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Methods for preparation of carbon nanotubes

E G Rakov

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Abstract. The most important methods of synthesis and purification of carbon nanotubes, a new form of material, are described. The prospects for increasing the scale of preparation processes and for more extensive application of nanotubes are evaluated. The bibliography includes 282 references.

I. Introduction

Immediately after they had been discovered in 1991,[1] carbon nanotubes (nanotubulenes, hereinafter, NT) attracted so much attention of scientists of various professions that the discoverer, Iijima, soon became and still remains one of the most cited researchers in the field of nano-sized materials. The reason for this interest is not the unusual structure of these compounds, as in the case of fullerenes (although this also plays a certain role) but rather the prospects that are opened by the properties of NT for materials science.

The journal *Fullerene Science and Technology*, having the word 'technology' in its title, was founded in 1992; during the decade which has passed since the discovery of fullerenes (by 1995), 150 patents for their use were granted in the USA;[2] reviews dealing with commercialisation of the manufacture and use of fullerenes appeared;[3] however, there are still no data on the large-scale implementation of any patented method or, even more so, on the appearance of a new line of research in the materials science.

The situation with NT is absolutely different: as early as 1992 – 1993, the main fields of their potential application took shape and design of the first prototypes of future devices started. Some applications of NT were inherited from fullerenes (electrodes for chemical cells, safe sources of hydrogen in transport devices, optical filters), other applications coincide with those of carbon fibres (high-strength composites), and some fields of application are due to the unique properties of NT themselves (semiconductor devices, field emitters, probes of tunnelling microscopes, 'quantum wires'). It is clear that this is by no means the full list of currently known applications of NT. It is not without reason that a recent review [4] is entitled 'Nanotubes: a revolution in materials science and electronics'. As Buchachenko has noted vividly, carbon nanotubes made it possible 'to pass from fine words to impressive deeds'. [5]

Certainly, fullerenes, too, are finding and will be finding application (the rapidly progressing chemistry of fullerenes is now at an early stage of development); however, NT as materials have already clearly separated from their three-dimensional relatives.

Defect-free carbon NT are formed as a result of rolling of planar atomic network graphite sheets (graphenes) into seamless cylinders with diameters of ~ 1 to 120 – 150 nm and with lengths of up to hundreds micrometers. There exist three forms of NT: achiral NT of the 'armchair' type (two sides of each hexagon are oriented perpendicular to the NT axis), achiral 'zigzag' NT (two sides of each hexagon are parallel to the NT axis) and chiral or helical NT (each pair of the hexagon sides is arranged at an angle other than 0 or 90 ° relative to the NT axis).

The structures of NT are usually described by means of two indices, n and m, which are related unambiguously to the NT diameter (d) and the chiral angle (θ, characterising the deviation from the 'zigzag' configuration and ranging from 0 to 30 °) (Fig. 1).

$$d = \frac{a\sqrt{3(n^2 + m^2 + mn)}}{\pi},$$

where a are the interatomic distances in the planar network,

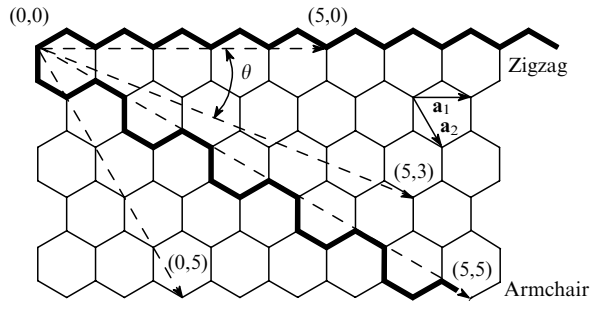


Figure 1. Scheme illustrating the structure of idealised NT.

E G Rakov D I Mendeleev University of Chemical Technology of Russia, Miusskaya pl. 9, 125047 Moscow, Russian Federation.
Fax (7-095) 490 75 23. Tel. (7-095) 948 54 67

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$$\theta = \arctan\left(-\frac{\sqrt{3m}}{2n+m}\right).$$

Thus achiral NT of the 'armchair' type are characterised by indices (n, n), those of the 'zigzag' type have indices (n, 0) and chiral ones are described by (n, m).

Nanotubes can be single- or multi-walled; the number of walls is theoretically unlimited but normally it does not exceed a few dozen. The distances between the neighbouring shells are close to the interlayer spacing in graphite (0.34 nm); thus, the smallest diameter of carbon NT is $\sim$0.7 nm. The diameter of the second and subsequent coaxial atomic layers is stipulated by the diameter of the innermost layer. In this connection, the structure of NT resembles that of onion fullerenes; if the inner shell is C_{60}, the second shell is C_{240}, the third one is C_{540}, *etc*. The spatial accordance of the structures of NT layers, *i.e*. retention of interatomic distances close to 0.34 nm is possible only provided that the chiral angle changes on passing from layer to layer.

The specific structural features of NT can hamper their use as materials — synthesis gives NT with different structures. Multi-walled NT are much more diversified; therefore, more uniform single-walled NT, which, in addition, usually contain fewer defects, are preferred for the design of functional materials.

In most cases, the tips of NT are covered by hemispherical or conical caps, which contain not only hexagons but also pentagons, in which the configuration of the carbon atoms is less stable. These caps are somewhat more chemically reactive than the lateral surfaces. The hemispherical caps resemble 'halves' of fullerene molecules. Thus the NT (10,10), isolated rather frequently, are capped by halves of spherical C_{240} fullerene.

Synthesis of NT can give a tough precipitate consisting of sintered NT, a somewhat softer precipitate of densely stacked NT, a rubbery material consisting of entangled NT ('paper,' 'mats'), a three-dimensional network of long fibres ('lace collar', 'web'), or a textured material consisting of parallel or nearly parallel (but arranged at a distance from one another) NT on a substrate ('forest'). Structures looking like a 'sea-urchin' and NT as helices (see below) have also been described.

Nanotubes tend to form relatively stable aggregates (they are referred to as bundles or 'ropes'), in which the axes of individual NT are parallel to one another, the shortest distance between them being $\sim$0.32 nm (Fig. 2). These aggregates arise due to van der Waals forces.

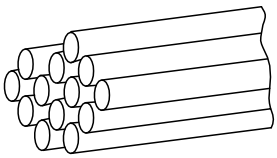


Figure 2. Schematic structure of bundles of single-walled NT.

In the majority of cases, the synthesis of carbon NT is accompanied by the formation of other carbon modifications — fullerenes, nanoparticles and amorphous carbon. The yields of NT and side products are determined by the conditions of synthesis; the removal of side products is an important stage in the synthesis of NT.

Good prospects for the design of new functional and structural materials are opened by modification of carbon NT, which can be accomplished by the following methods:

(1) filling of the inner cavities of NT with substances which alter their electronic, magnetic or mechanical properties;

(2) 'grafting' of functional groups to the tips of NT;

(3) replacement of some of the carbon atoms in NT by atoms of other elements;

(4) partial or complete cleavage of double bonds on the lateral surfaces of NT by adding one or another reagent;

(5) intercalation (insertion) of 'guest' atoms or molecules into the intertubular space of NT bundles.

In addition, NT can be used as templates in the template syntheses of nanotubular or nano-rod materials for various purposes.

The scope of this review is restricted to the methods of synthesis of NT because these methods are important for the development of studies and projects related to NT. They should lay the grounds for the future commercial manufacture. Attention is focussed on recent studies.

The publication in 1999 of a Russian review devoted to the structure, electronic properties and morphology of NT [6] facilitated the performance of this task. Earlier Russian reviews dealing with the mechanisms of the formation of fullerenes, nanoparticles and NT [7, 8] were also useful; however, they are somewhat less significant because lots of newer studies have appeared.

Apart from carbon NT, those containing B and N atoms are also briefly considered in this review. These NT can be synthesised either from carbon NT or simultaneously with them.

II. Electric-arc synthesis

It is known that an electric arc develops a temperature of up to 4000 °C, its 'burning' being accompanied by transfer of a substance between the electrodes. In 1990, electric arc-synthesis with graphite electrodes under an atmosphere of inert gases was first used to prepare fullerenes in relatively large amounts.[9] It is among the products of arc synthesis that Iijima discovered carbon NT in 1991.[1] Subsequently, this procedure has been modified and used in many laboratories of different countries.

1. Principles of the method

The first synthesis of NT in relatively large (gram) amounts was also performed in Japan.[10] The electric-arc synthesis was carried out under a helium atmosphere using graphite electrodes — an anode 8 mm in diameter and a cathode 12 mm in diameter — located at a distance of less than 1 mm from each other. The current in the arc reached 100 A (current density $\sim$150 A cm^{-2}) and the voltage was 10 to 35 V. The rate of the growth of the cathode deposit was $\sim$1 mm min^{-1}. Some of the graphite evaporated from the anode turned into carbon black and soot, which were deposited on the walls of the reaction chamber, and some was deposited at the cathode. The outer solid layer of the cathode deposit contained sintered NT and nanoparticles, which could not be separated. The purity and yield of NT depended appreciably on the helium pressure — the formation of NT started at $\sim$13 kPa, and at 66–332 kPa, the cathode deposit contained only NT and nanoparticles. The optimum pressure was 67 kPa; in this case, $\sim$75% of the electrode material consumed was deposited at the cathode, the yield of NT, which were accumulated in the inner, black, relatively soft part of the deposit being $\sim$25%.

The yield of NT attained in an argon flow was much lower than that in a helium flow.

Analysis of the results of the first studies on the structure and synthesis of NT [10–14] allowed Ebbesen [15, 16] to note some characteristic features. The material formed has a hierarchical structure, in which tens or hundreds of individual multi-walled NT with diameters of 2–20 nm and nearly equal lengths (microns or tens of microns) are joined into regularly organised bundles resembling ropes. These ropes are combined into fibres with a diameter of $\sim$50 μm, while the fibres are joined into threads having even greater diameters (about a millimeter) and visible with the naked eye. The larger the bundle, the more disordered can it be.

The formation of columns $\sim$50 μm in diameter consisting of NT and arranged parallel to the electrode axis has been reported.[17] This study is notable due to the setup used; it had movable vertical electrodes with a diameter of 19 mm, which (as well as the arc area) could be cooled during the process. (In the conventional arc syntheses, the cathode and anode diameters are different, the anode diameter being smaller than the cathode

diameter.) Using this setup controlled by a computer, the researchers were able to deposit ~90% of the substance at the cathode and to obtain thus high-quality multi-walled NT. The current in the arc of this setup reached 250–300 A, although the current density at the beginning of the process was even lower than the standard value and amounted to 70–80 A cm^{-2}. Upon annealing in air at 650 °C, the columns were etched being replaced by channels surrounded by entangled NT.

An increase in the electrode diameter normally causes sintering and cracking of NT. A dense greyish product is accumulated in the inner part of the cathode deposit, instead of the easily extractable black material. This phenomenon was initially explained by insufficiently high temperature of the synthesis;[18] however, the assumption that the temperature was, conversely, too high seems more reasonable.[17]

The decrease in the anode diameter from 12.7 to 8.0 mm with the cathode diameter (25.4 mm) and current density (140 A cm^{-2}) remaining the same increased the yield of NT. An increase in the pressure of helium (which is believed to quench NT) from 6.6 to 101 kPa also resulted in an almost proportional increase in the rate of growth of the deposit.[18] However, according to Ando and Iijima,[19] variation of the yield of NT as a function of gas pressure passes through a maximum, the position of which corresponds to 7 kPa in the case of Ar or CH_4 and to 3 kPa for He. In the opinion of Wang *et al.*,[18] the discharge used in the synthesis of NT is quasi-continuous and has a characteristic interruption frequency of ~8 Hz. The discharge is initiated between the closest sections of the electrodes and, after some amount of graphite has been evaporated from the anode (which extends the discharge), it 'jumps' to the neighbouring section and thus becomes shorter. Travelling of the arc over the electrode surface changes presumably the sites of localisation of NT.

Lozovik *et al.*[7] believe that an arc discharge between graphite electrodes has two modes of operation, a noisy and a quiet one, transition from one mode to the other being induced by changes in the current density. A high current density and a low inert gas pressure (noisy mode) result in the predominant formation of fullerenes, while nanoparticles and NT are formed predominantly at a relatively low current density and a high pressure (quiet mode).

A thorough investigation of the cross-sections of bundles obtained by the arc method showed that NT do not have, as a rule, a cylindrical shape.[20] The cross-sections of NT look like polyhedra or ellipses with numerous defects including edge dislocations. The structures of NT are intermediate between the 'Russian doll' model (coaxial seamless cylinders) and the 'folded carpet' ('scroll') model. In earlier studies, either model has been preferred, although the methods used in the investigations did not allow one to reveal the differences between them.[21] Moreover, it was found that the 'scroll' model is too regular to describe many NT and, in some cases, the 'papier-mache' model (separate fragments applied onto one another) should be accepted (Fig. 3).[22]

Some disordering of the structure is due to the fact that NT are formed in the arc under non-equilibrium conditions and to the stress arising upon joining of individual NT into bundles. The presence of a large number of defects in multi-walled NT obtained in an electric arc is confirmed by experiments on their intercalation.[23, 24]

It has been suggested[25] that bundles are formed under the influence of an electric field, their length, diameter and the manner of laying being dependent on the electric field strength. However, in reality, bundles can be formed even without electric fields. Nevertheless, it is beyond doubt that the field has an influence on the morphology of the products of arc synthesis.

The yield and shape of NT formed in an arc discharge plasma depend not only on the main arc discharge variables (the voltage between the electrodes, the current strength and density, temperature of the plasma) and parameters related to the discharge



Figure 3. Structure models of multi-walled NT. (*a*) 'russian doll'; (*b*) 'scroll'; (*c*) 'papier-mache'.

variables (the pressure and composition of the inert or reacting gas) but also on the gas flow rate, on the dimensions of the reaction chamber, and on the duration and the scale of the process. The configuration of cooling devices if they are present (determines the size and shape of temperature fields) and the power of cooling devices (determines the heat removal), the nature and purity of the electrode materials and several other parameters that can hardly be quantitatively evaluated are also significant.[10, 15–19, 26] The main parameters governing the yield of NT — the rates of NT growth and quenching — depend on numerous variables which are far from being fully taken into account in experimental studies. This accounts for some contradictions, hampers comparison of the results and often makes them poorly reproducible. The absence of theoretical models (related to the setup geometry), which makes scaling impossible, might be due to the same reasons.

The mechanism of the formation of NT in an arc discharge has not yet been unambiguously elucidated, although it is discussed in many studies. There exist two main opposing models. According to one model, growth of NT advances due to the addition of carbon atoms or fragments from the vapour phase to the dangling bonds at the tips of open NT, whereas according to the other model, they add to the topological defects in the caps of closed NT. In recent years, preference is given to the former model, because the occurrence of 'edge-to-edge' ('lip–lip') interactions has been proved. They prevent the formation of caps in multi-walled NT due to the formation of 'fluctuating' (closure–rupture) C–C bonds at the tips of two or three neighbouring coaxial NT.[27, 28]

The role of the electric field in the mechanism of the formation of NT is obviously overstated in some publications. It has been shown[16, 29] that this role is far from being paramount, the NT growth involving simultaneously charged (C^+ *etc.*) and neutral (C_2 *etc.*) carbon species. The difference between the main carbon sources might account for the formation of two types of condensed products, NT and polyhedral particles. It is also unlikely that the tips of NT growing at the cathode in an arc discharge are opened due to strong electric fields.[30]

The experimental studies considered above describe the preparation of multi-walled NT. The formation of single-walled NT was first observed by Ajayan and Iijima,[31] but this study has not been adequately appreciated, later studies being regarded as the pioneering ones.[32, 33] Both groups of researchers cited[32, 33] performed the synthesis in the presence of catalytic additives. This opened up a new chapter in the history of NT.

2. The influence of catalytic additives

The pioneering studies[32, 33] somewhat contradict each other in details but coincide in the main point stating that the introduction of small amounts (1%–2%) of transition metals such as Fe, Co, Ni or their mixtures into the graphite anode influences appreciably the shape and the yield of NT and, in some cases, also localisation of the NT-containing product in the reaction chamber.

Subsequently, admixtures of Li, Cu, Ag, Zn, Cd, B, Al, In, Y, La, lanthanides, Si, Ge, Sn, Ti, Hf, Pb, Sb, Bi, S, Se, Cr, W, Mn, Ru, Pd, Pt, mixtures of two metals or of a metal with a nonmetal and several carbides and oxides were tested.[28, 34–37] It was found that vaporisation of an anode containing Co, Co–Ni, Co–Y, Co–Fe, Ni, Ni–Y, Ni–Lu and Ni–Fe gives deposits looking

like a lace collar or a soft belt being formed around the cathode deposit. They contain single-walled NT mixed with amorphous carbon and metal particles, the NT having diameters of 1.2–1.4 nm and being joined into more or less ordered bundles. The tips of single-walled NT are closed and contain no metal particles. Upon evaporation of graphite anodes with Ni–Y and Co–Y admixtures, the content of single-walled NT in the deposits reaches 70%–90%.[37] The yield of NT also markedly increases when a Co–Pt mixture is used.[38]

Some catalysts (Cu; Cu with Ni, Pt, Y or Fe; Ni; Ni with Y, Lu or Fe) caused the formation of a 'web', which hung between the cathode and the walls of the chamber. This web, as well as the deposit on the chamber walls, contained fullerenes, amorphous carbon, flat graphite particles and small amounts of single-walled NT. In some cases, a rubber-like deposit was formed on the walls; it could be detached as pieces or ribbons (Fig. 4).[39]

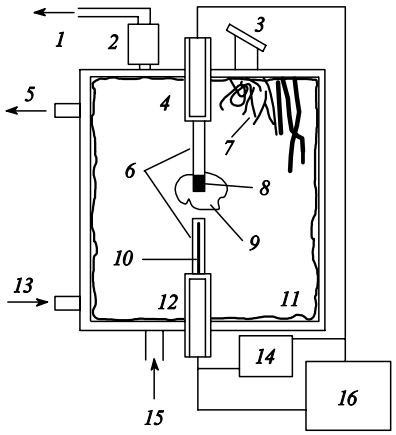


Figure 4. Setup for electric arc synthesis and localisation of various products;
(*1*) to vacuum pump; (*2*) filter; (*3*) viewing window; (*4*) cathode; (*5*) nozzle for the removal of the cooling water; (*6*) graphite electrodes; (*7*) web-like precipitate; (*8*) cathode deposit; (*9*) rubber-like deposit around the cathode; (*10*) filling material (a mixture of powdered graphite with a metal); (*11*) fullerene- and NT-containing soot on the walls; (*12*) anode; (*13*) nozzle for the supply of cooling water; (*14*) voltmeter; (*15*) helium inlet; (*16*) power supply.

The addition of sulfur to a Co catalyst also resulted in a greater amount of the web-like product and higher NT yields and in a quite noticeable scatter in the NT diameters (from 1 to 6 nm).[40] Evaporation of Co and S simultaneously with graphite changed the shapes of the resulting products and led to the evolution of multi-walled NT in the middle of the cathode deposit, multi- and single-walled NT together with many other particles in the rubber-like deposit around the cathode, and single-walled NT in the web-like material.[39]

Kiang *et al.*[40] believe that the multi- and single-walled NT are formed *via* different mechanisms and that Co and S induce the formation of single-walled NT directly in the gas phase and prevent the NT tips from closing. Since sulfur itself does not catalyse the formation of NT, its role seems to reduce to the stabilisation of dangling bonds.

The addition of Bi and Pb also causes an increase in the NT diameter. The carbon ring structures formed in the gas phase are believed to play an important role in the mechanism of formation of single-walled NT. The most stable ring structures are those containing 10 to 40 carbon atoms, which form Co_mC_n clusters together with Co atoms. It is these clusters that function as catalysts, while S, Bi and Pb stabilise the ring structures.[41]

The results of studies on the catalysed arc synthesis of single-walled NT are summarised in Table 1.[42] It can be seen that the diameter of NT obtained in this way varies from 0.6 to 6 nm.

Table 1. Characteristics of NT prepared by arc discharge synthesis in the presence of catalysts.[42]

Catalyst	Diameter of NT /nm		Composition of crystallites [a]
	limits	average	
Fe	0.7–1.6	0.80, 1.05 [b]	Fe_3C
Fe	0.6–1.3	0.7–0.8	–
Co	0.9–2.4	1.3, 1.5 [b]	Co
Co	0.6–1.8	–	Co in a graphite shell
Ni	1.2–1.5	–	Ni in polyhedral particles
Ni	0.6–1.3	0.7–0.8	–
Fe + Ni	0.9–3.1	1.7	–
Fe + Ni	>0.6	1.3–1.8	–
Co + Ni	>0.6	1.2–1.3	–
Co + S	1.0–6.0	1.3, 1.5 [b]	Co and Co in polyhedral particles
Co + Bi	0.8–5.0	1.2, 1.5 [b]	–
Co + Pb	0.7–4.0	–	–
Co + Pt	~2	–	CoPt
Y	1.1–1.7	–	YC_2 in polyhedral particles
Cu	1–4	–	Cu in polyhedral particles
None	>2	–	–

[a] The crystallites are located inside NT or polyhedral particles (see Section III.3). [b] The curve for the distribution of NT over diameters exhibits two maxima.

The mechanism of the catalytic action of metals in the formation of single-walled NT implies adsorption of carbon atoms on the surface of metal particles and their free migration over the surface to the base of a growing NT.[43] It was shown experimentally that the catalytic reaction can follow either of two routes, depending on the size of the metal catalyst particles. If the particle size (average diameter) is several tens of nanometers, which is much greater than the NT diameter (~1 nm), many closed NT sprout from one particle. If the particle size is not larger than the NT diameter, the particle moves together with the growing NT tip. The results of molecular dynamics modelling[43] confirmed the probability of the former pathway, involving migration of adsorbed carbon atoms to the NT base and the 'root' growth of NT. It should be borne in mind, however, that this model is of limited utility. It does not take into account the fact that NT formed in arc synthesis contain lots of defects and that a stream of carbon atoms directed towards growing NT has the greatest intensity near the NT tips. In addition, the conditions of vapour condensation in different sections of a setup, as well as in different setups are nonequivalent, which results in the formation of particles with dissimilar morphologies.

Nevertheless, the modelling made it possible to explain why multi-walled NT are not formed in the presence of catalytic additives (this would require cooperative processes, associated with consistent interaction of numerous particles), why single-walled NT always have relatively small diameters (the growth of NT is initiated on the surface bulges of metal particles and the diameter of these bulges is small with respect to the height), and why mixed catalysts are often more efficient than one-component ones (this is due to the enhancement of carbon adsorption, to the change in the activation energy of the NT growth, and to the formation of a surface with a large number of bulges).

Apparently, single-walled NT are even more prone to form bundles, which are combined in 'ropes' with a two-dimensional triangular crystal lattice.[37, 44, 45]

Journier and Bernier,[26] who surveyed studies on catalytic arc synthesis, have rightly stated that the yield and the shape of NT can differ substantially even when the same metal is used, depending on the metal concentration, pressure of the inert gas, current strength (or density), and the geometry of the arc setup.

A special role in the arc synthesis of NT is played by boron, the introduction of which as B, B_2O_3 or BN induces the formation of a large number of well graphitised long (up to 20 μm) NT with boron-containing caps.[46] In this case, B_4C crystals, large fullerenes and BC_3 nanotubes are produced in addition to carbon NT. The presence of boron in the gas phase decreases appreciably the concentration of C_2 fragments in the plasma zone and the contents of fullerenes in the wall deposit.[47] Since the C_2 clusters are the main source of condensed structures, the introduction of boron can change the mechanism of the formation of NT. Note that the arc setup used in the study cited [47] differed only slightly in geometry and electric parameters from the conventional setups used for the synthesis of carbon NT [anode and cathode diameters 6 mm (a cathode with a diameter of 200 mm was also tested), distance between the electrodes 1 mm, current 80 or 150 A, voltage 25 or 40 V, respectively, gas pressure 27 – 67 kPa].

In some studies the formation of carbon NT, separate areas of which were made of BN has been noted.

Under certain conditions, for example, upon evaporation of BN or mixtures of B or BN with graphite, boron carbides, nitride, and carbonitrides can form 'self-contained' NT.[48 – 51] The use of HfB_2 (see Refs 52, 53) or ZrB_2 (see 54, 55) electrodes for the electric arc synthesis in a stream of N_2 results in the formation of BN nanotubes. If BC_4N serves as the electrode material,[56, 57] NT containing B, C and N (or BN) are produced; when the electrodes are made of graphite with the addition of BN ,[48] the process yields NT containing BC_2N and BC_3 . However, in the latter case, the composition of NT is nonuniform along the length of the tubes.

Unique multi-walled NT have been prepared by Suenaga *et al.*,[58] who also used HfB_2 and graphite as the electrode materials; several inner shells consisted of carbon, several central shells (embracing the carbon shells) were made of BN, and some outer shells were again carbon. The mechanism of formation of these NT (they evolved together with polyhedral particles, which also contained layers with different compositions) is totally unclear. The inner layers might grow upon diffusion from an NT tip; however, the probability of this process is low. Since the electronic properties of C and BN layers are different, this result brought about the idea of designing electronic devices with radial heterojunctions.

Studies on the catalytic synthesis have much in common with the studies on the synthesis of NT the inner cavity of which is filled with one or another substance.

3. Preparation of filled nanotubes

Filling of the inner cavity of NT (encapsulation) is a route to the development of a great number of novel nanomaterials of various classes and functions (materials with specific electronic, magnetic, optical, or mechanical properties, catalysts, sorbents). Some of them could be used as a type of 'NT – filler' nanocomposite, while other require that the carbon shell be removed (burned out). Particular attention is devoted to the preparation of 'quantum wires', *i.e.*, conducting materials with a diameter of several nanometers, whose conductivity is close to truly one-dimensional conductivity. The possibility of using NT and nano-rods in nanotechnological devices is being discussed.

The first study on filling NT was performed in 1993.[59] Mixtures of NT with Pb were annealed in air at ~400 °C. In the presence of O_2, the molten metal opened the tips of NT, removed the hemispherical caps and was sucked into the inner cavities of the NT by capillary action. However, it has been reported [60] that lead is able to fill NT only at pressures of 1000 to 10 000 atm; hence, under the conditions described above, NT were filled by lead compounds rather than by lead metal. Indeed, it has been shown that heating of a mixture of Pb_3O_4 with NT for 9 h at 700 °C results in opening and filling of the NT.[61] Encapsulation of molten V_2O_5 , PbO, Bi_2O_3 (see Refs 62, 63), MoO_3 (see Ref. 64) and $AgNO_3$ (see Refs 65, 66) into open NT has also been reported.

Even before the discovery of NT, the arc method has been used to prepare endohedral fullerenes [67] and nanoparticles encapsulated into a multilayered graphite shells.[68, 69] Therefore, it comes as no surprise that filling of NT can occur directly during the arc synthesis. Ordinary and filled NT are obtained under different conditions, in particular, filled NT are formed at lower temperatures (1000 to 2000 °C).

Yttrium carbide was the first substance detected inside NT prepared in an arc.[70 – 72] According to an estimate,[35] yttrium is encapsulated into NT more easily than many other metals, although this feature can hardly be related to the enthalpy of formation of YC_2 . Later, carbides of other lanthanides and Mn have also been encapsulated into NT.[73 – 75] Carbides have been formed when metal-doped graphite anodes have been used because carbides are the species most stable in the presence of carbon. However, in some cases, elementary substances have also been detected inside NT, for example, Mn,[76] Cu, Ge [77 – 79] and even small amounts of Y.[72] These elements either do not form stable carbides or are liberated in an arc discharge under an H_2 atmosphere.

Thus copper forms no stable carbides and does not catalyse the formation of NT or fullerenes; therefore, the mechanism of its encapsulation differs from the mechanism of insertion of other metals.[78] Evaporation of a graphite anode in a hydrogen plasma in the presence of copper gives rise to polycyclic aromatic hydrocarbons, which form graphite shells around Cu particles.[78, 79] The formation of filled NT upon joint evaporation of pyrene and Cu or Ge (this was done using a Cu anode with a cavity filled with pyrene and a W cathode) [80] was considered [78, 79] as direct evidence supporting the above statement.

Metals with different volatilities show different behaviour during encapsulation.[81] Some substances fill long NT giving continuous crystals with lengths of up to 1 μm (Cr, Ni, Sm, Gd, Dy, Yb, S, Se, Ge, Sb); other substances fill only short NT (Al, Bi, Te), and some other elements form inclusions separated from one another inside NT (Co, Fe, Pd).[36, 82 – 85] In a study of encapsulation of high-melting transition metal carbides (NbC, TaC, MoC), an exceptionally stable face-centred form of the carbide MoC was discovered. [85] Nanotubes containing B_4C in the inner cavity have also been prepared. [86]

The operation conditions used in these studies [70 – 83] did not differ much from those used for the synthesis of NT. Thus Setlur *et al.*[78] used electrodes with a diameter of 10 mm located at a distance of 0.25 to 2.0 mm; the current was 100 A, the voltage was 20 V and the gas pressure ranged from 1.3 to 6.7 kPa. In another series of studies,[82 – 84] the corresponding parameters were 9 mm, 1 mm, 100 – 110 A, 20 – 30 V and 60 kPa.

Sulfur plays a special role in the formation of filled NT.[84] Sulfur can be contained in a graphite anode as a minor impurity; it promotes filling of NT with other elements. In some cases, sulfur enters NT as a sulfide but more frequently it is not present in the filling material. This effect of sulfur has been explained [84] by the fact that sulfur forms clusters with carbon in the gas phase; this ensures transportation of sulfur to the growing NT, where it promotes graphitisation of NT and reconstruction of a metal surface, resulting in the exposure of catalytically more active crystallographic planes. At the final stages of the process, sulfur is removed from the graphite shell of the NT. These results are similar to the data reported in earlier publications.[39, 40] In some cases, sulfur suppresses the formation of single-walled NT.

The technique of filling NT under the conditions of arc synthesis suffers from a severe drawback — this process is hardly controllable. The yield of filled NT and the composition, structure and morphology of encapsulated substances cannot be governed in the majority of cases.

4. Modifications of arc synthesis

The use of an alternating-current arc and electrodes with identical diameters changes substantially the pattern of the process, namely, the products are formed on the chamber walls rather than at the electrodes, new forms of NT being produced together with the known ones.[87, 88] The yields and forms of some products

also depend on whether the electrodes are mounted in the vertical or horizontal position.

A series of publications [19, 89–91] deal with the formation of multi-walled NT under a methane atmosphere. This process differs from the conventional one (performed under an inert gas) in the fact that, under some conditions, the formation of NT is not accompanied by evolution of fullerenes or nanoparticles. At high partial pressures of methane, relatively thick multi-walled NT are formed and at low pressures (1–3 kPa), thin and long multi-walled NT are produced. The optimal conditions for the formation of thin NT for the vertical mounting of electrodes with a diameter of 6 mm are the following: methane pressure 2.7 kPa, current 30 A.

Later, the authors of the above series of studies arrived at the conclusion that, since CH_4 decomposes in an arc to give C_2H_2 and H_2, the synthesis of NT should better be performed in a stream of H_2 (see Refs 92–95).† Some advantages of using H_2 have been mentioned above in the consideration of copper encapsulation. A certain role in the formation of NT can also be attributed to the high heat capacity of H_2, owing to which it can efficiently quench NT.[96] When the process is performed at 'plasma' temperatures, the fact that the energy of ionisation (the first ionisation potential) of H_2 is half that of He also becomes significant.

Rather long NT are formed even at an H_2 pressure of 7 kPa; their yield at a pressure of 13 kPa is comparable with the yield attained in the atmosphere of He at 66 kPa. Many NT prepared in a flow of H_2 have a narrow inner channel; they are open and usually high-quality NT (having few nanoparticles on the outer surface). The thinnest and longest multi-walled NT were prepared at H_2 pressures of 6.7–11 kPa.

The arc synthesis in an atmosphere of H_2 differs appreciably from the synthesis in inert or hydrocarbon media because the temperature developed in the atmosphere of H_2 is higher. This provided grounds for assuming that C^+ ions participate in the formation of NT in an H_2 medium.[92] It is also assumed that either H_2 molecules or H atoms add to the dangling bonds of growing NT and thus prevent closure of these bonds and, in addition, eliminate the possibility of the formation of amorphous carbon.[92] The addition of H_2 is evidenced by the fact that an increase in the partial pressure of H_2 results in higher yields of open NT. The mechanism involved may be similar to the mechanism of the formation of diamond from the gas phase. Particles of various natures are produced; however, under a hydrogen atmosphere, the most reactive ones are completely or partially gasified (etched).

Yokomichi *et al.*[97] have attempted to prepare NT in a CF_4 medium. It has been assumed that the F atoms formed upon decomposition of CF_4 would attach to the dangling bonds and prevent them from closing, thus influencing the process of NT formation. This assumption largely proved to be correct; in any case, no fullerenes were formed together with NT. The synthesis was carried out using a setup with electrodes 5 mm in diameter at a current of 20–60 A and a CF_4 pressure ranging from 2.7 to 53 kPa. Under the optimal conditions (20–40 A, 6.7–13.3 kPa), multi-walled NT were synthesised with an outer and inner diameters of 20 and 5 nm, respectively; they did not differ much from the NT obtained in a flow of He.

The researchers cited[97] studied the influence of the main parameters of the process (medium, gas pressure and current) on the yield of NT and polyhedral particles and on the length of NT and compared their data with those reported in other publications; the results were summarised in a table (Table 2). In particular, it follows from this table that the processes occurring in an atmosphere of CF_4 and CH_4 are fairly similar. However, the data of Table 2 should be treated with caution because this way of presenting the information does not show, for example, that in some cases, the plots for the variation of the yield *vs* current pass through a maximum.

Table 2. Influence of the increase in the gas pressure and in the current on the main characteristics of electric-arc synthesis of NT under atmospheres of various gases.[97]

Medium	Yield of NT	Length of NT	Yield of nanoparticles
CF_4	decreases	increases	decreases
He	increases	does not change	does not change
CH_4	decreases	increases	does not change
H_2	decreases	does not change	does not change

Koprinarov *et al.*[98] have attempted to devise a continuous electric arc process and to make up for the consumption of graphite due to evaporation by supplying CH_4. For this purpose, they used the 'reverse method', *i.e.* the area of the anode in the setup used was an order of magnitude greater than the area of the cathode. The products of electric-arc synthesis were found to contain fullerenes, polyhedral particles and single-walled and multi-walled NT. The nanotubes had different lengths and structures. Some of them were partly single-walled and partly multi-walled structures; this indicates that various sections of NT grew at different rates. The 'reverse method' offers no advantages over the conventional method.

Carbonised coal can be used as the electrode material instead of graphite;[99] however, the presence of non-volatile impurities causes contamination of NT; hence, in the majority of studies, high-purity graphite is the material of choice.

The main drawback of the arc method is low output. This is demonstrated by a publication [37] in which synthesis in a He flow in the presence of Ni and Y introduced in a graphite anode gave only 2 g of NT over a period of 2 min. After that, the setup had to be disassembled to replace electrodes and take the products out.

III. Laser-assisted synthesis

Fullerenes were first obtained by the laser method in 1985; however, only 10 years later, this method was employed to prepare NT.[100, 101] The first setup was a 50-cm quartz tube with a diameter of 2.5 cm containing a graphite rod 1.25 cm in diameter arranged along the tube axis. The tube was evacuated and simultaneously heated to 1200 °C. After that, Ar was supplied (pressure 66.5 kPa, linear gas velocity 0.2–2.0 cm s^{-1}). The target was exposed to a laser beam with a wavelength of 532 nm (Nd laser), a pulse frequency of 10 Hz, a pulse power of 250 mJ, and a pulse duration of 10 ns. The surface of the target was scanned by a laser spot with a diameter of 3 or 6 mm. The products of evaporation (multi-walled NT and nanoparticles) were collected on a cooled copper finger, on the walls of the tube, and on the reverse side of the graphite target (Fig. 5).

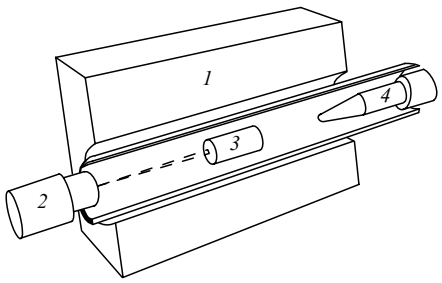


Figure 5. Scheme of the laser setup;
(*1*) furnace heated to 1200 °C; (*2*) neodymium laser; (*3*) graphite target; (*4*) water-cooled collector.

† Subsequently, the same conclusions have been drawn by other investigators.[96]

The daily output of the first setup was up to 80 mg of a nanomaterial containing NT. The process had to be terminated because the tube was clogged near the target with a web-like material which also contained NT. By using a tube with a diameter of 3.8 cm, all other conditions remaining almost the same, another group of researchers attained a higher yield of a rubbery material containing single-walled NT. In this case, the output was 200 mg per experiment (3–5 h).[102] It was noted that distribution of the NT over diameters depends on the radiation wavelength (either 532 or 1064 nm).[102]

An increase in the diameter of the reaction tube to 5 cm was even more effective. This setup can afford ~1 g of the material (containing 60%–90% of NT) per 24 h.[103]

Subsequently, one laser was replaced by two lasers (wavelengths 532 and 1064 nm), which emitted alternately, the interval between the pulses being 42 ns, and the power of a pulse was increased to 490 and 550 mJ, respectively.[103] This made it possible to 'knock down' the plums formed. Subsequently the tube diameter was doubled once again; in addition, alternation of the side of the target exposed to radiation and beam scanning were used. As a consequence, the yield of products containing 40%–50% of NT reached 20 g during 48 h of continuous operation.[103]

Yudasaka *et al.*[104] used a modified setup with two targets, one made of a graphite powder and the other made of a metal or an alloy.

Study of the influence of the pressure of Ar and the furnace temperature on the yield and properties of the laser ablation product has shown that at pressures below 13 kPa only amorphous carbon is formed, while NT appear in the products, together with amorphous carbon, above 26 kPa.[105]

An increase in the furnace temperature from 780 to 1050 °C resulted, in the presence of catalysts, in an increase in the average diameter of single-walled NT from 0.8 to 1.51 nm, although the yield of NT at low temperatures was relatively low.[106]

The yield and the shape of NT prepared by the laser method are determined by fewer parameters than those of the NT obtained by the electric-arc synthesis. Perhaps, this is why markedly higher yields of NT have been attained in the laser-assisted synthesis. The temperature of the area from which graphite is evaporated and the temperature gradient in the gas phase near this area can be considered to be the crucial factors. Unfortunately, in the experiments described above these parameters have been determined insufficiently definitely if at all (the measurements were hampered by the beam scanning over the target surface). Instead, properties influencing the temperature of evaporation were measured (the furnace temperature, laser radiation power, diameter of the light spot on the target, the velocity of the spot migration, the gas pressure, and the gas flow rate).

The introduction into graphite of small amounts of catalysts led to the formation of single-walled NT, which, unlike those obtained in arc, were only slightly covered by amorphous carbon particles.[101, 107] Mixtures of Co with Ni (0.6 at.% each) and of Co with Pt (0.6 at.% and 0.2 at.%) proved to be the best catalysts. When these mixtures were used, the yield of single-walled NT exceeded 70%, which is tens or hundreds times higher than the yields attained using individual metals as the catalysts. High yields have also been obtained with mixtures of Ni with Pt.[100]

The use of a mixture of two noble metals, Rh and Pd, mixed with graphite in a laser-assisted synthesis afforded single-walled NT with diameters of 1.0–1.5 nm.[108] Only mixtures of Cu with Ni were found to be substantially less active than copper itself.[100]

The mechanism of the catalytic formation of single-walled NT upon laser ablation proposed by Thess *et al.*[107] was defined as the 'scooter' mechanism. According to this mechanism, individual atoms of Ni, Co or other catalytically active metals are adsorbed on the open tips of the curved C_n ($n \leqslant 50$) graphene fragments and 'scoot' around the tips, thus promoting removal of all carbon structures except for the energetically preferred ones.

Clusters comprising 10 to 100 closed-tip nanotubes formed 'ropes', 10 to 50 of which composed bundles. A more detailed study of the 'ropes' showed that they are polycrystals, the sizes of separate grains ranging from 10 to 100 nm (the typical size is 10 to 20 nm); their cross-sections are oval and the predominant aspect ratio is ~3.[109]

Some of the NT are clustered into 5–15 nm thick 'ropes' forming rings with diameters of 300–500 nm.[110]

The products of laser-assisted synthesis were found to contain an interesting type of NT, so-called 'nano-peas', which are chains composed of spherical C_{60} molecules located inside single-walled NT with a diameter of 1.3–1.4 nm.[111]

The laser method also makes it possible to prepare NT from BN;[112–115] however, the experimental conditions employed in this case differed sharply from those used to prepare carbon NT; specifically, high and superhigh pressures were used. The process induced by laser heating of hexagonal BN in a diamond anvil at a high pressure under an atmosphere of N_2 has an interesting feature, namely, cubic BN appears at the bottom of the NT formed.[115] The mechanism of formation of NT from BN upon laser evaporation at superhigh pressures might include a stage of surface diffusion of molecules from the bottom of an NT to its tip, which implies restriction of the NT length.[116]

Laser ablation of a complex target (C, Si, BN) at near-atmospheric pressure accompanied by chemical reactions can be used to synthesise axial NT. This type of NT with diameters of several tens of nanometers and with lengths of up to 50 mm contained a core of β-SiC, an intermediate layer of amorphous SiO and an outer shell of BN and C.[117] The study cited aimed at designing coaxial nano-sized electronic devices with heterojunctions.

In addition to the neodymium laser, a CO_2 laser has also been tested for the synthesis of carbon NT.[118]

IV. Other methods of graphite vaporisation

The conclusion that fullerenes and NT are formed in the vapour phase, irrespective of the way used to vaporise graphite or another form of carbon, was drawn fairly long ago and has been confirmed in a number of publications. Thus Ebbesen *et al.*[119] proved, using isotope dilution, that NT (as well as fullerenes) are formed exactly from carbon vapour. Apart from the arc- and laser-induced evaporation of graphite considered above, NT are also prepared using resistivity vaporisation and vaporisation induced by electron or ion beams or by sunlight.

1. Resistivity vaporisation

Heating a 0.5-mm graphite foil by Joule heat *in vacuo* (10^{-6} Pa) and cooling the resulting vapour to −30 °C resulted in NT being deposited on the surface of single-crystalline graphite.[120–123] The rate of deposition of NT with a diameter of 1–4 nm was 0.5 A s^{-1}. The NT were capped and combined in arrays. This method permits the preparation of particles having diverse shapes — single-walled and multi-walled NT, NT bundles and nano-cones, the yield of single-walled NT ranging from several percent to 80%–90%.

2. Electron- or ion-beam vaporisation

The first experiments on the preparation of NT by electron-beam vaporisation of high-purity (99.99%) reactor grade graphite *in vacuo* (10^{-3} Pa) and deposition on various substrates (Si, quartz, graphite, ceramics, anodised Al) were performed in Russia back in 1992.[124] The resulting condensate was a 0.01–10-μm thick film consisting of NT with a diameter of ~1 nm. Separate NT were joined in fibres ~5 nm in diameter, while the fibres were clustered in cables with a diameter of 10–30 nm. The tubular texture was retained throughout the whole film thickness; moreover, variation of the angle between the direction of the stream of carbon particles and the substrate surface resulted in the formation of inclined

textures. Kosakovskaya *et al.*[124] measured a large number of film characteristics and noted anisotropy of film properties.

Nanotubes have also been formed on bombardment of high-purity graphite with Ar^+ ions with an energy of 60 keV in a high vacuum at a normal angle of incidence.[125] Polyhedral nanoparticles were isolated together with NT.

Exposure of hexagonal BN to an electron beam gave NT;[126] as in the study described above,[115] in this case, too, the formation of seeds of cubic boron nitride at an initial stage was assumed. The irradiation with electrons with a current density of 10–20 A cm^{-2} at a voltage of 300 kV resulted in annealing of most of defects and in almost complete ordering of the BN walls of the NT.[112] An electron beam with a current density of 150 A cm^{-2} at an accelerating voltage of 400 kV ensured the formation of multi-walled coaxial BN clusters. [127]

Irradiation of boron-containing carbon with electrons gave carbon NT doped with boron.[128]

The role of the gas phase in this process and in other processes described above is obscure; therefore, the term 'vaporisation' is used only conditionally.

3. Sunlight-induced vaporisation

The studies dealing with the use of solar concentrators for the preparation of NT have been briefly surveyed in a publication.[26] These studies were carried out only in France. A setup producing a temperature of about 3000 K at the focus was developed. Evaporation of pure graphite gave only a small amount of soot, whereas vaporisation of a graphite powder with catalysts gave rise to NT. The type of NT formed (single-walled, multi-walled or bamboo-like) and the amount of impurities were governed by the catalyst and the gas pressure in the process, *i.e.*, by the same parameters as in the case of electric-arc and laser-assisted syntheses, described above and studied much more extensively. In the presence of Co, single-walled NT with a diameter of 1–2 nm were found in the soot deposit and NT bundles with diameters of more than 20 nm containing no admixture of amorphous carbon were found in the web-like deposit.

V. Pyrolysis of hydrocarbons and decomposition of CO

1. Catalytic pyrolysis

Catalytic pyrolysis of hydrocarbons had been used to prepare carbon fibres even before the discovery of NT and fullerenes. Nanotubes were first synthesised by this method in 1993.[129] The course of the process is influenced by the temperature, the overall pressure, the initial hydrocarbon used and its partial pressure, the nature and characteristics of the catalyst (first of all, the particle size, which could determine the diameter of the NT), and the nature of the catalyst support. The pyrolysis can result in layers of amorphous carbon or graphite formed around catalyst particles, carbon fibres and multi-walled or single-walled NT.[26] The length of NT and the degree of their coverage by amorphous carbon particles depend on the duration of the process.

a. Pyrolysis of acetylene

Acetylene is used most often for pyrolysis. José-Yacamán *et al.*[129] carried out acetylene pyrolysis at 500 °C and atmospheric pressure over a graphite catalyst containing 2.5% of Fe. The concentration of acetylene in the diluent (N_2) was 9%. It was noted that graphite particles are formed initially around the Fe particles and this is followed by growth of NT with diameters of 5–20 nm and lengths of up to 50 μm. Nine different catalysts (Fe, Co, Ni and Cu supported on three materials — flake graphite, SiO_2 or HY zeolite) have been assayed;[130, 131] the effects of the flow rate, the temperature and duration of the pyrolysis on the yield and quality of NT have been studied. An increase in the temperature from 500 to 800 °C influences only slightly the length of NT but increases the yield of amorphous carbon (amorphous carbon constitutes up to 50% of the deposit even under the optimal conditions). Longer pyrolysis times result in higher relative yields and greater lengths and diameters of NT. The replacement of the inert diluting gas by H_2 barely influences the growth of NT. In all cases, the structure of NT was defective. A graphite coating was formed around the catalyst particles and multi-walled NT were 'extruded' from it.

Testing of Fe catalysts prepared by various procedures showed [132] that Fe supported on SiO_2 provides the best results. The greatest yield of NT was attained when C_2H_2 was pyrolysed at 700 °C. The outer and inner diameters of NT were, on the average, 10–20 and 5–8 nm, respectively.

As a further development of the study cited,[132] pyrolysis of C_2H_2 over Fe particles in mesoporous SiO_2 has been carried out.[133] The catalyst was prepared by hydrolysis of tetraethoxysilane in a solution of $Fe(NO_3)_3$ followed by reduction with an H_2-N_2 mixture at 550 °C. The diameter of NT (~30 nm) obtained at 700 °C from an acetylene–nitrogen gas mixture (9% of C_2H_2) was nearly equal to the diameter of pores in SiO_2. It has been assumed that NT with a smaller diameter can also be obtained in this way. Each NT contained 40 to 50 shells and was located at a distance of ~100 nm from the closest neighbours; thus, the deposit looked like a 'forest' consisting of nanotube 'stems' parallel to one another. The rate of the growth of NT was about 25 μm h^{-1}. In the initial stages, NT were free from the amorphous carbon impurity; however, as the duration of the pyrolysis and, correspondingly, the length of NT increased (the NT grew to a length of 50–100 μm over a period of 2–5 h), the 'stems' bent and amorphous carbon appeared on their surface. The main obstacle hampering the conducting of larger-scale process is the difficulty of manufacturing substrates with large dimensions because they are subject to shrinkage and cracking.

An improved method for the synthesis of a supported Fe catalyst has been proposed.[134, 135] The method was based on the deposition of a film of a $Fe(NO_3)_3$-containing gel onto a 30–50 μm quartz plate, the removal of excess water and other solvents and drying at 80 °C. As this was done, the gel cracked into pieces with an area of 5–20 mm^2 each. These pieces were calcined *in vacuo* and then the iron was reduced to give small (5–50 nm) iron particles distributed uniformly over the surface.

Pyrolysis of a $C_2H_2-N_2$ mixture containing 9% of acetylene at 600 °C and a pressure of 24 kPa in the presence of this catalyst made it possible to obtain NT in very high yields. The outer diameter of NT amounted to 30–40 nm and the inner diameter was 10–15 nm. They consisted of 10–30 coaxial layers. Individual NT were located at distances of ~100 nm from one another. The rate of the growth was 30–40 μm h^{-1} and the length of NT (attained in 48 h) was ~2 mm. The greatest area coated by NT was 15 mm^2. No formation of polyhedral particles was detected. The layer of NT was easily separable from the substrate.

A mechanism consisting in the NT growth on the side of a free tip, which is covered by a catalyst particle, has been proposed for this process.[135] The micrographs of NT obtained by the transmission electron microscopy, which are presented in a study cited,[135] show an iron particle at the tip of the NT and a top-shaped cavity at the NT base. These results are at variance with the data of José-Yacamán *et al.*[129] It has been considered initially that the reaction mechanism should include the formation and decomposition (upon supersaturation) of 'active' metal carbides. This mechanism was consistent with the fact that the growth of NT, which has stopped after cooling of the carbonised catalyst, is resumed after the subsequent heating. The root growth of NT can proceed by a mechanism described previously and assuming the surface diffusion of carbon atoms to the bulges on the catalyst surface;[43] in this case, dehydrogenation of C_2H_2 on the catalyst surface to give H_2 rather than mere adsorption of carbon can be the first stage of pyrolysis. A mechanism involving immersion of small C_n clusters into the caps of NT has also been considered. It should be stated that catalytic pyrolysis of the same hydrocarbon (C_2H_2) present in the same concentration in N_2 (9%) at similar temperatures (500 and 600 °C) can follow absolutely different

mechanisms depending on the pressure in the system, the method used to prepare the catalyst and other factors.

Pyrolysis of C_2H_2 over Fe-containing catalysts supported on various materials including SiO_2 has been considered in several other publications.[136–139] It was noted that, in addition to the NT described above, helical and even branched NT can be formed.

Apart from iron, cobalt also exhibits high activity in the pyrolytic decomposition of C_2H_2.[136] The materials used as supports for this metal include SiO_2,[137,140,141] NaY zeolite[137] and Al_2O_3.[142] The procedure for the preparation of Co catalysts, in particular, the pH of precipitation of the metal salt from a solution, influences appreciably the quality of NT.[141] Biro *et al.*[143] have classified NT into two groups: 'raft-like arrays' with a diameter of 1 nm and single ones with a diameter of 10 nm. Remarkable NT with a coil structure were also isolated upon pyrolytic decomposition of C_2H_2 over Co.

Nanotubes of this type have been studied in detail.[144] It was shown by high-resolution electron microscopy that the coils consist of several straight sections, the junctions of which can contain disordered areas. The convolutions closely adjoin one another, the NT forming them being 'flattened', *i.e.* compressed along the coil axis.

A certain catalytic activity in the formation of NT from C_2H_2 is displayed by Ni and Mn oxides, while platinum metals proved to be poor catalysts.[136] However, a catalyst promoting the formation of very long NT was prepared from $Pt_5(CNC_8H_9)_{10}$.

Catalyst particles can be introduced into a support by impregnating it with aqueous solutions of salts followed by decomposition of the salts, by chemical vapour deposition using organometallic compounds, or by electrodeposition. The size of metal particles can range from several nanometers to tens of nanometers.

Zeolites, especially NaY zeolite, make good supports for the catalysts of acetylene pyrolysis.[137]

The synthesis described in Refs 133–135 should actually be categorised as a template synthesis. Membranes prepared by anodic oxidation of Al are also good templates for the catalytic synthesis of NT.[139] These membranes contain parallel closely packed hexagonal channels (pores) running throughout the whole bulk. By varying the conditions of anodic treatment, one can control the pore diameter (2–500 nm), the membrane thickness (50–500 mm) and the pore density (10^7–10^{12} cm^{-2}). The Al_2O_3 membranes are transparent and stable up to a temperature of at least 1000 °C; the chemical properties of their surface can change upon the addition of hydroxy groups.

Recently a template synthesis of NT by pyrolysis of C_2H_2 in the presence of a mixed catalyst has been performed.[145] Commercial zeolite samples were impregnated with aqueous solutions of Co and V acetates and used in the process immediately after drying. The pyrolysis was carried out at 700 °C. This procedure yielded well graphitised and relatively thin NT (10–12 shells, outer diameter 8–10 nm, inner diameter 2.5–2.8 nm). The role of the vanadium additive is unknown; the mechanism proposed in the study cited[145] and involving the transition of metal compounds to the gas phase seems doubtful.

b. Pyrolysis of methane, ethylene and propylene

It has been noted in a publication[137] devoted to the pyrolysis of acetylene that the use of methane, ethylene or propylene instead of acetylene either does not give NT or gives them in low yields. However, in some studies, conditions have been selected under which pyrolysis of these compounds does yield NT. Thus a deposit consisting of NT to an extent of 90% was obtained from CH_4 at 600 °C in the presence of the $Ni_xMg_{1-x}O$ catalyst, prepared from Ni and MgO, in which some Ni atoms were located on the catalyst surface as aggregates.[146,147] The synthesis of NT with a length of > 20 μm from a CH_4–H_2 mixture in the presence of Fe particles has been reported.[148] An interesting point in this study[148] is that NT were synthesised using a microwave setup (Fig. 6), widely employed for the preparation of diamond films. However, the

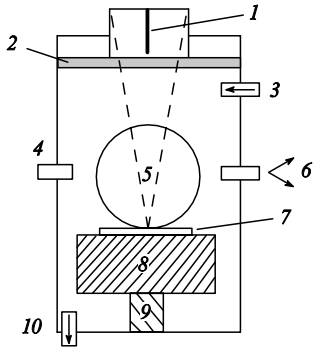


Figure 6. Setup for plasma-activated chemical deposition from the gas phase. The pressure of the mixture of CH_4 and H_2 at the inlet is 0.13 Pa, the substrate temperature is 370–950 °C;
(*1*) microwave antenna; (*2*) quartz window; (*3*) gas inlet; (*4*) viewing window; (*5*) plasma discharge; (*6*) to the optical emission spectrometer; (*7*) substrate; (*8*) an energy-sensitive graphite stand; (*9*) drive to a stepper motor; (*10*) to a vacuum pump.

synthesis of single-walled NT carried out at Stanford University (USA) appears the most impressive.[149,150] In this study, methods of nanotechnology were employed. The catalyst was applied to a silicon plate as micron-sized islets. To this end, square holes were made in a poly(methyl methacrylate) film by electron-beam lithography and then the catalyst precursor was deposited onto the film from a methanol solution containing $Fe(NO_3)_3$, $MoO_2(acac)_2$ and Al_2O_3 particles. Subsequently the solvent and the film were removed, the catalyst was heated in argon, and, finally, pyrolysis of CH_4 was carried out.

During pyrolysis, very straight NT with diameters of 1–3 nm and lengths of up to 20 μm containing no topological defects were formed on the catalyst islets over a period of 10 min. Some NT served as bridges between neighbouring catalyst islets and thus formed electric contacts. An increase in the process duration to several hours resulted in thicker NT.

This method is rather straightforward and easily reproducible; it can be used to prepare NT on substrates having large areas.

The $CoSi_2$ formed upon the deposition of cobalt onto silicon also catalyses the formation of NT from CH_4.[151]

The use of ethylene for the template catalytic synthesis of single-walled NT on porous Al_2O_3 plates has been described.[152,153] Pyrolysis of propylene[132,137,139] and pyrolysis of polyethylene over a Ni catalyst have been reported.[154,155]

c. Pyrolysis of benzene and other aromatic compounds

Benzene can also serve as the initial hydrocarbon for the synthesis of NT; this synthesis can be carried out using the equipment designed for the preparation of carbon fibres from C_6H_6.[156] It was noted that the growth of NT and carbon fibres follow different mechanisms; indeed, catalyst particles were detected at the tips of the fibres, whereas the NT usually had conical caps free from inclusions. The preparation of NT from a C_6H_6–H_2 mixture over an Fe catalyst requires as a rule lower partial pressures of C_6H_6 and lower temperatures than the synthesis of fibres. In some cases, the growth of NT is replaced by the growth of solid fibres. Solid fibres and NT prepared from the same hydrocarbon in single-type equipment differ markedly in mechanical properties — the fibres are easily broken on bending, whereas NT exhibit flexibility and elasticity.

Pyrolysis of C_6H_6 over Co supported on SiO_2 affords simultaneously bent and helical NT and fibres,[157] the ratio of the yields of NT and fibers being determined by the size of the catalyst particles and the composition of the reaction mixture. A catalyst containing a higher proportion of Co (5 mass %) and consisting of larger particles (11 nm) results in a higher proportion of fibres than a catalyst with a lower metal content (0.5 mass %) and a

medium particle size (7 nm). The replacement of the gas diluent H_2 by N_2 increases the yield of NT.

The helical NT resulting from the pyrolysis of C_6H_6 differ from those formed upon the pyrolysis of C_2H_2 (see above [144]); they are multi-walled NT, the distance between the shells being intermediate between the corresponding distances in ordinary and turbostratic graphites. The shells themselves are largely disordered.[157] Among other reasons, the formation of such structures might be due to the addition of hydrogen (the diluent of benzene) to the dangling bonds of NT. However, the catalyst particles exert a greater influence. This hypothesis is consistent with the model proposed by Amelinckx *et al.*,[158] which assumes that the growth of NT progresses on the side of a free tip having an encapsulated catalyst particle.

Deposits of NT with a definite texture can be obtained from gaseous C_6H_6. Thus pyrolysis of C_6H_6 on a profiled substrate with scratched parallel grooves gives rise to NT arranged parallel to the substrate surface and growing from the upper edges to the centres of the grooves.[159] It was suggested that irregularities on the upper edges of the grooves exhibit enhanced catalytic activity.

A similar expedient has been used in the pyrolysis of 2-amino-4,6-dichloro-*s*-triazine.[160, 161] A 10- to 100-nm thick Co film was sprayed onto a SiO_2 plate. Then 1 to 20 μm wide tracks spaced 100 – 200 μm apart were etched on the substrate using a laser. The substrate was placed in a furnace the coating downwards and pyrolysis was carried out at 950 °C. This gave rise to NT bundles having a strictly identical length and very close outer diameters (30 – 50 nm). The NT obtained in this way contained up to 5% of nitrogen. When the plate was placed in the furnace the coating upwards, the situation changed sharply; strongly twisted NT were formed.[161] This outcome has not yet been adequately interpreted.

The researchers believe that etching of the Co film gives rise to energy-saturated metal or metal oxide clusters, which are deposited along the track edges. Hydrogen chloride, arising upon decomposition of triazine, can convert Co into volatile $CoCl_2$ and thus influence the catalytically active particles at the tips of NT. The growth of NT is terminated when the catalyst species have lost activity or have been completely evaporated as the chloride.

Pyrolysis of tris(aminotriazine) (melamine) and cyanuric acid over etched Co, Ni, or Fe films occurred in a similar way.

A mixture of gaseous phenylacetylene and thiophene with He [162] and a mixture of 2-methyl-1,2′-dinaphthyl ketone with He [163] in the presence of a Ni catalyst have also been used for the pyrolytic synthesis of NT. It is noted in both studies that at the first stage of pyrolysis, Ni particles are coated with a graphite layer; this is followed by the nucleation and growth of NT. The temperature of choice is 700 °C. Yudasaka *et al.*[163] proposed an original procedure for the preparation of the catalyst. They sputtered a metal film on a quartz glass substrate and heated it *in vacuo*. The size of the Ni particles thus formed was determined by the thickness of the deposited film; in the optimal case, it was 20 – 30 nm. It has been concluded [162] that NT are 'extruded' from Ni_3C particles; Yudasaka *et al.*[163] noted an important role of the shape of Ni nanoparticles.

2. Pyrolysis in the presence of a 'floating catalyst'

A conventional supported catalyst is coated, sooner or later, by a layer of the products of pyrolysis of hydrocarbons and is thus deactivated. The introduction into the system of catalyst precursors as volatile compounds which decompose to give catalytically active species directly in the reaction area could, in principle, permit one to avoid the catalyst deactivation and to bring the process of pyrolysis closer to a continuous process.

There are only a few publications in which this approach has been employed. Thus decomposition of Ni phthalocyanine at 700 and 800 °C has resulted in the synthesis of NT containing some nitrogen.[164] These NT were multi-walled particles with large (~200 nm), small (10 nm) or variable diameters, their length reaching 6 μm. It has been assumed [164] that the mechanism of the NT growth includes encirclement (encapsulation) of Ni particles with a carbon layer, graphitisation of this layer, the change in the shape of Ni particles, the appearance of seeds and the growth of NT. The Ni particle inside the NT can either migrate from the substrate to the growing tip or remain in a particular section of the NT, forming a node point.

Decomposition of Fe and Co phthalocyanines is also accompanied by the formation of NT, whereas Cu phthalocyanine gives neither NT nor graphitised particles.

Ferrocene has been used as the 'floating catalyst' in the pyrolysis of thiophene.[165] Unlike the study cited above,[164] in this case, single-walled NT were produced. The process was carried out at 1100 – 1200 °C for 1 to 30 min. This yielded a large amount of long and relatively thick 'ropes' and ribbons coloured silvery black. Some of the ribbons were semitransparent and not attached to the surface. The longest 'ropes' were 3 – 4 cm long and had a diameter of 0.1 mm, while the ribbons were up to several millimeters wide. Each 'rope' and each ribbon consisted of several thousands of vaguely oriented threads, comprised by bundles of well oriented closely packed single-walled NT. The diameter of the bundles ranged from several to forty nanometers, the average diameter of the NT being 1.7 nm. It was found that the bundles are formed in the reaction area and carried away with the gas stream; outside the area they stick together forming 'ropes' or ribbons.

Pyrolysis of ferrocene and its mixtures with C_2H_2 has also been studied.[166]

3. Decomposition of CO

Thermal decomposition of CO (disproportionation to CO_2 and carbon) differs sharply from the pyrolysis of hydrocarbons from the thermodynamic viewpoint; at atmospheric pressure and low temperatures (300 – 750 K), the equilibrium yield of carbon is nearly quantitative, while at higher temperatures and lower pressures, it diminishes. Conversely, the yield of carbon in the pyrolysis of C_2H_2 and CH_4 increases as the temperature rises and the pressure is reduced and approaches a quantitative yield at 1250 – 1500 K.

In this respect, carbon monoxide may seem to be a less convenient starting compound for the synthesis of NT. However, for kinetic reasons, a hydrocarbon is more difficult to heat to a temperature above 800 – 900 °C (before it is brought in contact with the catalyst) than CO; hence, carbon monoxide offers some advantages.

The first study [167] on the catalytic decomposition of CO to give NT was carried out in 1995, *i.e.* much later than NT were synthesised by other methods. Decomposition of a $CO - CO_2$ gas mixture (20% of CO) was carried out at 500 °C over the Ni/Al_2O_3 catalyst. A graphitised shell was formed around the Ni particle; nanotubes protruded out of this shell. The introduction of hydrogen into the gas mixture changed appreciably the morphology of the deposit.

Thermal decomposition of neat CO over a Ni – Co catalyst supported on Al_2O_3 was performed at 1200 °C at a pressure somewhat higher than atmospheric.[168] This process gave rise to single-walled NT.

The preparation of an active molybdenum catalyst used for the synthesis of NT from CO was an important achievement. The catalyst was prepared by impregnation of alumina with a methanol solution of bis(acetylacetonato)dioxomolybdenum followed by heating to 200 °C. The diameter of NT formed in the presence of this catalyst was 1 – 5 nm. Catalyst particles with sizes of several nanometers were detected on the tips of many of the NT. This provided grounds for proposing a mechanism of the growth, which was called the 'skull-cap' mechanism. According to this mechanism, a catalyst particle promotes dehydrogenation of the hydrocarbon molecules deposited on the particle from the gas phase. Carbon diffuses to the open tip of the NT (where the catalyst particle is located) over the catalyst surface or through the bulk and is embedded in the NT structure. It is the coating

consisting of chemisorbed carbon atoms on the surface of the catalyst particle that is referred to as 'skull-cap'. It prevents the formation of dangling bonds. Micrographs of single-walled NT with catalyst particles located on the open tip and having a size equal to the NT diameter were reported.[168]

Testing of the Ni–MgO,[146,169] Co–MgO[170] and Ni–$AlPO_4$[169] systems as catalysts for decomposition of CO gave positive results. Not only multi-walled NT[147] but also single-walled NT containing no deposit of amorphous carbon on the external surface have been synthesised from CO.

None of the proposed mechanisms[171] is able to explain the influence of the nature of the initial gas on the morphology of NT and other structures.

4. Synthesis of nanotubes containing B–C–N, C–N and B–N

It has been noted above that the catalytic pyrolysis of triazine gives rise to nitrogen-containing NT.[160] The pyrolysis of $CH_3CN \cdot BCl_3$ at 900–1000 °C over a Co powder afforded fibres and NT of the composition $B_xC_yN_z$ with various morphologies.[172] Nanotubes of the composition $C_{38}N$, the properties of which differed markedly from those of carbon NT, were obtained from pyridine in the presence of a Co catalyst; the nanotubes $BC_{28}N$ were synthesised from the adduct $(CH_3)_3N \cdot BH_3$.[173] All the nanotubes thus prepared were multi-walled. Since the yield of NT in the pyrolysis of the adduct $NH_3 \cdot BH_3$ was very low, it was proposed that coating of metal particles with graphite is a necessary initial stage in the formation of boron- and nitrogen-containing NT.

The data available to date are still inadequate for drawing definite conclusions about the reaction mechanisms, although the shape of some NT provided grounds for speaking about the unusual phenomenon of periodic motion of the catalyst particles located inside the NT along the NT axis.[172] Previously a similar mechanism had been described for purely carbon NT with a bamboo-like structure.[174]

VI. Growth of nanotubes by decomposition of metal carbides

When performing arc synthesis, researchers have noticed that particles of catalysts (carbides) are first covered by an envelope of several graphitised layers, which serve as the source for the growth of NT.[175] The mechanism of formation of such a structure (which has been termed 'sea-urchin') includes the formation of supersaturated solutions of carbon in a metal or metal carbide, subsequent segregation of carbon from these solutions and the 'root' growth of NT. 'Sea-urchins' were formed on particles of YC_2,[71,175] LaC_2,[176] GdC_2,[177] Ni_3C,[178] TiC[179] and other carbides.

Heating of silicon carbonitride under a static atmosphere of N_2 at 1400 °C or in a flow of N_2 at 1850 °C resulted in the synthesis of multi-walled NT with a diameter of 10–25 nm and with a length of up to 1 μm.[180] According to a publication which appeared almost simultaneously,[181] laser ablation of α-SiC resulted in sublimation of silicon and the formation of NT on its surface. Soon this process was even more simplified; in particular, laser treatment was replaced by resistivity heating of powdered[182] or single-crystalline[183] silicon carbide. Heating of powdered silicon carbide *in vacuo* at 1600–1700 °C allowed preparation of NT on a relatively large area over a period of 10–15 min. These NT grew at right angles to the external surface of the powder; they were substantially shorter than those obtained by the arc method but longer than those prepared by the laser ablation of SiC. Even more uniform NT ('a forest') were synthesised at a temperature of 1700 °C and a pressure of 1.3×10^{-2} Pa on a $3 \times 5 \times 0.34$ mm plate. They grew to a length of 0.15 μm over a period of 30 min and were distinguished by a fairly regular mutual orientation. Apparently, this procedure is the simplest way of producing cathodes for field electron emitters.

Small amounts of NT were formed in Fe–Ni and Fe–Ni–Co alloys containing carbon[184,185] and in complex solid solutions containing Fe_3C.[186] During subsequent studies, this procedure could be modified for the preparation of NT-containing composites possessing specific properties.

VII. Other methods

1. Synthesis in the flame

Combustion of hydrocarbons in oxygen is employed for the synthesis of diamonds (see, for example, Ref. 187) and fullerenes.[188] Nanotubes can also be prepared in this way.[189] It is of interest that the C : O ratios, which were equal to 1.06, 1.07 and 0.86–1.00 for the combustion of C_2H_2, C_2H_4 and C_6H_6, respectively, are close to the optimal values for the synthesis of diamond. However, these processes were carried out under different conditions — in the synthesis of diamond, the inner cone of the flame was directed at a substrate cooled to a particular temperature, whereas in the preparation of NT, catalysts were used.

The data on the synthesis of NT in flames are too scarce to analyse them, as has been done for the synthesis of diamonds (see, for example, Refs 190, 191). It is possible that NT, like diamonds, can be synthesised using any carbon compound, no matter what other chemical elements (halogens, sulfur, nitrogen, phosphorus, silicon, boron, *etc*.) are contained in the compound.

2. Electrolysis of molten salts

Nanotubes can also be synthesised without participation of a gas phase, namely, in ionic salt melts. The electrolysis of molten LiCl at temperatures above 600 °C in a cell with carbon anode and cathode causes a heavy erosion of the cathode and appearance of sludge in the melt, which can be washed by water and toluene after cooling the melt.[192] In addition to spheroidal and polyhedral particles, multi-walled (2–10 walls) NT with a diameter of 2–10 nm were detected in the sludge. The current density has a strong influence on the yield of NT. The yield and the quality of NT also depend substantially on the temperature of the melt and the nature of the salt used (LiCl, NaCl or KCl).[193] The electrolysis should not be carried out for a long time because the sludge can short circuit the electrodes.

The electrolysis of a LiCl–$SnCl_2$ melt resulted in the synthesis of NT filled with β-Sn, *i.e*. a nanowire.[85]

3. Chlorination of carbides and other methods

According to a publication,[194] back in the 1960s, multi-walled NT were obtained by chlorination of SiC and TaC at 800–850 °C; the electron micrograph of these NT was published in 1978 in a book.[195] Presumably, the coke that had been prepared using a graphite electric heater (with a temperature of at least 2500 °C) and employed for the synthesis of carbides, served as the source of NT.

There also exist other methods for the synthesis of NT, for example, pyrolysis of the powdered polymer prepared by polyesterification of oxalic acid and ethylene glycol,[26] and the reaction of metallic Cs with nanoporous carbon, prepared from a mixture of polyfurfuryl alcohol and polethylene glycol, carried out at 50 °C.[196]

A method for the synthesis of NT similar to that described in Ref. 148, has been proposed by Küttel *et al*.[197] The researchers prepared NT in a microwave discharge using a setup for the plasma synthesis of diamond coatings and a CH_4 (2%) – H_2 (98%) mixture at a pressure of 0.4 kPa; Ni or Fe islets were applied preliminarily on the substrate, the temperature of the substrate being only slightly higher than the optimum temperature for the synthesis of diamonds (900–1000 °C). The deposit had a 'spaghetti' structure and consisted of NT with a diameter of 20–60 nm and a length of up to 100 μm entangled with one another and firmly attached to the substrate. The catalyst particles remained near the NT 'roots' during the synthesis.

The same researchers were able to perform the synthesis of NT using the 'classical' setup used for chemical vapour deposition of diamonds, namely a hot-filament reactor. Since setups similar to that used by Küttel *et al.*[197] are widely employed in dozens of laboratories in many countries and do not need to be modified for switching to the preparation of NT, further development of these methods for the synthesis of NT may be expected.

Recently, syntheses of NT by heating carbon black with boron at 2200 °C and by detonation of 2,4,6-triazidotriazine have been described.[198] An interesting feature of the latter method (explosive synthesis) is that it permits preparation of NT with a record-breaking inner diameter equal to 80–120 nm (although they are formed in a very low yield).

VIII. Purification and opening of nanotubes

Detailed investigaton into the properties of NT and some of their practical applications require individual and uniform open-tip NT containing no impurities. However, they are usually obtained as bundles consisting of NT with different lengths, capped at one tip and contaminated with impurities. Therefore, techniques for purification and opening of NT are as important as the methods used to synthesise them.

Unlike fullerenes, neither individual NT nor, all the more so, bundles are soluble in any solvent, which complicates the problem of their purification. Nevertheless, several techniques which permit more or less successful purification of NT have been proposed. The methods are based on the following characteristic features of NT.

The materials that typically contaminate NT (fullerenes, polyhedral graphitised particles, amorphous carbon) are more reactive than NT and some of them (for example, fullerenes) are soluble in organic solvents. Sections of NT with a higher density of defects also exhibit higher reactivity than defect-free NT. This refers first of all to the caps at the NT tips, which contain not only six-membered but also five-membered carbon rings. The carbon atoms in these rings are more reactive. The sections on the lateral surfaces of bent NT possess similar properties because kinks would be impossible without insertion of either five-membered (positive curvature) or seven-membered (negative curvature) carbon rings in a net consisting of standard six-membered rings. Finally, enhanced reactivity is also characteristic of the atoms at the edge dislocations of NT (the 'scroll' or 'papier-mache' structure), in which dangling bonds are concentrated together with defects arising upon replacement of carbon atoms by atoms of other elements.

Multi-walled NT, which are normally more defective than single-walled ones, are more reactive, whereas NT annealed at high temperatures (annealing leads to elimination of defects) are less reactive. Nanotubes filled with metals or metal carbides differ in density from empty NT.

The methods used to purify nanotubes can be divided into three groups — chemical, physicochemical and mechanical.

1. Chemical methods

The simplest method for opening NT is selective oxidation of the caps, which can be carried out by gases, melts or aqueous solutions.

The gaseous oxidants used for this purpose are O_2 (see Ref. 62), air,[199] CO_2 (see Ref. 200) and oxygen plasma.[201] The maximum rates of oxidation with air are attained at 420 °C for C_{60}, at 645 °C for graphite and at 695 °C for NT or nanoparticles.[199] Oxidation with O_2 or with air proceeds most efficiently at 650–750 °C.

Even at 550 °C, a gas flow containing 1% of O_2 causes disordering of the outer shells of NT and formation of wells with a diameter of 2–10 nm on their surface; as a consequence, thin NT swell up.[202] At 750 °C, gasification readily occurs at the sites of cracks, defects or deformations.

After opening of NT, the oxidation slows down, whereas oxidation of nanoparticles goes on until they are completely eliminated.[203] However, complete elimination of nanoparticles requires that more than 99% of the initial material be oxidised. Meanwhile, even after 95% oxidation, a sample contains only 10%–20% of the initial NT. This is due to the fact that not only caps but also lateral walls of the NT are oxidised. As this takes place, multi-walled NT become thinner and some of them are completely gasified.

To purify multi-walled NT in air, heating by IR radiation can be used.[204] In particular, a 0.1-mm thick spongy paste with an area of ~ 10 mm^2 consisting of multi-walled NT was obtained in this way from the products of arc synthesis in an H_2 flow. In some cases, it is sufficient to heat the material in air at 500–600 °C for 30 min.[205]

Purification can also be carried out in hydrogen plasma.[201] However, in practice, purification of multi-walled NT from amorphous carbon is carried out by treatment in an H_2–N_2 mixture at 900 °C.[137]

The method of oxidation in melts[59,61] has not been further developed.

In the case of single-walled NT, oxidation in aqueous solutions is apparently the most important method. The most frequently encountered procedure is refluxing in concentrated (60%–70%) HNO_3.[109,203,206–208] The products of catalytic synthesis are freed simultaneously from the inevitable metal impurities. After refluxing for 4.5 h, the loss of mass in the material obtained by the arc method was less than 2%; as a result, 80% of NT became open.[206] Refluxing of 10 g of the initial material produced by the laser ablation method in 1 litre of a 2–3 M solution of HNO_3 for 45 h resulted in a 70% loss of weight.[108]

Apart from treatment with nitric acid or after this treatment, NT are made to react with mixtures of HNO_3 with H_2SO_4 and of H_2SO_4 with H_2O_2 (see Ref. 103). In some cases, H_3IO_5 and $HClO_4$ (see Ref. 209) or solutions based on concentrated HCl[210] have been used instead of HNO_3. Other compounds used as oxidants include H_2O_2, $K_2Cr_2O_7$, $KMnO_4$, solutions of Ru and Os chlorides in a solution of $NaIO_3$, *etc*. Some of the oxidants (acidic solutions of H_2O_2 and $K_2Cr_2O_7$) proved to be much less selective and efficient than HNO_3, some other (solutions of $KMnO_4$ containing MnO_2 or CrO_3) exhibited medium activity, and a group of reagents (solutions of Ru and Os chlorides in a solution of $NaIO_3$) exhibited a very high reactivity and ensured opening of up to 80%–90% of NT at 100 °C.[211,212]

Oxidation in solutions can be combined with filling of NT (for this purpose, a soluble metal salt is added to the solution[206,210]) or with chemisorption of metals on the NT surface.[213] Chemisorption is due to the fact that upon treatment with an acid, the surface of NT is coated with the acidic groups COOH, which can react with metal ions. The quantity of the Pd^{2+} ions absorbed was found to be strictly correlated with the concentration of acidic groups on closed or open NT.[213] An especially high density of acidic groups is attained by using a mixture of H_2SO_4 with HNO_3; these groups promote deposition of finely dispersed metal clusters on the NT surface (see, for example, Ref. 214). The data on wetting, filling and coating of NT have been briefly surveyed in a publication.[215]

Foreign particles can be removed using organic solvents, for example, toluene, carbon disulfide and other solvents, while metal particles can be removed with the aid of acids.

In a pioneering study dealing with purification of NT,[216] chemical modification of NT by grafting dichlorocarbene to the graphene wall at a double bond has been proposed. In a later publication,[217] preparation of soluble NT has been reported. The researchers attached a long-chain amide in place of the carboxy groups at the tips of cut single-walled NT. This was attained by treatment of NT with thionyl chloride (70 °C, 24 h) and then with octadecylamine (90–100 °C, 96 h). The product was readily soluble in chloroform, dichloromethane, aromatic compounds

and CS_2. These studies open up new prospects for the development of more facile methods for the purification, separation, study, description and application of NT.[218]

2. Physicochemical and mechanical methods

In recent years, a number of physicochemical and mechanical techniques for the purification of NT have been proposed. They are briefly described below. A physicochemical method, chromatography, has been used to purify both multi-walled [219] and single-walled NT.[220] The initial NT are dispersed in aqueous media, the dispersions being stabilised by adding surfactants. After separation of the material into fractions using a column with a porous glass packing (with an average diameter of pores of 300 nm), NT are isolated from the individual fractions by centrifuging. Thus not only impurities are removed but, in addition, NT of different lengths are separated.

'Cutting' of NT into 100 – 300-nm long sections has been reported.[221]

The foundations of an electrophoretic method for the purification of NT (as a suspension in isopropyl alcohol) have been outlined in a study.[222]

Various mechanical procedures for the purification of NT are known. They include sonication, microfiltration and centrifuging.[103, 199, 206 – 208, 223 – 225] Many of these procedures are labour-consuming and include large numbers of stages; in some cases, they are used only in combination with chemical methods. Sonication increases the density of defects, especially, in multi-walled NT. The ability of individual NT to form bundles ('ropes') manifests itself not only during the synthesis but also in the purification — in some cases, the purified material contains bundles with greater diameters than the initial material. Under some conditions of sonication in acids, the bundles of NT assume a ring shape with a diameter of 0.25 – 0.55 μm.[226]

Particular examples of combined strategies for the purification of single-walled NT can be found in the literature.[103, 208]

IX. Conclusion

Methods for the synthesis of NT are fewer in number, judging by reviews,[3, 7] than methods for the synthesis of fullerenes. Nevertheless, the main range of these methods has already taken shape and now the question is what of these methods are best suited for the large-scale synthesis of NT.

Different methods can only be compared conventionally because in most cases, the necessary characteristics are not fully available or not reported at all. First of all, methods that require vacuum or elevated pressures should be distinguished from the procedures of synthesis at ambient pressure. The former are less productive. The vaporisation of graphite induced by electron or ion beams and the use of diamond anvils also imposes some restrictions on the productivity. It is also expedient to classify as a separate group those methods that cannot be easily made continuous, for example, electrolysis or explosive synthesis.

Many investigators agree in the opinion that the most widely used electric-arc and laser-ablation methods are applicable only on a laboratory scale, whereas pyrolysis should become the most important commercial method.[131, 156, 165, 227] This method is similar in many respects to the pyrolytic method long employed for the production of carbon fibres both in the presence and in the absence of catalysts. The necessary equipment is relatively simple. It is the pyrolytic method that was used to prepare the longest known thread-like bundles of NT and macroscopic ribbons ('mats') of interwoven NT.[165]

The advantages of the pyrolytic method are manifested especially clearly in the production of ordered structures by deposition of NT onto a smooth substrate with a supported catalyst or onto a porous template. Neither arc nor laser methods can give such structures. Mechanical expedients have been developed which allow laying of NT of any origin parallel to one another (for example, dispersion in a matrix made of a polymeric resin followed by cutting thin slices of the composite [228] or microfiltration of a suspension in ethanol through specific ceramic filters followed by transfer onto a plastic surface [229]). However, they are all much more complicated and much less elegant than catalytic pyrolysis and cannot in full measure compete with it.

Ordered structures from NT prepared by the pyrolytic method are best suited for template synthesis, *i.e.* application of metals, for example, Ni or Co on their surface,[142, 230, 231] for deposition of oxides,[63] carbides [232 – 235] or gallium nitride,[236] for the preparation of catalysts, sorbents, membranes for electrochemical cells,[152] field emitters and artificial muscles (actuators).

Pyrolysis of hydrocarbons in flame [188] and in plasma [196] are also promising because both methods are facile and can be implemented in a continuous mode. Diamond coatings are already prepared on an industrial scale by means of plasma devices; the principal (perhaps, the only) condition for using them for the synthesis of NT is the presence of an appropriate catalyst on the substrate.

However, it may happen that NT meant for particular purposes will be prepared by other methods which have not yet been tested, for example, in plasma jet devices. However, the use of solar energy concentrators for the preparation of NT can hardly be expected in Russia, because the intensity of solar radiation in Russia is relatively low and the level of development of this method does not surpass that for other methods of heating.[237]

Studies of carbon NT have provoked interest in the preparation of nanotubes consisting of other inorganic compounds. Tubular structures are possible for a fairly large number of inorganic compounds of various classes.[238] Studies on the synthesis of NT from BC_x, BN, BC_xN_y and CN_x are only at the beginning; however, in this case, too, pyrolytic methods would apparently prove to be the most convenient.

The problem of the synthesis of NT with identical geometries might be solved using the method proposed by Smalley, namely, selection of homogeneous seed NT and their further growth by pyrolysis of hydrocarbons (http://www.dtic.mil/dusdst/agenda/agenda31999.html).

A complicated synthetic task would be routine preparation of NT with reproducible heterojunctions (variation of diameter, chirality or chemical composition); some enthusiasts believe that this could serve as the basis for the nascent nanoelectronics. The design of nanomechanical devices in which NT are expected to serve as important and abundant parts will also require great efforts.

* * *

Since this manuscript was prepared for the publication, new journal papers and Internet sites devoted to the synthesis of carbon NT have appeared (or become available).

Thus the mechanism of formation of carbon NT, nanowires and nanoparticles in an electric arc burning under a hydrogen atmosphere has been described. The participation of polycyclic aromatic hydrocarbons in the synthesis of NT has been confirmed. A direct correlation between the ability of H_2 to remove graphenes from an anode and the yield of NT has been elucidated.[239]

It was found that only three platinum metals, Rh, Pd and Pt, induce the formation of single-walled NT in an electric arc, whereas mixtures of metals (Ru – Pd, Rh – Pd, Ru – Rh, Ru – Pt and Pd – Pt) exhibit low or zero activity; only a Rh – Pt mixture (1 : 1 or 5 : 2) is active in this process.[240] At a helium pressure of 78 kPa over a Rh – Pt catalyst, NT with approximately equal diameters (1.28 ± 0.07 nm) were formed. A 10 – 12 fold decrease in the helium pressure resulted in the growth of nanotubes of different diameters (0.7 – 1.3 nm).

A novel method for the synthesis of NT in a pulsed arc setup has been developed.[241] The highest yield of NT was attained in a

flow of Ar or Kr at temperatures of > 1000 °C and pulse duration of > 1 μs.

Interesting results concerning growing of NT by the electric-arc method have been obtained in a study by Chang *et al.*,[242] who used an anode with a diameter of 6 mm and a 10-mm thick disk 30 mm in diameter as a cathode. Both electrodes were intensely cooled with water and the electrolysis was carried out in a self-sustained mode (interelectrode distance 3–4 mm, voltage 20 V, current 55–65 A, helium pressure 67 kPa). The cathode deposit was formed on an area with a diameter close to the anode diameter. The morphology of the deposit differed appreciably from the standard morphology. A bed of chaotically entangled slightly bent NT (diameter 10–40 nm, length > 30 μm), the axes of which were oriented randomly, was located under a thin tough shell. These NT had no defects, contained no amorphous carbon impurity and could be purified from the nanoparticle impurity by merely keeping in air (850 °C, 1 h). The intense cooling of the electrodes and gases near the cathode as well as the large distance between the electrodes, which influences the mode of the current passage, is assumed to be largely responsible for the sharp change in the morphology and properties of the arc synthesis products.

A detailed study of some parameters of the laser-induced thermal synthesis of NT has been reported.[243, 244] In particular, it was found that the amount of carbon being vaporised from the target is determined by the intensity of laser radiation, while the course of the chemical reaction yielding NT is governed by the temperature in the furnace. The rate of evaporation of catalysts (Ni and Co) is affected by both parameters. The laser radiation intensity has a slight influence on the diameter of NT, while a decrease in the furnace temperature results in smaller diameters.[243] The increase in the delay between single laser pulses from 0.1 to 120 s has almost no influence on the structure of single-walled NT but decreases the yield of the web-like product.[244] It has been shown theoretically [245] that the use of shorter pulses (picoseconds instead of nanoseconds) and higher frequencies (tens of megahertz) brings the synthesis of NT closer to a quasi-continuous mode.

It has been shown [246] that the laser-assisted synthesis of NT in the presence of Ni and Co can also be performed in a flow of N_2.

The application of a continuous-wave CO_2 laser to the synthesis of NT without additional furnace heating of the target is a method new in principle.[247] In this study, a vertical setup was used with a rotating target moving along its axis (a rod 6 mm in diameter) and made of a mixture of graphite with a catalyst. A hot zone with a diameter of ~1 cm was formed around the laser spot; this resulted in local heating of the gas flow and prevented the plasma from cooling too fast. The synthesis was carried out under Ar. When the radiation power was 250 W and the diameter of the laser spot was ~1 mm, the vaporisation rate reached 200 mg h^{-1}. The yield of single-walled NT in the presence of Ni–Y or Ni–Co catalysts was ~20% based on the amount of the vaporised material.

French investigators have successfully tested a prototype of a 1000-kW solar concentrator for the synthesis of NT (http://www.uiuc.edu/cnrs/Cnrspresse/en352a3.htm).

The formation of NT on irradiation of graphite with high-energy Ne^+, Kr^+ and Xe^+ ions has been studied.[248]

Numerous publications in 1998–1999 were devoted to the pyrolytic synthesis of NT. For instance, the influence of the substrate on the catalytic pyrolysis of C_2H_2 in the presence of Co or Fe has been considered. [249] The influence of the natures of the catalyst (Fe_2O_3, CoO, NiO or their mixtures) and the support (Al_2O_3 or SiO_2 with a specific surface area of 100 and 300 $m^2\ g^{-1}$, respectively) on the formation of single-walled NT in the pyrolysis of pure CH_4 has been studied.[250] Relying on the fact that the tips of growing NT contained no catalyst particles, the researchers [250] concluded that the process followed a 'root' growth mechanism. The highest yield of individual NT was attained with the Fe_2O_3/Al_2O_3 catalyst.

The pyrolysis of metallocenes and $Fe(CO)_5$ mixed with C_2H_2 or C_6H_6 has been studied.[251, 252] It was found that the content of the amorphous carbon impurity can be diminished by introducing H_2 into the gas phase.

The conduct of the pyrolysis of C_2H_2 by means of a hot filament with plasma activation permitted the substrate temperature to be decreased to 650 °C.[253, 254] Yet another novelty was the use of an NH_3 admixture, which was found to function as a catalyst. The diameter of the NT produced in this way was dictated by the thickness of the Ni film sprayed preliminarily onto a glass substrate and varied from 20 to 100 nm. The growth rate was several times higher than that attained in earlier studies (see, for example, Ref. 133) and was equal to 120 μm h^{-1}.

Pyrolysis of naphthalene vapour in the presence of $Cr(CO)_6$ vapour with 'anode field activation' was performed for the first time.[255] The process at a voltage of 4–6 kV, an anode temperature of 1100–1200 °C and a vapour pressure of ~8 Pa afforded carbon NT with Cr nano-rods protruding from their inner cavity. These rods had a strictly invariant diameter (~10 nm) along the full length (up to 0.5 μm). The attempts to accomplish a similar process with $Mo(CO)_6$ or $W(CO)_6$ failed.

Yet another modification of the pyrolytic synthesis of NT includes two-stage heating *in vacuo* (first at 350–450 °C and then at 500–800 °C) of tripropylamine introduced in the channels of $AlPO_4$-5 single crystals.[256] The NT thus formed had equal diameters and equal lengths; however, they proved to be unstable with respect to HCl.

Nanotubes consisting of a new promising material, carbon nitride, have been prepared on a graphite substrate from a C_2H_2–N_2 mixture in a microwave plasma using a bias potential.[257] A peculiar method for the synthesis of B,N-containing NT is based on the replacement of C atoms in carbon NT by B and N atoms upon the reaction of NT with B_2O_3 vapour diluted with N_2.[258] The preparation of multi-walled NT filled with molten UCl_4 or its mixtures with KCl has been described.[259]

A method for purification of NT (prepared by the pyrolysis of C_2H_2 over Co introduced into NaY zeolite) has been described, which involves dissolution of impurities in hydrofluoric acid and subsequent oxidation of NT with a solution of $KMnO_4$ or air.[260]

A fairly comprehensive study [261] is devoted to the behaviour of NT treated with a mixture of concentrated HNO_3 and H_2SO_4. The presence of acid functional groups on the surface of these NT makes it possible to prepare viscoelastic gels; on drying, solid materials or films with specific structures and properties can be obtained. Under particular conditions, the dispersions can be converted into a material reminiscent of liquid crystals.

Fullerenes have been synthesised by irradiation of C_6H_6–O_2 or C_6H_6–N_2O mixtures with a CO_2 laser in the presence of SF_6.[262] This method might also enable the synthesis of NT.

The preparation of Langmuir–Blodgett films from matrix-diluted single-walled NT and application of the films onto various surfaces using micelle-like aggregates has been reported.[263] Soluble carbon NT coated with poly(phenylacetylene) have been synthesised.[264]

Many of the studies mentioned above were reported at the conference on commercialisation of the achievements in the large-scale production of carbon NT (USA, Washington, April 1999; http://www.knowledgefoundation.com/carbon.html). The prospects for the investigation and use of NT-based materials were also discussed at the conference of the Materials Research Society (USA, Boston, December 1998), which has been described in a brief review. [197]

Studies on the application of NT in electronics were surveyed by Johnson at the International Conference on Solid-State Circuits (USA, San-Francisco, January 1999; http://www.eet.com/story/OEG19990217S0045).

Several new promising fields of application of NT have appeared quite recently. The greatest interest was aroused by the development of a prototype of artificial muscles, actuators, activated by application of a low electric potential, which was

reported by an international group of scientists [265–268] (see also M Fox *Infoseek News* May 21, 1999; http://www.mpg.de/news99/news26_99.html; and http://www.msnpc.com/news/271534.asp). A new route to the design of NT-based parts of electronic devices (amplifiers, switches, logical elements) was discovered.[269] The possibility of isotope separation with the aid of NT [270] and of using NT for nanolithography [271] was demonstrated. An electrode manufactured from a single NT was developed and tested.[272, 273]

Recent reviews and issues of journals devoted to NT are also worth mentioning.[274–282]

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