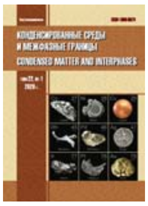

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NEXAFS and XPS Studies of Cr/MWCNT Composites

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Abstract

Nanocomposites obtained by MOCVD through deposition of pyrolytic chromium layers of different thickness on the outer surface of multi-walled carbon nanotubes (MWCNTs) using the "Barkhos" chromium-organic liquid were studied.. These pyrolytic Cr coatings have high microhardness, heat resistance, hydrophobicity, and chemical resistance to hydrochloric and sulphuric acids and alkali melt.

The unique physical properties of chromium coatings as well as chemical resistance in a wide temperature range and large external surface of MWCNTs offer great opportunities for the possible applications of the studied nanocomposites. An important problem in this case is the determination of the mechanisms of chromium adhesion to the chemically inert surface of MWCNTs.

A promising method of studying the interface between the MWCNT surface and the coating layer is ultra-soft X-ray spectroscopy in the NEXAFS 1s carbon ionization threshold region. However, there are practically no publications on such studies for chromium compounds due to the superposition of the structure of NEXAFS Cr2p absorption spectra on the NEXAFS C1s ionization threshold region. In the present paper, nanocomposites were studied by the total electron yield method using the unique technique of suppressing and measuring the contribution of multiple orders near the C1s absorption edge.

The studies of the nanocomposite (pyrolytic Cr)/MWCNT performed by NEXAFS and XPS methods showed: (i) the initial MWCNT features are preserved in the composite spectrum; (ii) there is no significant destruction of the outer layers of MWCNTs; (iii) the interface between the MWCNT and the pyrolytic chromium coating is a multilayer structure. This structure includes the outer surface of the MWCNT, the atoms of which form C–O and C–Cr bonds with the pyrolytic chromium coating, chromium carbide monolayer, and the chromium oxide (Cr_2O_3) coating layer. The effective thickness of the chromium oxide and chromium carbide coating layers is 1.5 and 0.3 nm respectively, were determined for the studied samples.

Keywords: multi-walled carbon nanotube, absorption cross section, photoelectron output depth, metal coating, NEXAFS, XPS, MOCVD.

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1. Introduction

Composites based on multi-walled carbon nanotubes (MWCNTs) with a metal containing coating offer great opportunities for use in various scientific and technical applications. The most common methods of composite synthesis are the electrochemical reduction of metallic salts using the sol-gel method, metal organic chemical vapor deposition (MOCVD), and physical deposition (electron-beam sputtering, thermal spraying, etc.). In our earlier studies, it was shown that MOCVD, due to its technological characteristics, is the most appropriate method for the synthesis of MWCNT composites with a metal containing coating [1–4].

The present paper is devoted to the investigation of an MWCNT composite with a pyrolytic Cr coating. Unlike pure Cr, pyrolytic Cr coatings have high microhardness, heat resistance, hydrophobicity, and chemical resistance to hydrochloric and sulphuric acids and alkali melt. Therefore, they can be used in the aviation (friction joints in aircraft control systems), petrochemical (anticorrosive coatings highly resistant to aggressive environments high in hydrogen sulphide), and steel (foundry and pressing equipment, thermocouple protection tubes) industries.

The chemical composition of the MWCNT outer surface, pyrolytic chromium coating, and the interface between the coating and the MWCNT surface was studied using NEXAFS (Near Edge X-ray Absorption Fine Structure) and XPS (X-ray Photoelectron Spectroscopy) methods.

2. Experimental

The initial MWCNTs were synthesized by MOCVD through thermal decomposition of the mixtures of ferrocene with toluene in a quartz reactor in a argon flow at atmospheric pressure. Deposition of pyrolytic chromium coatings on the MWCNT surface was also performed by the MOCVD method using as a precursor the “Barkhos” chromium-organic liquid, consisting of a mixture of bis-arene chromium compounds. The details of the preparation technique of the studied samples are described in the following works [1, 3, 4].

The study of the initial MWCNT surface, the chemical composition, and measurement of Cr coating thickness as well as the study of the Cr/MWCNT interface were conducted by NEXAFS spectroscopy using a a synchrotron radiation of Russian and German source at BESSY II [5]. Spectral dependence of absorption cross section in a wide energy range of 250–900 eV and near the C1s and Cr2p absorption edges of initial MWCNTs, Cr/MWCNT composite, and chromium oxide Cr_2O_3 were measured in the Total Electron Yield (TEY) mode. The studied samples were prepared by rubbing MWCNT powder and Cr/MWCNT composite into the pure surface of a Cu plate. An additional thin-film Ti filter with a thickness of 160 nm installed on an Au grid in front of the sample in the path of incident radiation was used for the suppression and estimation of the radiation reflected from a diffraction grating in multiple diffraction orders and long-wave diffuse background radiation [6]. The tracking of the contribution of background radiation is especially important for the Cr/MWCNT composite as the structure near the Cr/MWCNT composite absorption edge of the Cr coating in the second order diffraction is applied to a thin structure near the NEXAFS C1s absorption edge of the MWCNT.

XPS measurements of the Cr/MWCNT composite were performed using the equipment of the Center for Studies in Surface Science of Research park of St.Petersburg State University – Combined Auger, X-ray and Ultraviolet Photoelectron spectrometer Thermo Fisher Scientific ESCALAB 250Xi with an ion-electron system for charge compensation. An X-ray tube with an Al-anode was used as a source of radiation. Energetic positions of all peaks were calibrated against the C1s peak at 284.6 eV

3. Results and discussion

The analysis of NEXAFS C1s spectra (Fig. 1a) shows that the structures (π* and σ* resonances) typical for a initial MWCNT are preserved in the spectrum of the Cr/MWCNT composite, which indicates the absence of significant destruction of the outer layers of MWCNTs. However, an additional structure A (287.1 eV), B (287.7 eV), C (288.4 eV), and D (290.4 eV) was observed in an intermediate region between the π* and σ* resonances. The positions of these peaks are in good agreement with the energetic positions of the elements of NEXAFS C1s absorption spectrum of graphite oxide [7] corresponding to the ordinary (C–O, band A), epoxide (C–O–C, band B), and double (C=O, band C) bonds and the carbonate group $[CO_3]^{2-}$ [8]. It should be noted that in the quantum energy 285–287 eV range there may be a structure related to the possible formation of carbides [9], absorption transition in these compounds may make a contribution to A and B peak intensity in the C1s-spectra.

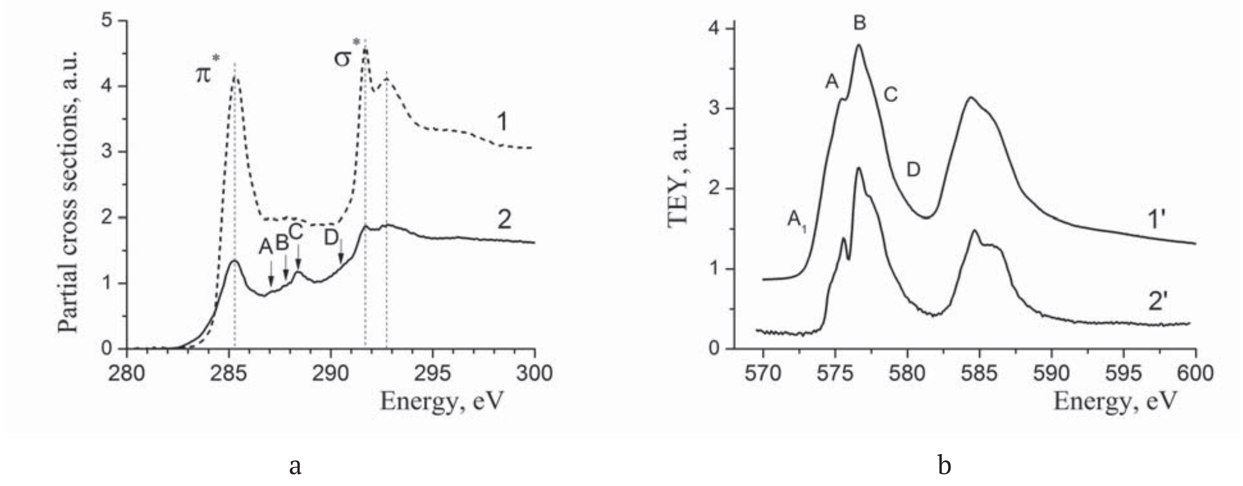
The presence of the elements typical for Cr_2O_3 (Fig. 1b) in the NEXAFS Cr2p edge allows assuming that the layer of chromium deposited on the surface is oxidised completely due to contact with atmospheric oxygen.

According to the data of the NEXAFS C1s spectra of MWCNT and the Cr/MWCNT composite, the effective thickness of the oxide coating (Cr_2O_3) was assessed according to the ratio:

$$d_{\mathrm{eff}} = \lambda \ln\left(\frac{S_1}{S_2}\right), \qquad (1)$$

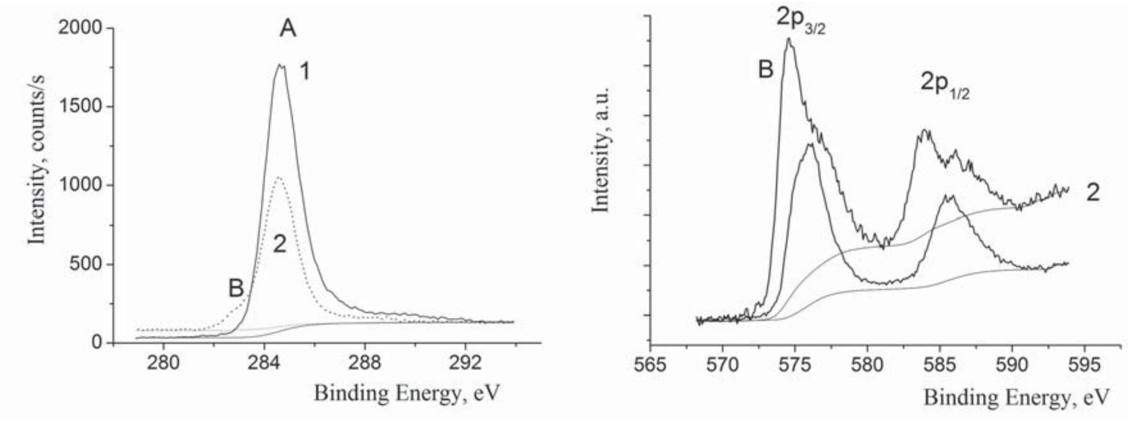
λ = 1 nm photoelectron escape depth from the surface of Cr_2O_3 [10]; S_1 and S_2 – areas under the spectral dependence of absorption cross section of MWCNTs, and the composite Cr/MWCNT, respectively ($S_1/S_2 = 2.6$); $d_{\mathrm{eff}} = 0.96$ nm.

Photoelectron studies are traditionally used for examining the phase composition of nanocomposites, in particular they can be used to determine the presence of the chromium carbide layer on the MWCNTs surface as well as to assess the characteristic thickness of the layers of chromium compounds covering the nanotubes. Fig. 2 shows XPS spectra in the C1s and Cr2p ionization thresholds region, both for the studied composite and for the initial nanotubes. The comparison of integral intensities of bands A in the carbon spectra of the initial MWCNT and the composite Cr/MWCNT ($S_1/S_2 = 1.91$) also allowed assessing the thickness of the Cr_2O_3 coating that equalled $d_{\mathrm{eff}} = 1.5$ nm (in this case the free path was $\lambda = 1.89$ nm [11]), which agrees with the above-mentioned assessment according to the NEXAFS spectra data. The appearance of additional B bands, both in 1s carbon spectra and 2p chromium spectra, should be noted while examining the XPS spectra of the composite. Their energetic position correlates well with the ionization thresholds in chromium carbides [12–13], which allows assuming that the carbon atoms of the nanotube interact with the chromium atoms and Cr-C chemical bonds are formed. At the same time, taking into account the free path of photoelectrons in the MWCNT layer $\lambda = 3.11$ nm [11], the ratio of bands A and B in the XPS C1s spectra of the composite allows assessing the thickness of the carbide layer as $d_{\mathrm{eff}} = 0.3$ nm. Thus, the chromium atoms coating formation process on the nanotube surface is as follows: at the initial stage, during the process of MOCVD, chromium atoms form a chemical bond with carbon atoms on the MWCNT surface forming a thin layer of chromium carbide that is covered with a layer of metal oxidised to Cr_2O_3 when the composite is subsequently exposed to the air.



a b

Fig. 1. Spectral dependences of a) the partial absorption cross sections of MWCNTs (*1*) and the Cr/MWCNT composite (*2*) in the NEXAFS region of the C1s absorption edge; b) TEY signals of the Cr/MWCNT (*1'*) and Cr_2O_3 (*2'*) composite in the NEXAFS region of the Cr2p absorption edge



a b

Fig. 2. XPS spectra a) in the region of the C1s edge of the ionization of the initial MWCNTs (*1*) and the Cr/MWCNT composite (*2*) and b) in the region of the Cr2p edge of the ionization of Cr_2O_3 (*1*) and the Cr/MWCNT composite (*2*)

4. Conclusions

The analysis of the data obtained by NEXAFS and XPS methods allowed establishing that, as a result of the interaction of chromium atoms with the outer surface of MWCNT, a multilayer structure is formed, consisting of the outer surface layer of MWCNT, a thin layer of chromium carbide covered with the of chromium oxide Cr_2O_3 layer with an effective thickness 0.3 and 1.5 nm respectively.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work presented in this paper.

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