon nanotubes, interface, ion irradiation, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS).

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Currently, a special attention is paid to the development of supercapacitors based on new composite electrode materials with increased power, long service life and high charge/discharge rate [1]. The use of nanocomposites based on multi-walled carbon nanotubes (MWCNT) and electrically conductive polymers as a material for supercapacitor electrodes makes it possible to increase the capacitance characteristics of supercapacitors because of the large surface area, which increases the capacity of the double electric layer, and because of the additional contribution of pseudo-capacity [2]. One of the important problems of the practical application of this class of materials is the weak adhesion of MWCNT to a current-collecting substrate, which is currently solved by adding polymer binders to the system, such as polyvinylidene fluoride, carboxymethylcellulose, styrene butadiene latex, etc. [3]. However, their use results in a significant decrease of the conductivity of the electrode material and, as a result, in the need to search for new binder compositions, as well as other mechanisms to increase the adhesion of the electrode material to the substrate [4]. Another method to improve adhesion is based on the ion-assisted sputtering of thin films [5]. But the amorphization of the substrate occurs in this case.

A new approach to increasing the interfacial adhesion of MWCNT to the surface of a metal (titanium) substrate is proposed in this paper, based on the modification by a continuous ion beam of the surface of MWCNT layers

deposited by aerosol spraying on the surface of Ti-foil while preserving the structural characteristics of the layer.

Commercial MWCNTs were used in this study (MWCNT-2, produced by the Catalysis Institute of the Siberian Branch of the Russian Academy of Sciences) [6]. The MWCNT layer was deposited on the surface of the titanium foil by aerosol spraying of a suspension of MWCNT powder in isopropyl alcohol. The MWCNT layer was irradiated with argon ions with an average energy of 20 keV and a duration of 2, 5 and 10 min. The interfacial adhesion in the MWCNT/Ti system was evaluated by the visual inspection of the condition of the MWCNT layer on the surface of Ti-foil after 1 min treatment in an ultrasonic bath (Jeken Ultrasonic Cleaner model PS-06A).

The morphology of the MWCNT layers was studied by scanning electron microscopy (SEM) using JEOL JSM-6610 LV electron microscope. The analysis of the MWCNT electronic structure and the MWCNT/Ti interface was performed by X-ray photoelectron spectroscopy (XPS). The core-level C 1s, O 1s and Ti 2p photoelectron (PE) spectra were recorded using a laboratory spectrometer LAS-3000 (Riber, France) using AlK α -radiation with photon energies of $h\nu = 1486.6$ eV. The binding energy scale was calibrated using the Au 4f $_{7/2}$ peak (84.0 eV) and the Fermi level recorded on a plate of pure gold. Core-level PE spectra were processed using CasaXPS 2.3.16.

SEM data (Fig. 1) indicate the presence of a sparse MWCNT layer on the Ti-substrate. The nanotubes in the layer are located mainly parallel to the substrate, forming

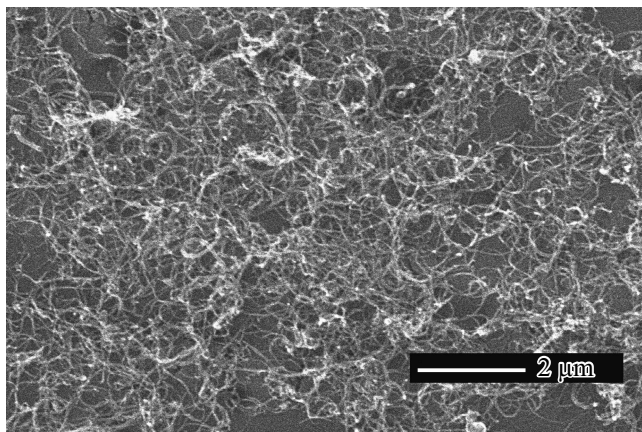


Figure 1. SEM-image of a thin layer of MWCNT on a titanium substrate.

Quantitative elemental composition of the MWCNT/Ti system before and after irradiation (according to the XPS data)

Sample	Concentration, at. %			
	[C]	[O]	[Ti]	[O]/[Ti]
MWCNT/Ti	61.4	26.1	12.5	2.1
2 min of irradiation	69.6	22.0	8.4	2.6
5 min of irradiation	67.1	24.0	8.9	2.7
10 min of irradiation	61.0	27.5	11.5	2.4

many intersections and overlapping each other. SEM images show areas of the substrate up to $1 \times 1 \mu\text{m}$ in size that are not coated with nanotubes, due to the small thickness of the MWCNT layer. There was no significant change of the morphology of the surface and disturbance of the MWCNT layer after irradiation for all irradiation modes.

The results of the elemental analysis performed using the XPS method are listed in the table. The oxygen concentration in the MWCNT sample before irradiation is 2 times higher than the titanium concentration, which is explained by the presence of an oxide layer TiO_2 on the foil surface, limiting the depth of probing of metallic titanium. An increase of the $[\text{O}]/[\text{Ti}]$ ratio to a value of 2.6 is observed after irradiation, which, apparently, is attributable to the formation of structural defects and broken chemical bonds on the surface of the MWCNT, on which oxygen-containing functional groups (OCFG) are attached [7].

The degree of interfacial adhesion of the MWCNT layer to the surface of Ti-substrate was visually qualitatively assessed based on the condition of the MWCNT layer after ultrasonic treatment described above. Fig. 2, *a* clearly shows that the MWCNT layer on the Ti surface is completely removed during ultrasonic treatment without ion beam treatment, which indicates a low adhesion of the MWCNT layer to titanium. The surface of the MWCNT layer irradiated with ions, even with minimal exposure time, practically did not

change its appearance after ultrasonic treatment as the color and uniformity of the coating were not affected (Fig. 2, *b*).

A detailed analysis of the C 1s, O 1s and Ti 2p-PE spectra of MWCNT/Ti samples both before and after ion beam irradiation allows obtaining a more detailed understanding of the mechanisms of interfacial adhesion in irradiated samples. The components corresponding to sp^2 -hybridized carbon C=C (~ 284.6 eV, C1), carbon in the structural defects (~ 285.4 eV, C2), carbon in C–O (~ 286.5 eV, C3) and C=O (~ 287.5 eV, C4), as well as OCFG: COOH– and $(\text{CO}_3)^{2-}$ (~ 289.0 eV, C5) are present in C 1s-PE spectrum of the MWCNT/Ti sample before irradiation (Fig. 3, *a*) [7].

The examination of the C 1s-PE spectrum of the MWCNT/Ti after ion beam irradiation reveals a significant increase of the full width at half maximum (FWHM) of the C 1s PE line from 0.8 to 1.6 eV, which suggests a change of the chemical state of carbon atoms in the MWCNT/Ti system. Moreover, a decrease of the relative intensity of component C1 (~ 284.6 eV) and an increase of the intensities of components C2 (~ 285.4 eV), C3 (~ 286.5 eV), C4 (~ 287.5 eV) and C5 (~ 289.0 eV) is observed [7]. In general, this indicates the formation of structural defects on the surface of the MWCNT and the attachment near the last OCFG. The absence of a noticeable PE signal in the spectrum in the region of binding energies of ~ 281.3 eV [8] indicates that the formation of bonds between titanium and carbon atoms and, consequently, TiC_x compounds does not occur.

Fig. 3, *b* shows Ti $2p_{1/2,3/2}$ spectra of MWCNT/Ti of samples before and after irradiation with argon ions for 10 min. Next, we will consider only the most intense Ti $2p_{3/2}$ spectrum. There are components corresponding to metallic Ti (~ 454.0 eV, Ti1) and oxidized states of titanium TiO_{1-x} (~ 455.5 eV, Ti2), TiO_{2-x} (~ 456.5 eV, Ti3) and TiO_2 (~ 458.6 eV, Ti4) in this spectrum of the MWCNT/Ti system before irradiation [8]. Thus, the titanium foil can be characterized by oxide compounds of titanium atoms with varying degrees of oxidation in the presence of a certain proportion of atoms of Ti^0 .

A noticeable decrease of the relative intensity of the Ti1 component is detected after irradiation in the case of Ti $2p_{3/2}$ spectrum of the MWCNT/Ti. In turn, the Ti2 and Ti3 components shift to the region of higher binding energies ($\Delta E \sim 0.2$ eV), which may be attributable to the oxidation of titanium atoms during irradiation.

Fig. 3, *c* shows that the O 1s-PE spectrum of a non-irradiated MWCNT/Ti sample can be described by three components O1, O2 and O3 corresponding to oxygen atoms bonded to a titanium atom (~ 530.6 eV, O1), as well as to the carbon atoms in the C=O (~ 532.1 eV, O2) and C–O (~ 533.3 eV, O3) groups [8]. An increase of the relative intensity of the O2 and O3 components corresponding to oxygen chemically bonded to carbon is observed in the O 1s PE spectrum of the irradiated sample, which is in good agreement with the data of quantitative XPS-analysis. Thus, it is possible to conclude that the chemical bonding between

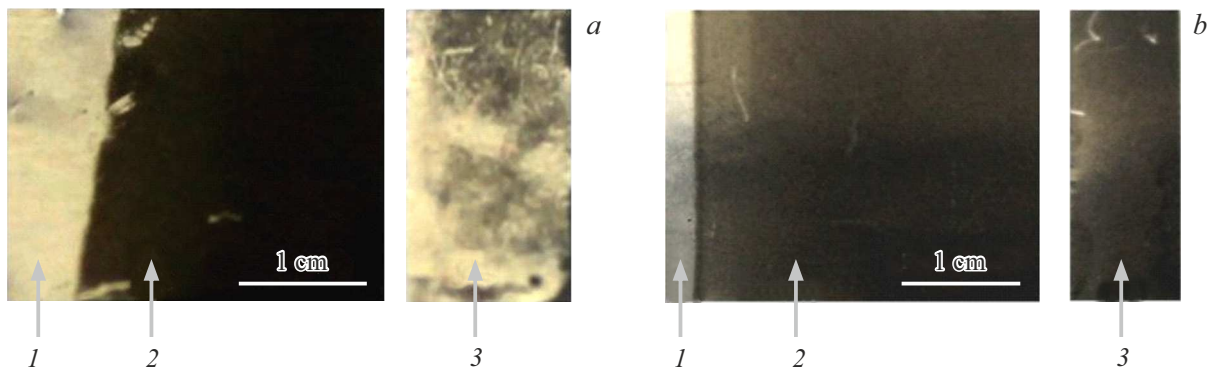


Figure 2. Photos of the surface of the MWCNT layer before and after ultrasonic treatment. *a* — non-modified MWCNT layer; *b* — modified MWCNT layer after 2 min irradiation with argon ions. 1 — the area of the substrate not coated by the MWCNT layer, 2 — the MWCNT layer on the substrate, 3 — a fragment of the MWCNT/Ti sample after ultrasonic treatment.

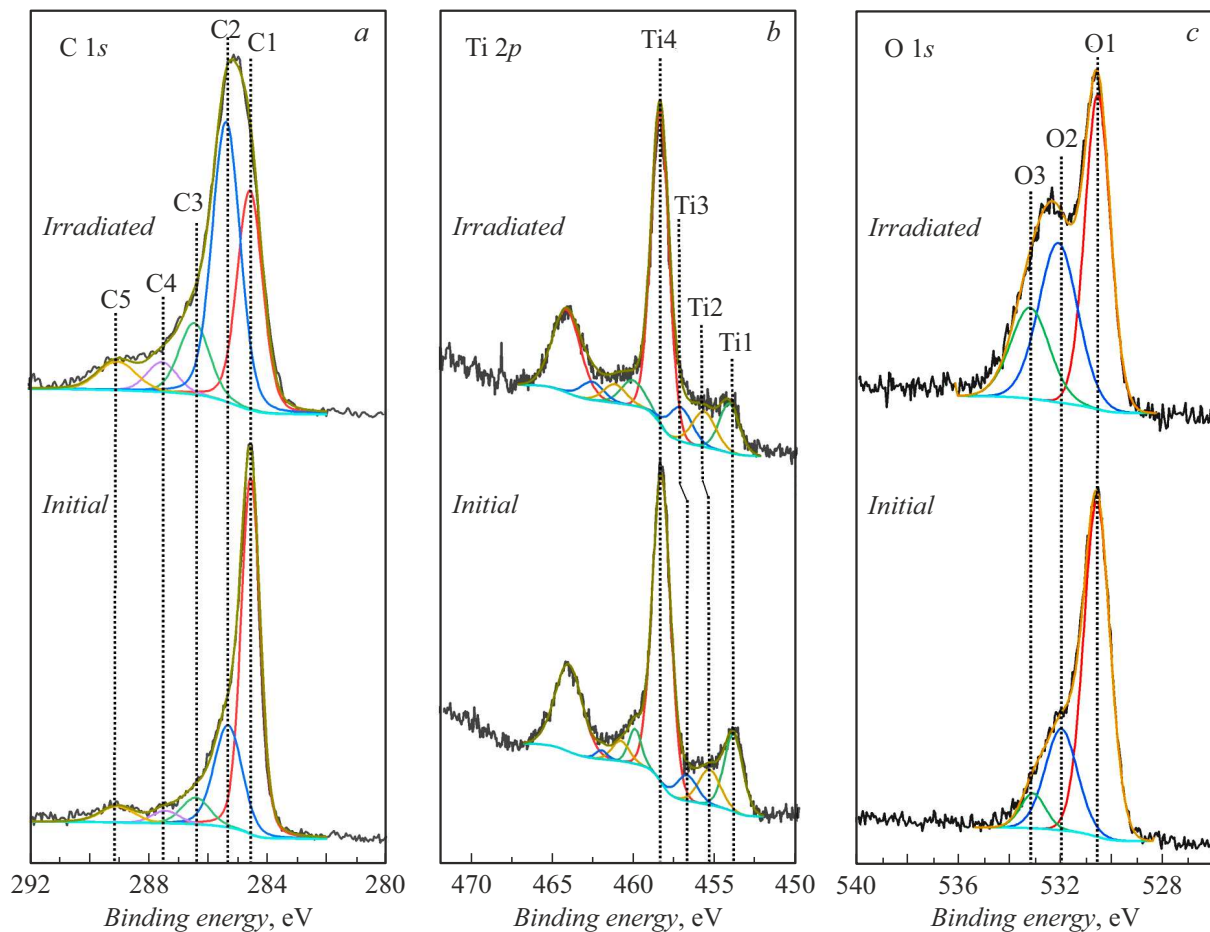


Figure 3. Core-level C 1s- (*a*), Ti 2p- (*b*) and O 1s- (*c*) PE spectra of the surfaces of the MWCNT/Ti samples before and after 10 min irradiation with an argon ion beam.

atoms of metallic titanium and oxygen in OCFG on the surface of the MWCNT formed near structural defects in the walls of nanotubes is the most likely reason for the increase of the adhesion of the MWCNT layer to the titanium substrate as a result of irradiation of the MWCNT/Ti system with a beam of argon ions.

The studies performed in this paper showed that the treatment of MWCNT layers on the surface of a titanium foil with argon ions can significantly increase the interfacial adhesion at the MWCNT/Ti interface. The acquired result can be used for the development of new supercapacitor electrodes with increased energy characteristics based on

electrically conductive polymers and carbon nanotubes without using any binder.

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Conflict of interest

The authors declare that they have no conflict of interest.

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