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Nickel-Containing Carbon Nanotubes and Nanoparticles Prepared in a High-Frequency Arc Plasma

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Abstract—This paper presents the results of an investigation of nickel-containing carbon nanostructures prepared by plasma-chemical synthesis in a carbon–helium plasma jet at atmospheric pressure with the arc fed by a high-frequency current. It is demonstrated that, under these conditions, the conversion of graphite into a carbon condensate reaches 98 wt % and the contents of carbon nanotubes and nickel in this condensate are 72 and 10 wt %, respectively. Sequential treatment with nitric and hydrochloric acids has made it possible to extract purified carbon nanotubes and nickel nanoparticles coated with a carbon shell (approximately 50 nm thick) in which the nickel content is 4 wt %. Data are presented on the diameters of the prepared nanotubes and on the state of carbon in the samples.

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1. INTRODUCTION

At present, carbon nanotubes have been studied in sufficient detail. Owing to its unique properties, this material can be widely used for solving various problems in electronics, materials science, and many other fields of engineering and technology. The application of carbon nanotubes has been substantially hampered by the high cost of their production. Carbon nanotubes exhibiting unique electrical, magnetic, optical, and strength properties have promised a revolution in materials science and electronics. Moreover, by virtue of the nanometer-scale dimension of carbon nanotubes, their use instead of components of similar purposes in the already existing devices has become particularly attractive. Carbon nanotubes filled with 3*d* metals and their compounds have revealed interesting magnetic and electrical properties [1]. In this respect, their preparation and investigation are important not only from the fundamental viewpoint but also in view of promising applications.

There are many methods for preparing carbon nanotubes. The majority of these methods are based on condensation of carbon from a gaseous phase at a low pressure with the use of catalysts, usually, transition metals, which provide a means for preparing more ordered structures. Group VIII metals (Fe, Co, Ni), when used as catalysts, facilitate the preparation of single-walled nanotubes.

Laser ablation makes it possible to obtain up to 96% of carbon nanotubes only in the carbon condensate, but it is a rather expensive and laborious method. In order to produce one gram of defect-free carbon nanotubes, it is necessary to strictly maintain a temperature of 1200°C and a pressure of 66500 Pa for several hours; moreover, the use of catalysts entails a rather laborious preparation of an irradiated target [2].

The most commonly employed methods for preparing carbon nanotubes are laser ablation, chemical vapor deposition, and thermal sputtering of a graphite electrode in an arc discharge plasma in a helium atmosphere. When carbon nanotubes are synthesized using an electric arc deposition, the content of the carbon nanotubes in the cathode deposit has usually not exceed 60%. The rest of the carbon condensate, which is formed on the cooled walls of the discharge chamber, contains a rather small amount of carbon nanotubes. Furthermore, carbon nanotubes on the cathode surface congregate into cylindrical bundles and, under an unstable arc current, show a tendency toward agglomeration. Extraction of carbon nanotubes from

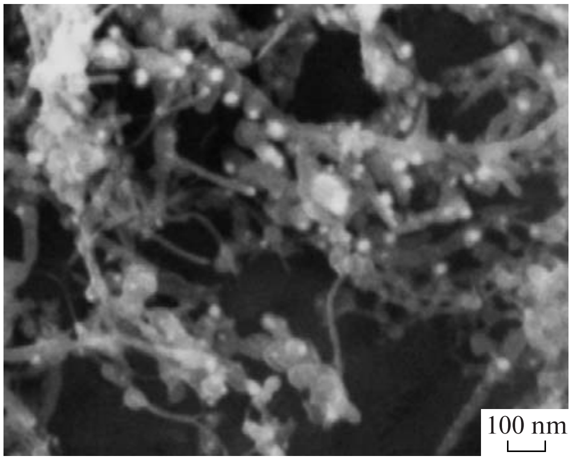

Fig. 1. Electron microscope image of sample **1**.

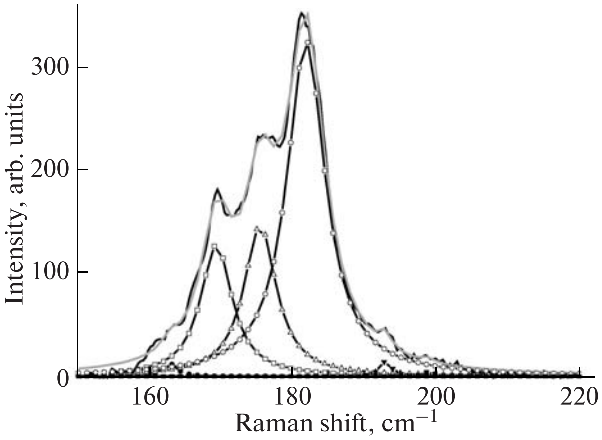

Fig. 2. Raman spectrum of sample **2** in the region of the breathing mode of the carbon nanotubes.

the cathode deposit is a laborious and expensive process. However, it is well known that the conversion of graphite into a carbon condensate containing carbon nanotubes and fullerenes without the formation of a cathode deposit is feasible when the electric arc is fed by an alternating current in the high-frequency range [3].

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

In this work, we extracted and investigated the components of the condensate produced by cooling the plasma consisting of carbon, nickel, and helium, which was formed in a high-frequency arc at atmospheric pressure [3]. The arc was ignited between two horizontally located graphite rods 5.5 mm in diameter. Finely dispersed nickel powder with a particle size of 0.5 μm was placed in an axial hole of the graphite rod electrodes. The ratio of the nickel introduced into the plasma to carbon was 1 : 7. The arc was fed by an electric current of 350 A at a frequency of 66 kHz, which made it possible to transform almost all electrode material (98%) into a condensate formed on the walls of the water-cooled chamber. The condensate (sample **1**) from the chamber walls was subjected to boiling at a temperature of 90°C in a strong nitric acid for 3.5 h. The precipitate filtered through an FS-III paper filter was insoluble in the acid and amounted to 76 wt % of the initial condensate. It was washed in distilled water to remove the acid and salt products and then was dried under normal conditions (sample **2**).

The solution, which was obtained upon boiling carbon black in the acid, was evaporated; then, the residue was washed in distilled water at a temperature of 60°C until the solution reached the pH value of 5. The precipitate thus obtained was dissolved in a dilute hydrochloric acid at a temperature of 90°C and then was filtered off. The undissolved residue again was washed in distilled water and dried (sample **3**).

The structure and composition of the samples were investigated using X-ray powder diffraction (DRON-4 diffractometer), X-ray fluorescence analysis (Bruker Pioneer S4 spectrometer), Raman scattering (Horiba Jobin Yvon T64000), and X-ray photoelectron and Auger electron spectroscopies (SPECS ultrahigh-vacuum photoelectron spectrometer). Electron microscope images of the samples were obtained with a JEOL JSM-7001F field-emission scanning electron microscope.

3. RESULTS AND DISCUSSION

The X-ray fluorescence analysis of samples **1**–**3** has demonstrated that the samples contain 10, 5, and 4 wt % Ni, respectively. The electron microscopic analysis of samples **1**–**3** has revealed that the carbon condensate, for the most part, exists in the form of carbon nanotubes containing metal particles with the size ranging from a few nanometers to several tens of nanometers (Fig. 1).

The Raman spectra of samples **1**–**3** are characterized by a set of vibrations of carbon nanotubes in the frequency range from 10 to 3500 cm^{-1}. All the spectra in the region of 180 cm^{-1} exhibit a vibration corresponding to the breathing mode (or to radial vibrations of the carbon nanotubes). The Raman spectrum of sample **2** in the region of the breathing mode of a single-walled nanotube is shown in Fig. 2. The maxima of the Lorentz components are observed at frequencies of 163, 169, 175, 182, 193, and 199 cm^{-1} and correspond to carbon nanotubes with diameters of 1.44, 1.38, 1.33, 1.29, 1.21, and 1.78 nm, respectively [4].

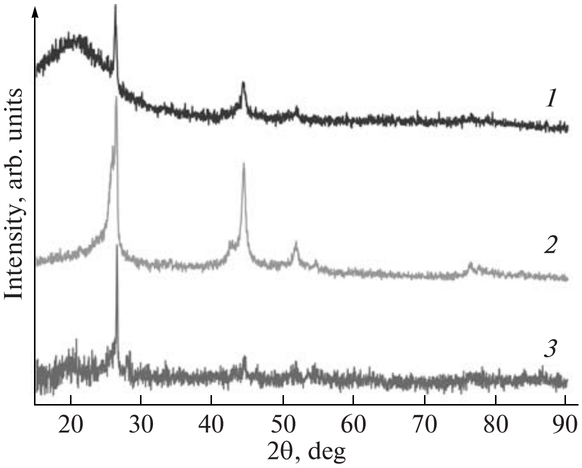

Fig. 3. X-ray powder diffraction patterns of samples (*1*) **1**, (*2*) **2**, and (*3*) **3**.

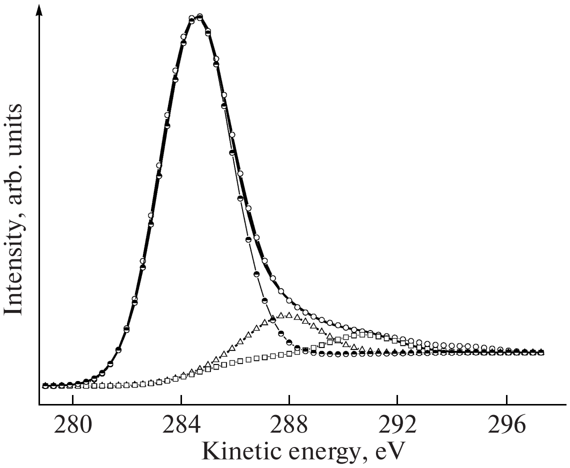

Fig. 4. Photoelectron spectrum of sample **2** in the region of the C 1*s* line.

The X-ray powder diffraction patterns of sample **1**–**3** contain reflections from nickel (44.3° and 51.7°) and graphite (26.4°) (Fig. 3). Apart from these reflections, the X-ray powder diffraction pattern of sample **2** exhibits reflections of lower intensity that correspond to nickel (76.4°) and graphite (42.6° and 54.5°). The reflection observed at 25.8° in the X-ray powder diffraction pattern of sample **2** corresponds to a graphite structure with an interlayer spacing of 3.42 Å. This reflection is revealed after the removal of finely dispersed carbon from the condensate. The X-ray powder diffraction pattern of sample **1** in the angle range 10°–30° contains a halo associated with the amorphous part of the sample, which disappears after the sample is treated with nitric acid (sample **2**).

The photoelectron spectrum in the region of the C 1*s* line of sample **2** containing purified carbon nanotubes is presented in Fig. 4. The Gaussian–Lorentzian deconvolution of the experimental C 1*s* line of sample **2** made it possible to separate a component corresponding to the C–C bond with the sp^2 hybridization characterizing the carbon nanotubes (E = 284.6 eV) [5] and components characterizing the double and single bonds of C and O (E = 288.0 and 290.9 eV) [6]. The component of the C 1*s* line, which corresponds to the double and single bonds of C and O, is also observed in the spectrum of sample **1**. According to the photoelectron and Auger spectroscopic data, sample **3** does not contain oxygen. The Gaussian–Lorentzian deconvolution of the C 1*s* line in the spectrum of sample **3** made it possible to separate components corresponding to the C–H bond (E = 283.0 eV), the C–C bond with the sp^3 hybridization characterizing carbon nanotubes (E = 284.6 eV) [5], and the C–C bond with the sp^2 hybridization (E = 285.2 eV) [6] characterizing the bending of the carbon nanotubes. Thus, the method used made it possible to determine the contents of carbon nanotubes in samples **1**–**3**, which are equal to 72, 81, and 56 wt %, respectively. The Ni 2*p*3/2 line in the spectra of samples **1**–**3** is shifted by 0.4 eV toward higher energies with respect to the line of metallic nickel; moreover, in the spectrum of sample **3**, this line is revealed only after etching the surface with an ion beam to a depth of approximately 50 nm.

4. CONCLUSIONS

The performed investigations have demonstrated that the method used for preparing carbon nanotubes in a high-frequency arc plasma is one of the most effective synthesis methods. In the carbon–helium plasma with nickel used as a catalyst, we obtained a carbon condensate containing nickel nanoparticles (approximately 10 wt %) with a graphite conversion of approximately 98%. In the initial carbon condensate and the carbon condensate remaining after treatment with nitric acid, the contents of carbon nanotubes were 72 and 81 wt %, respectively. Sequential treatment with nitric and hydrochloric acids made it possible to extract nickel particles coated with carbon. The nickel content in these particles was 4 wt %, and the thickness of the carbon shells were no less than 50 nm. The carbon nanotube diameters determined from the Raman spectrum were found to be 1.44, 1.38, 1.33, 1.29, 1.21, and 1.78 nm.

In the future, we are planning to publish the results of investigations into the magnetic properties of samples **1**–**3**.

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