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GROWTH OF CARBON NANOTUBES ON CATALYST

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ABSTRACT

One of the convenient and cheap methods for growing carbon nanotubes (CNTs) is the catalytic pyrolysis process of acetylene. The growth of carbon nanotubes was studied experimentally. Scanning electron microscopy showed that in the presence of CoCl2 and NiCl2, carbon nanotubes are collected on the top of the porcelain calcification boat through the catalyst and are divided into smaller particles and are located in the inner spaces of CNTs. The boundary conditions leading to the separation and encapsulation of the catalyst drop in the inner space of the CNT have been determined.

АННОТАЦИЯ

Одним из удобных и дешевых методов выращивания углеродных нанотрубок (УНТ) является процесс каталитического пиролиза ацетилена. Рост углеродных нанотрубок изучался экспериментально. Сканирующая электронная микроскопия показала, что в присутствии CoCl2 и NiCl2 углеродные нанотрубки собираются на вершине фарфоровой кальцифицирующей лодочки через катализатор, разделяются на более мелкие частицы и располагаются во внутренних пространствах УНТ. Определены граничные условия, приводящие к отрыву и инкапсуляции капли катализатора во внутреннем пространстве УНТ.

Keywords: nanoparticles, catalyst, carbon nanotubes, encapsulation.

Ключевые слова: наночастицы, катализатор, углеродные нанотрубки, инкапсуляция.

Introduction

Carbon nanotubes (CNTs) have been one of the most promising and discussed materials in the scientific community since their discovery in 1991. Due to the unique physicochemical properties of CNTs, their fields of application are constantly expanding, including nanoelectronics, composite materials, catalysis, medicine, energy storage, etc. [1–3].

Among the methods of synthesis of carbon nanotubes, there are two main groups: vaporization of graphite at a high temperature of 2700-3700 °C, followed by condensation of steam during cooling and catalytic pyrolysis of carbon-containing compounds at temperatures not higher than 1000 °C. The second group of methods is the most promising, as it is more suitable for industrial production. This method allows obtaining large quantities of CNTs, availability of large number of starting reagents, relatively low energy consumption, and simplicity of instrumentation. The growth process and properties of carbon structures are significantly influenced by factors such as the composition of the precursor gas mixture, the nature and size of the catalyst particles, the type of substrate, temperature, pressure and duration of the process, etc. Fe, Ni and Co are often used as catalysts for the formation of individual and their mixtures of CNTs, with the addition of promoters. [2, 4–7].

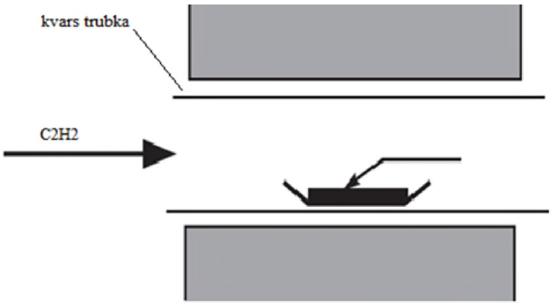


Figure 1. Schematic diagram for the synthesis of CNT for the catalytic cracking of hydrocarbons

Studies on the laws of controlled synthesis of carbon nanotubes are distinguished by the presence of a wide range of possibilities for their application due to a number of special electrical, mechanical and sorption properties of these natural objects. There are many publications devoted to the problem of monitoring the growth of CNTs [4-6], many aspects of the growth of CNTs are still insufficiently studied. In particular, the reasons for the often-observed instability of the catalyst particles in the upper part of the CNT and their encapsulation in the inner spaces of the nanotubes are not completely clear.

The purpose of this work is to determine the factors and conditions affecting the stable position of the catalytic particle on top of the CNT and, as a result, to determine the stable growth of CNTs during the catalytic pyrolysis of acetylene.

Experimental technique

The method of thermal catalytic decomposition of acetylene C_2H_2 was used to synthesize CNTs [6]. To catalyze the growth of CNTs, nano dispersed particles of cobalt chloride (CoCl2) and nickel chloride (NiCl2) obtained by vacuum condensation were deposited on porcelain calcifying boat plates. (Fig 2)

Pyrolysis of acetylene was carried out in the temperature range of 600-1100 °C. C2H2 gas was supplied to the reaction zone through silk gel and glycerin. The flow rate of the gas mixture was set in the range (0.5-1.5) l / min, the molar ratio of components [H2] / [C2H2] was set in the range from 1:4 to 10:1. During the experiments, the gas mixture delivery time was set from several minutes to half an hour, and the obtained nanotubes were cleaned with toluene $C_6H_5CH_3$. The formed samples of carbon deposits containing nanotubes were studied using scanning electron microscopy SEM, X-ray microanalysis.

Results and discussion

The carbon product deposited from the gas phase as a result of the catalytic pyrolysis of acetylene includes a number of CNTs, as well as a small amount of amorphous carbon. The outer diameter of nanotubes was in the range of 20-30 nm, and for nanotubes coated with amorphous carbon it was up to 200 nm. The length of the CNT was determined by the synthesis time and varied up to 100 nm. The mass and structure of UNTs depend on the type of catalyst, process temperature, location of the reaction zone in the reactor, etc. By changing the experimental conditions, the diameter of the nanotubes and their length can be changed in the range of 0.1-50.0 μm. Figure 2 shows a picture of an array of UNTs grown in the presence of nickel nanoparticles on the substrate. Catalyst particles were observed both in the upper part of the nanotubes and in their inner spaces (Fig. 3 a-b). Separated into smaller particles, the catalyst droplets are located in the inner spaces of the CNTs in the form of inclusions.

Encapsulation of catalyst particles within nanotubes is typical of all metals we have studied. As the growth temperature of CNTs increased from °C 620 to °C 800, an increase in the number of encapsulated particles inside the nanotubes was observed. Catalyst particles wrapped in nanotubes have an elongated droplet shape. This shape of encapsulated catalyst particles indicates their liquid phase state during nanotube growth at temperatures between 620 °C and 800 °C.

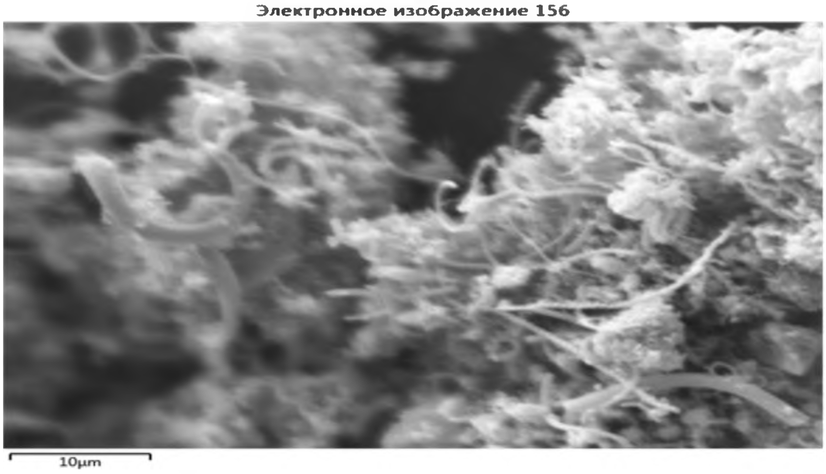
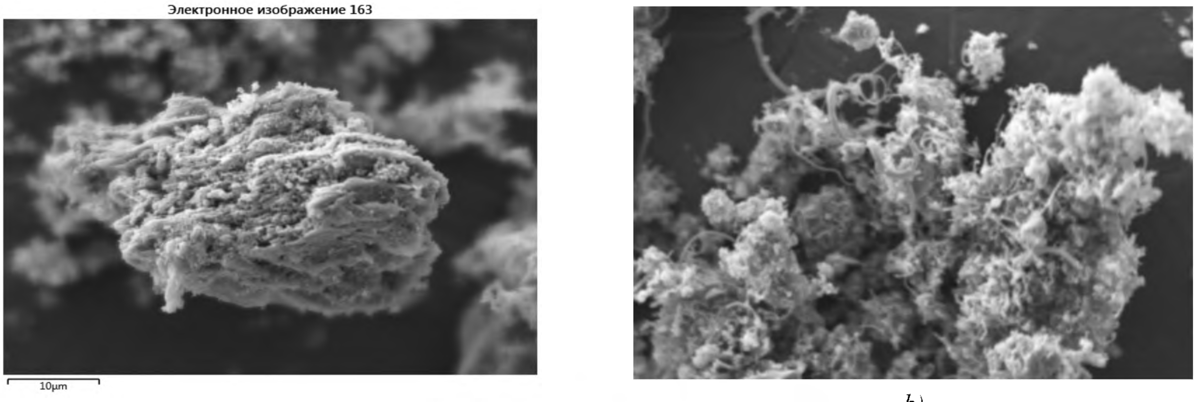


Figure 2. SEM results of the obtained nanotubes, view of the array of UNTs grown with catalytic NiCl2 nanoparticles

It is clear that the liquid nanoparticle is a carbon solution in the metal catalyst solution. Catalyst falling in mechanical equilibrium at the upper part of the UNT was considered. Catalyst falling at the top of the UNT is subjected to two opposing forces. The Laplace pressure, an uncompensated force due to PL, is applied to the opposite part of the droplet surface and pushes the droplet in the direction of UNT growth (F1). [6]

Similar to the frictional force, separation of the liquid droplet from the solid surface of the inner cavity of the nanotube (F2) occurs in the region of the rear part of the moving droplet.



a) b)

Figure 3. SEM images of UNTs containing encapsulated particles of nickel chloride and cobalt chloride are shown

The origin of the F2 force is related to the attraction of the liquid and the solid body on the surface on which it is located by the forces of intermolecular interaction. This interaction can be quantitatively characterized by the energy required to separate the liquid from the solid surface of unit area. Before liquid separation, the energy associated with the liquid-solid interface is equal to αSL per unit area. After the droplet detaches, when it moves in the direction of nanotube growth, two surfaces are formed like that: one of them is the free surface of the liquid droplet with energy αL, and the other is the free surface of the solid body with energy αS surface. Thus, the release energy of drops falling on a unit area is equal:

$$d\alpha=\alpha S + \alpha L - \alpha SL \qquad (1)$$

Whether the drop moves up or breaks depends on the ratio of F1 and F2 forces. For the droplet to break, the following condition must be fulfilled: F1 < F2. When a droplet is broken, a bridge (the narrowed part of the droplet) should form between the main part of the droplet and the small detached droplet. The force F1 pushing up the small drop can be estimated by assigning a certain value to the diameter of the bridge. The diameter of the bridge is equal to the diameter of the nanotube. If R is the radius of curvature of the back of the droplet, r is the inner radius of the nanotube, and the Laplace pressure is PL=2αL/R, then:

$$F1= \pi r2PL=2\pi r2\alpha L/R \qquad (2)$$

We find the force F2, considering the drop in contact with the inner surface of the UNT in a circle with a diameter of 2r. Let the drop inside the nanotube move completely through a distance h. In this case, energy consumption (work done) is equal to the product of the value of the area over which the liquid leaves the solid surface.

$$E=2\pi rhd\alpha \qquad (3)$$

Since the work is equal to the product of the force F2 and the distance h,

$$F2=2\pi rd\alpha \qquad (4)$$

Expressing the nanotube radius r as the radius of curvature R of the droplet

$$r=R\sin\theta, \qquad (5)$$

where θ is the wetting angle of the droplet.

Considering (2), (4) and (5), we write the condition F1 < F2 as follows

$$\alpha L\sin\theta< d\alpha \qquad (6)$$

It follows from the expression (6) that the catalyst droplet on the top of the CNT breaks and leaves the encapsulated liquid-phase inclusions inside the nanotube, if the specific release energy of the droplet is >2αLsina, in this case, the droplet leaving the liquid capsules leaves the solid surface of the nanotube. is more energetically beneficial than opening. We compare the value at with the value of 2αL, because when the droplet breaks off, two surfaces of the liquid are formed. If the value of da is less than 2αLsinα, the droplet moves in the direction of nanotube growth without leaving any particles. From the condition dα/αL>2sinα, the minimum value of the angle a can be found. It can be seen from expressions (1) and (6) that the cracking of the catalyst droplet is favored by good wetting of the carbon nanotube surface with liquid phase catalyst particles, that is, a small angle θ. Better wettability is achieved when CNT growth catalysts such as CoCl2, NiCl2, etc. are used. Therefore, the encapsulation of liquid phase particles inside nanotubes is observed with these metals. In addition, the smaller the difference in the free surface energy values of the liquid phase of the catalyst and the solid phase of the crystallized substance, the higher the stability of the drop on the top of the CNT, the lower the possibility of breaking the droplet and encapsulating the catalyst particles. As the growth temperature of CNTs increases, it is clear that the value of the surface energy αL is much weaker than the energy αS of the interface. This helps to achieve condition (6), below which the drop breaks up. Therefore, with increasing temperature, the number of encapsulated particles inside the nanotubes increases.

Therefore, in order to ensure the stable position of the catalyst droplet on top of the CNT during nanotube growth and to prevent its breakage and encapsulation, it is necessary to choose catalytic metals with a free surface energy close to carbon if possible. In order to keep the material and growth temperature to a minimum, any substances to be incorporated into the nanotubes, on the contrary, their surface tension should not be higher than 0.2 mJ/m2, which is higher than the surface energy of the carbon material (~ 2.0-2.5 mJ/ m2) is significantly less and simplifies the process.

Conclusion

During the growth of CNTs, it was experimentally determined that the stability of the catalyst precipitation is affected by the increase in the synthesis temperature. In particular, with an increase in the temperature of the CNT growth process in the presence of CoCl2, NiCl2 nanoparticles from °C 620 to °C 800, the percentage of nanotubes containing encapsulated catalytic nanoparticles in the form of inclusions in the internal spaces increases significantly. The boundary conditions leading to the decomposition and encapsulation of the catalyst drop in the inner cavity of the CNT are determined. The critical condition for the disintegration of the catalyst droplet and the formation of liquid phase inclusions in CNTs is the separation of the droplet from the inner surface of the nanotube, the specific energy of which is twice the free energy. Recommendations are given to ensure the steady state of the droplet during nanotube growth.

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