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PROCESSES OF HEAT AND MASS TRANSFER IN PLASMA

CATALYTIC SYNTHESIS OF CARBON NANOTUBES IN PULSED BARRIER DISCHARGE PLASMA

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It has been found that it is possible to activate the process of obtaining carbon nanotubes by vapor deposition due to the generation in the reaction zone of nonequilibrium plasma by the method of pulsed barrier discharge. It has been shown that depending on the catalytic substrate used (nickel wire, stainless steel, porous aluminum oxide with nickel deposited) in the pores, under the conditions of pulsed discharge both individual carbon nanotubes (straight or helical) and their ordered arrays can be obtained.

Introduction. The great deal of attention that has been paid in the last few years to the development of effective methods for obtaining carbon nanotubes is due to the fact that they exhibit unusual electronical, mechanical, and chemical properties [1]. Of particular interest is the possibility of growing ordered arrays and single fixed nanotubes, which opens up prospects for their application as field emitters [2], sensors [3], probes of atomic-force microscopes [4], electrode [5] and ultrahydrophobic materials [6], elements of nanoelectronics [7, 8], gamma optics, etc. Recently a number of methods for growing ordered structures from carbon nanotubes based, as a rule, on the processes of chemical vapor deposition on catalytically active substrates have been proposed and realized in practice [9, 10]. Particularly favorable conditions for oriented growth of carbon nanotubes can be provided by using, as a catalytic substrate, hexagonally ordered channel-porous anodic aluminum oxide, in whose pores nickel, cobalt, iron, or their alloys are deposited [11,12]. In this case, the growth of nanotubes is controlled by the structure of the pores [13], which in turn can be varied over a fairly wide range by choosing the conditions for obtaining porous anodic aluminum oxide and its subsequent chemical etching [14].

Growth of carbon tubes with the use of reactions of catalytic pyrolysis occurs at temperatures from 700 to 1000°C (depending on the organic compound used as a carbon source [9–13, 15]), which sharply limits the choice of catalyst carrier substrates. At the same time a considerable decrease in the working temperature can be attained due to the chemical deposition of nonequilibrium plasma in the reactor (for which, in particular, electron cyclotron resonance [16] or microwave generation [17] can be used). It is also essential that such plasma activation opens up new possibilities of controlling the growth of carbon nanotubes and is able to provide a radical increase in the process rate on the whole. The aim of the present work was to investigate the possibility of obtaining carbon nanotubes at atmospheric pressure in a pulsed barrier discharge plasma with the use of the reaction of carbon monoxide disproportionation.

Experimental Procedure. Plasmochemical synthesis of carbon nanotubes under the conditions of pulsed barrier discharge was carried out with the use of the facility schematically represented in Fig. 1. Carbon monoxide acting as a carbon source was fed together with the carrier gas (N_2) into the deposition reactor representing a quartz tube (diameter 20 mm, thickness of the walls 1.5 mm) with a coaxially arranged internal cylindrical electrode of diameter 10 mm from stainless steel and an external electrode from metal foil. Between the electrodes pulsed voltage (10 kV, pulse repetition rate 25 kHz) was applied. The catalytically active substrates were placed directly on the boundary of

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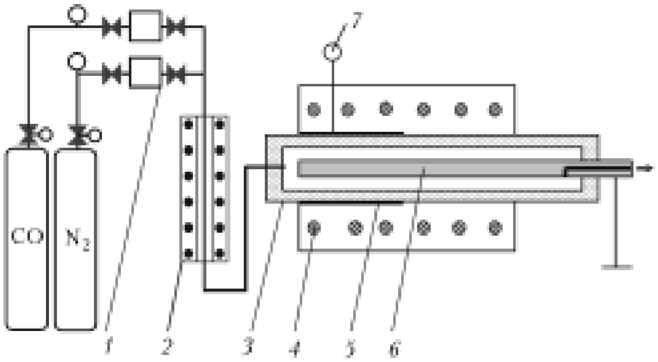

Fig. 1. Schematical representation of the facility for growing carbon nanotubes under the conditions of pulsed barrier discharge: 1) gas dosing system; 2) gas mixture heater; 3) tubular reactor; 4) reactor heater; 5, 6) electrodes; 7) pulsed source.

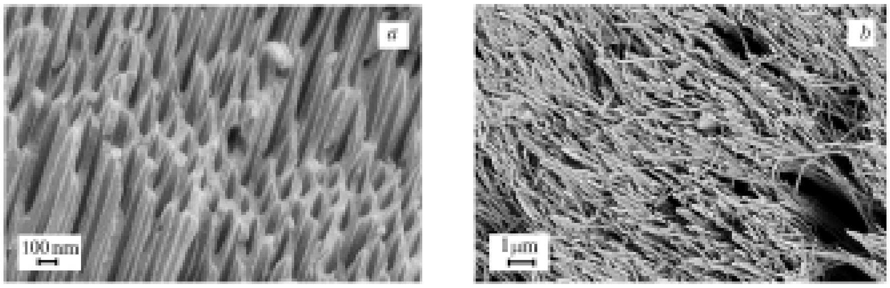

Fig. 2. Electron-microscopic images of: a) a spall of the channel-porous aluminum oxide film used as a nickel catalyst carrier; b) nickel fibers on the surface of the Ni/Al_2O_3 catalytic substrate formed after partial stripping of aluminum oxide.

the region of barrier discharge. The experiments were performed at a temperature of 500–700^{o}C and at atmospheric pressure. The flow rate of N_2 and CO was, respectively, 5 and 0.070 l/min. The deposition time of the carbon nanophase was 1 h in all cases. The luminescence spectra of the plasma were recorded by an SL40-2 spectrometer.

Porous anodic aluminum oxide films of thickness 50 μm with nickel deposited in the pores served as a substrate for growing carbon nanotubes. For comparison, in a number of experiments we used, as a substrate, nickel wire of diameter 0.1 mm and 50 μm-thick foil from stainless steel 12Kh18N9T pre-etched in 0.1 M solution of HCl. The electron microscopic study of the carbon nanotubes obtained was performed with the use of an LEO-906E transmission electron microscope and an LEO-1455VP scanning electron microscope.

Results and Discussion. *Obtaining a catalytic matrix based on anodic porous aluminum oxide.* Channel-porous oxide films acting as a metal-catalyst carrier were obtained by anodic oxidation of AMG-3 aluminum-magnesium alloy, which, as preliminary experiments have shown, permits providing a higher mechanical strength and a high resistance of anodic oxide to a heat shock. Before anodizing, metal specimens were subjected to mechanical treatment to attain a surface finish of class 12 and generate in the metal being anodized the required number of mechanical defects spaced at regular intervals, which created the conditions for the formation of highly ordered channel oxide with regular defect-free pores (Fig. 2) and made it possible to abandon the two-stage anodization traditionally used for obtaining porous aluminum oxide [18]. Anodization was carried out in an oxalate electrolyte ($H_2C_2O_4$ — 50 g/l, H_3BO_3 — 30 g/l) at a voltage of 45 V to provide the formation of channels of diameter ~50 nm at an occurrence density of ~10^{10} pores/cm^2. For further deposition of the metal the barrier layer in the oxide was degenerated by decreasing gradually the moulding voltage before completion of anodizing to the final value of 15 V.

Deposition of nickel in the pores of the thus formed anodic oxide was carried out with the use of a sulfate electrolyte ($NiSO_4$ — 50 g/l, H_3BO_3 — 30 g/l [19]) on alternating current of 50 Hz at a voltage of 15 V. The strip-

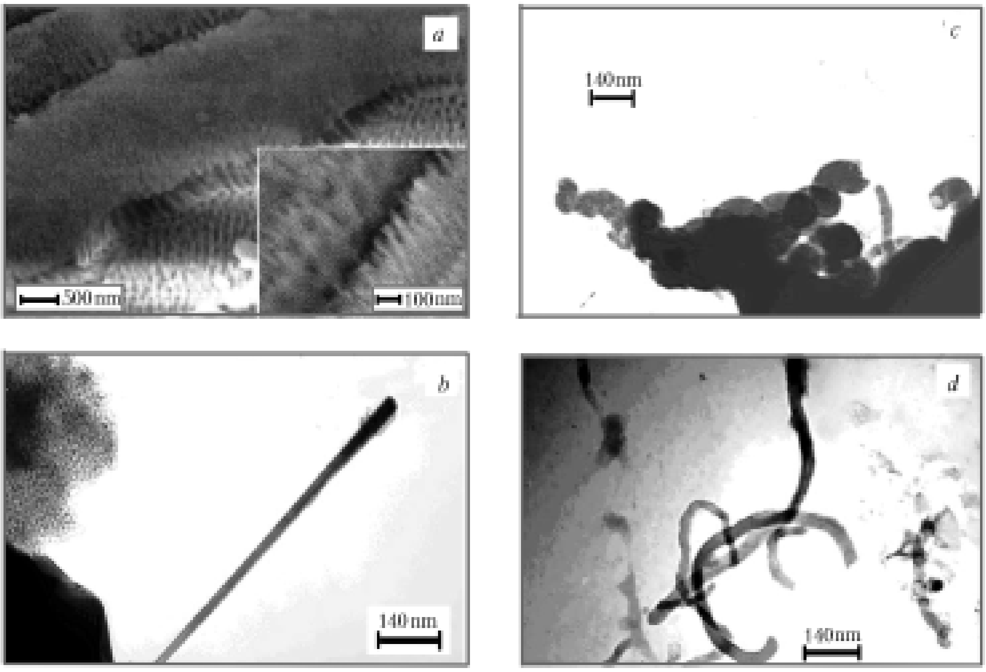

Fig. 3. Electron-microscopic images of: a) carbon nanotubes obtained under the conditions of pulsed barrier discharge with the use, as a substrate, of a porous aluminum oxide film, in which the channels are filled with nickel (the setting-in shows the structure of the array of nanotubes at a high resolution); b) nickel wire; c) stainless steel foil; and d) carbon nanotubes deposited on the reactor surface outside the barrier discharge zone. Scanning electron microscopy (a); transmission electron microscopy (b–d).

ping of oxide in a solution containing 20 g/l of CrO_3 and 20 g/l of H_3PO_4 permits judging the morphology of the nickel phase formed: As is seen from Fig. 2, the deposition on alternating current leads to a complete and uniform covering of pores with the metal. Analysis of the broadening of the X-ray diffraction lines points to the fact that the galvanic nickel sediment obtained under these conditions is formed mainly by crystallites with an average size of ~5 nm with an addition of a small amount (~5%) of larger crystallites of size ~30 nm, whose growth is obviously limited to the size of the pores in the oxide matrix.

The porous aluminum oxide films modified by the metal deposition were separated from the metal substrate by membrane etching with the use of 0.5 M HCl, which left the barrier layer intact. Since alternating-current deposition of metals is accompanied by their partial oxidation in the anode half-period, to reach the maximum activity, the patterned Ni/Al_2O_3 catalysts obtained were heated at 450°C in an oxygen current.

Plasmochemical synthesis of carbon nanotubes. In the absence of catalytically active substrates the formation of carbon nanotubes due to the disproportioning of CO in the barrier discharge was not observed. At the same time, on the Ni/Al_2O_3 catalyst surface under these conditions a close-packed array of carbon nanotubes of diameter ~30 nm and height ~0.4 μm oriented perpendicularly to the substrate is formed (Fig. 3). In so doing, nanotubes are formed only when the channels in the matrix are completely filled with the catalytic metal, i.e., in the presence of a good contact between the catalyst and the reactor medium in the process of growth of a carbon nanotube on it. The pronounced two-dimensional ordering of the nanotubes formed, which is observed despite the fact that the aluminum oxide matrix is able to provide their oriented growth only at the initial stage of synthesis, points to the high uniformity and defect-free character of carbon tubular structures aggregating by Van der Waals forces [20]. Another factor promoting ordering of the growing array is obviously the orientation of carbon nanotubes in an electric field under the conditions of a barrier discharge [16].

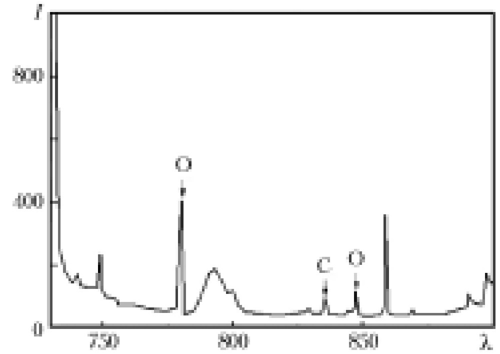

Fig. 4. Luminescence spectrum of the plasma in the pulsed barrier discharge reactor (the region of manifestation of atomic carbon and atomic oxygen).

Passing from the catalytic Ni/Al_2O_3 matrix to other substrates leads to a radical change in the morphology of the carbon nanophase formed. For instance, when nickel wire is used as a substrate, there appear individual strictly linear carbon nanotubes of diameter ~20 nm characterized by a high length-diameter ratio (reaching 100 or more) (Fig. 3). At the same time, on the surface of the stainless steel foil helical nanotubes (Fig. 3) similar to those formed in the process of pyrolytic decomposition of acetylene on iron-containing catalysts grow [21]. It should also be noted that tubular carbon fibers of irregular form are also revealed on the reactor walls outside the working zone (Fig. 3). The above discrete carbon nanotubes that appear in the process of catalytic synthesis in the barrier discharge are defective formations that have lost connection to the catalytic substrate.

The spectral dependence of the luminescence intensity I (rel. units) on the wavelength λ (nm) is given in Fig. 4. Along with molecular bands of carbon monoxide and the carrier gas (in the ionized and nonionized states), atomic lines of carbon (833.5 nm) and oxygen (777.4 and 844.6 nm) are also present in the spectrum. Thus, molecular carbon monoxide in the nonequilibrium plasma is given an excitation energy sufficient for the disproportioning reaction to proceed. The possibility of catalytic acceleration of the above process in contact with such metals as nickel, cobalt, and iron provides the conditions for the synthesis of coaxially cylindrical carbon nanoformations by the "carbide cycle" mechanism [22]. In the case of a Ni/Al_2O_3 substrate, the role of catalytic areas is played by the metal nanocrystallites forming a galvanic sediment in the oxide matrix channels. The fact that the size of these crystallites is smaller than the diffusion length of atomic hydrogen in the nickel catalyst provides the formation of nuclei of the carbon nanophase and its further growth [23]. In the case of nickel wire, the average size of nickel crystallites is much larger (~40 nm according to the X-ray diffraction data) and the growth of individual straight nanotubes obviously begins on the portions where small intercrystallite grains appear on the surface of faces (111), namely in the areas coinciding in symmetry and structure parameters with the flat grid (002) of graphite [24].

Conclusions. The results of the investigation show that carrying out a chemical deposition in a pulsed barrier discharge plasma makes it possible to grow carbon nanotubes at a relatively low temperature (500–700°C) and at atmospheric pressure. The process of isolation of carbon therewith has a catalytic character, and using various catalysts, one can obtain carbon tubular structures differing in morphology.

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