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MECHANICAL PROPERTIES OF CARBON NANOTUBES

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Approaches to template synthesis of nanotubular forms of materials are described. In this work the carbon nanotubes radial deformations with different wall thickness and different diameters were measured by AFM method. The dependencies of striking forse from deformation nanotubes three types were built: linear dependence in accordance with Hook's law for nanotubes by diameter 43 and 54 nm; quadratic one $F \sim \Delta D^2$ for nanotubes by diameter 22 nm and $F \sim \Delta D^5$ for the most thin single-wall nanotubes by diameter 1,6 nm.

Introduction

It would be expected that mechanical properties of carbon nanotubes (CNTs) can depend on geometrical parameters, thickness of the walls and interlayer distances. Discovery of carbon nanotubes, their identification, definition of atomic structure parameters, geometry are connected with the development of atomic-force microscopy (AFM). Investigations of their mechanical and material properties reveal that these materials possess very high stiffness and strength characteristics. A review of the available literature reveals that relatively few investigations have been conducted into the full range of mechanical properties of nanotubes [1, 2].

This work shows the own experience according to synthesis and definition elastic characteristics of nanotubes with different diameter and thickness of the walls under the radial pressure by the AFM method.

Experimental part

The carbon nanotubes were synthesized by a matrix method in the argon atmosphere under 500ºC during 5; 30 and 240 minutes in accordance with wall thickness of nanotubes ~ 2,4 and 11 nm correspondingly [3, 4]. Single-wall nanotubes were synthesized by electro-arched method. After the separation of the carbon nanotubes from matrix, their identification was carried out by transmission electron microscopy (TEM) and the AFM (NanoScope IIIa). Exploration of the lateral surface of the carbon nanotubes was made in regime of the periodical contact with frequency 250 kGts and amplitude 9,5-12 nm. The probe had the spherical form with curvature radius R=10 nm, the average hardness of cantilever made up 8,5 ***N***/m. Quantitative information of the interaction of the probe with the surface was defined by the changing of the amplitude of the probes oscillations ΔA. Force of the periodical probes pressure on the sample was changed by the regulation of the height of the position of console (set-point) [5]. The single- and multiwalled nanotubes which have external diameter 1,6; 43, 22 and 54 nm were investigated . The contact of silica probe ($E=1{,}5 \times 10^{11}$ Pa) was realized with cylindrical nanotubes under the forces in a diapason (3-21) $\times 10^{-9}$ N.

Results and discussion

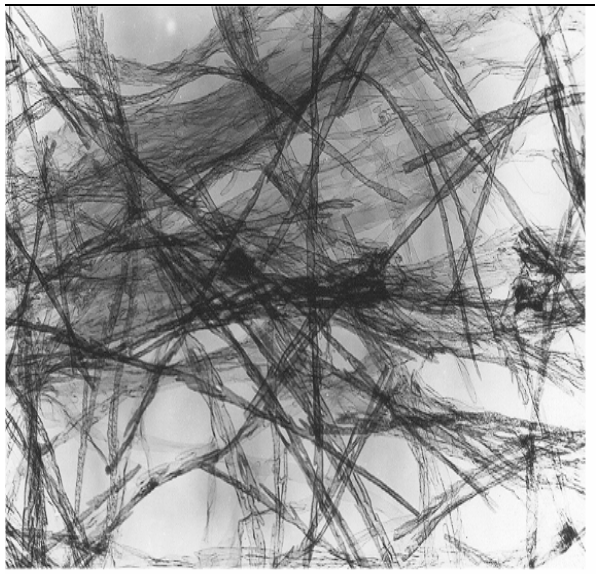
The template synthesis attracts our attention due to the ability to have the massive high density of well-regulated nanotubes. Choice of the precursor is defined by accessibility, price, conditions exploitation, its nature (saturated, non saturated hydrocarbon, atomic correlation of carbon to other atoms). We used the sources of carbon (precursor) the molecules of whish contained the carbon in the quantity C_1, C_2, C_7, (saturated molecules CH_3CN, CS_2 and unsaturated C_2H_2, C_7H_8). The choice of the carbons source mainly influenced on temperature of the pyrolitical synthesis CNT by template method, however we did not found out the direct dependence of temperatures of the synthesis on

carbon–carbon energy bonds of precursors. It is necessary to mark that the using of the same templates type – oxide aluminum membrane gave the possibility to compare to confront the peculiarities of the synthesis it their properties. Temperature interval of CNT synthesis from acetylene was 700-800ºC, toluol - 1000-1150ºC, dyhlormethane - 400-600ºC, acetonitryl - 700-1000ºC, mixture of carbon bisulfide with dychlormethane - 400-600ºC. Found that the using of the precursors CH2Cl2 was very successful concerning the lowering of the CNT formation temperature (by 250ºC in comparison with acetylene) [6, 7].

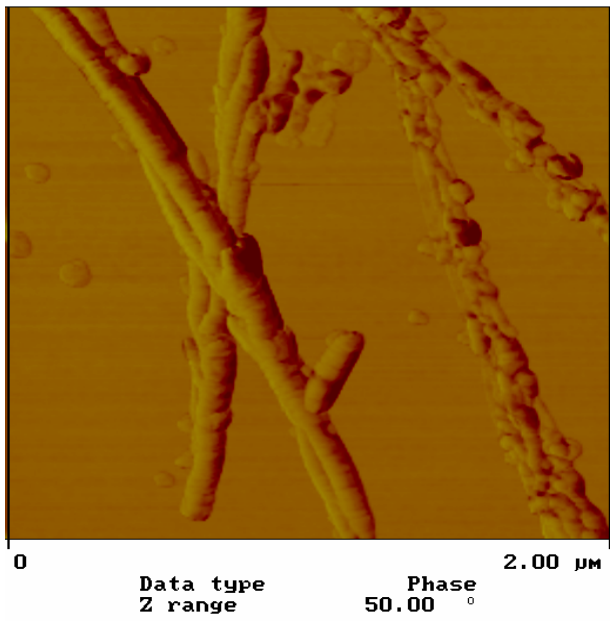
The TEM and AFM photo's of nanotubes [7] (the time of the synthesis of 30 minutes) are shown in figure 1. Their diameters are 40-60 nm. Sparse of the meanings of tubes external diameter connected with sparse of the meanings of the internal diameter nanopors of oxide aluminum, where the synthesis took place.

The results of the measuring of the carbon nanotubes radial deformation with different wall thickness, which were made with the help of AFM in regime of the periodical contacts of the probe with the model (tape-mode) [5], are shown in the table [8]. It is shown the heights of the lieing nanotubes under the pressure of the microscopes probe under the different meanings set-point.

It follows from the data that the amplitude of the oscillations of the cantilever free end, which is registered by the optical system, lessens from 12 to 9,5 nm under the approaching of the probe to the lateral surface of nanotube as the result of the elastic reaction of the pressing nanotube under the action of force. Very little radius of the curvature of the probes point (10 nm) leads to the significant contact pressure, which have to arose contact deformation. During deformation the nanotube external diameter lessens; it is registered by the reduction of the height AFM-profile under the various meaning of probe force influence. Value A – difference between amplitude of free oscillations of probe (A_0~12 nm) and amplitude of established oscillations under the contact with surface, used as the measured parameter. The value ΔA depends on elastic properties of the surface: the more rigid parts of the surface will crush less and the difference of



a



b

Fig. 1. TEM (a) and AFM (b) images of CNT

amplitudes oscillations ΔA will be less than for mildes models.

Previously the correction of the amplitude of free oscillations of probe was carried out in order to fulfil the condition of forces equality of the electrostatic repulsion and Van-

der-Valse forces of attraction (F=0) and curve F=f(D) passes through zero of decart coordinates. This position of probe in considered as the point of reading (D=0; F=0). Corrected meaning A_0 for different models distinguishes between each other a little and they are shown in the last line of the table.

Table

A set-point, nm	The height of the nanotube under pressure of the AFM probe, nm			
	Single-walled (wall, nm)	5 min (1,8)	30 min (3,8)	240 min (10,9)
9,5	0,997	41,675	20,759	52,001
10,6	1,112	42,565	21,305	54,029
11	1,606	42,527	21,615	54,412
12	1,610	43,366	22,079	
A_0, cor.	11,01	12,0	11,3	10,8

Kinetic energy of the striking cantilever on the surface of nanotube and defining by the quantity ΔA transforms into potential energy of the elastic deformed nanotube with the balanced diameter D_0 on value ΔD. The less diameter of nanotube the more the degree of the relative its deformation (ε). ε reaches 38 % for single-walled nanotube and ε sharply falls to 4-6 % for multiwalled nanotube.

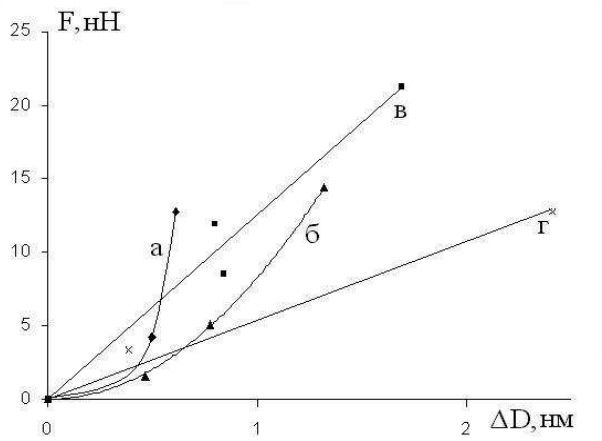


Fig. 2. The dependence of the force influence of probe over the nanotube from absolute deformation of the one for the single-walled nanotubes (**а**), multiwalled ones with diameter 43 nm (**б**), 22 nm (**в**) and 54 nm **(г)**

The curves dependence of interatomic force (F) on the value of absolute deformation (ΔD) for all investigated nanotubes are shown in figure 2. There are three types of dependence's: lines dependence in accordance with Hooks law for nanotubes by diameter 43 and 54 nm, quadratic one ($F\sim D^2$) for nanotubes by diameter 22 nm and for the most then single–walled nanotubes by diameter 1,6 nm $F\sim D^5$ under $\Delta D > 0{,}4$ nm. According to the facts the dependence of coefficient of probes elasticity of nanotubes (k) over their internal diameter is built (fig. 3). From the figure 3 we can see that coefficient of elasticity reduces monotonously while diameter of nanotube increases.

The absence of linear dependence F=f(D) for seconds mentioned models have to be attached to the beginning of the considerable contact pressures which lead for contact deformation due to very little radius of curvature of probes point (10 nm) and a small radius of cylindrical nanotubes (0,8 and 11 nm). It can be explained that contiguous bodies change in form and approach for some distance h thus some contact ground appears in the form of ellipsis by the area S=πab (a and b are semiaxes of ellipsis) m – stead of the point of contact under the action of needle over the model with some force F . This task is examined by Herts and gives the dependence like $F\sim h^{3/2}$ [9].

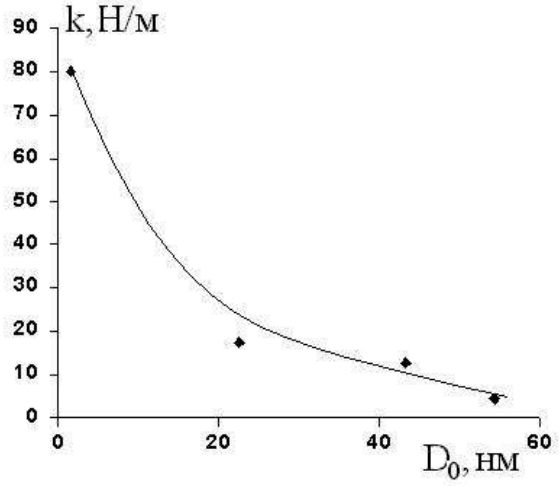


Fig. 3. The dependence of elastic coefficient of nanotubes over their diameter

Hert's law is fulfilled under the small changes (1-2 %) in comparison with radius of curvature of contact surfaces. Under these conditions the considerable contact pressures appear which give the contact deformation.

However during the investigation of DNK molecules which have cylindrical form by radius 1 nm by the AFM method, gives big deformation (18 %) and is not described by Hert's law. We can see the usual linear dependence.

Quite another type of dependence ($F \sim h^5$) is observed for single wall carbon nanotubes by radius 0,8 nm under $\Delta D > 0{,}4$ nm. The last means that short-acting Born-forces of repulsion dominate in single wall nanotubes under strong deformation for short distances. Their appearance is connected with overlapping carbon's atom electronic covers by reducing the distance between them (under flattening of cylinder) during the deformation process. Interaction takes place between atoms which are situated in semilayer from the side of probe and atoms – in semilayer from the side of support. Index of the degree reduces up to n = 2 under small degree of deformation for nanotubes by radius 11 nm ($\varepsilon \leq 6$ %) and for nanotubes by the biggest radius: 21,5 nm ($\varepsilon \leq 4$ %) and 27 nm ($\varepsilon \leq 4$ %) Hook's law (n=1) is fulfilled. The lower index of the degree in comparison with n=12 in the equation Leonard-Gohns points to overlapping of electronic covers only in some carbon's atom.

In a case of contact of spherical probe and cylindrical model (nanotube, virus part, molecule DNK, linear macromolecule and so on) Hert's correlation gives the law "3\2". Analysis of the heights of AFM representations of cylindrical virus partials by close meaning radius (10 nm) shown under different values of force influence of probe (radius r=25 nm) showed that the law "3/2" is just for the mentioned case in wide diapason of forces (0–175 nN), with the exception of branch of minimum influences [10] .

The results which were obtained for multiwalled nanotubes contradict AFM data for virus partials. Linear dependence between force F, influencing the lateral wall of nanotube by the biggest diameter D_0 and displacement ΔD may be conditioned by constant meaning of the area's contact $\Delta S = \pi ab$ during deformation. This may be connected with the presence of large cavities inside thin wall nanotubes due to which not only the local deformation in the nanotube takes place as the result of crush but the transforming of the cylindrical nanotube into nanotube in the form of ellipsis from the beginning. Elastic deformation of the wall nanotube depends on diameter of nanotube but the linear dependence $F = -k\Delta D$ may testify about "ideal" dempfiring ability of thin wall nanotube by large diameter (> 30 nm). There is no complete theory AFM of periodical contact which would allow quantatively connect parameters of the experiment (quantity of amplitude and displacement of phase oscillations of probe) with intensity of force influence of probe on the model and with local viscid elastic properties of the model. That's why AFM force modulation under the interpretation of experimental results is limited by qualitative analysis involving some model representations.

Conclusions

Thus template method ensures the necessary conditions for preparation of nanotubes. According to measurings the dependencies of striking force from deformation nanotubes of three types were built: lineas in accordance with Hook's law for diameter 43 and 54 nm; quadratic $F \sim D^2$ for nanotube by diameter 22 nm and for the most thin single wall nanotubes by diameter 1,6 nm $F \sim D^5$.

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МЕХАНІЧНІ ВЛАСТИВОСТІ ВУГЛЕЦЕВИХ НАНОТРУБОК

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Запропоновано темплатний метод синтезу. В роботі методам атомно силової мікроскопії були виміряні радіальні деформації вуглецевих нанотрубок з різною товщиною стінок і різним діаметром. Побудовані залежності сили зжиму від деформації нанотрубок трьох типів: лінійна у відповідності до закону Гука для нанотрубок діаметром 43 и 54 нм; квадратична ($F \sim \Delta D2$) для нанотрубок діаметром 22 нм і для одношарових діаметром кубічна 1,6 нм $F \sim \Delta D5$.