Structure, composition and magnetic properties of carbon nanotubes doped by Fe during the growth process

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Abstract. The results of complex investigations of the crystalline structure, composition and specific magnetization of the multi-wall carbon nanotubes (CNTs) filled by magnetic nanocomposite are performed. CNT arrays have been synthesized by the high temperature pyrolysis of fluid hydrocarbon - \( p \)-xylole \( \left[ C_8H_{10}\right] \) in the presence of volatile catalyst - ferrocene \( \left[ \text{Fe}(C_5H_5)_2 \right] \) at the walls of tubular-type quartz reactor of specially constructed equipment. It was revealed that the obtained CNTs constitute complex nanocomposite: C - Fe, C - Fe\(_2\)C - Fe\(_3\)C\(_2\) - Fe. The magnetic properties of such CNTs in the temperature region of 78\( \leq T \leq 1060 \) K are conditioned by the ferric carbide (in the form Fe\(_3\)C \( \equiv \) Fe\(_2\)C\(_2\)) and Fe.

1. Introduction

Carbon Nanotubes (CNTs) are carbon molecules that possess unique set of specific properties: mechanical, electrophysical, field-emission, optical and chemical. They have been surprising us by regularly discovered new effects and applications for over fifteen years [1].

Utilization of CNTs filled by nanoparticles of different materials comes as a significant step forward in the development of Nanotechnology [2]. The investigation of the properties of carbon nanotubes coupled with the magnetic materials is one of the most advanced directions of research [3]. In this case the ferromagnetic nanoparticles inside of CNTs could be as small as a domain size, and nanotube walls would serve as a nonmagnetic material between these nanoparticles. Such structures can demonstrate promising properties such as super paramagnetism, giant magnetoresistance and absence of hysteretic loop. They can be used, for example, for increasing the sensitivity of the magnetometer elements and the capacity of the magnetic record-read appliances.

The aim of the present research is the synthesis by CVD method of multi-wall carbon nanotube arrays filled by iron based nanocomposites and investigation of their structure, composition and specific magnetization in a wide temperature range.

2. Synthesis of CNTs filled by iron based nanocomposites

CNT arrays have been synthesized by the high temperature pyrolysis of fluid hydrocarbon - \( p \)-xylole \( \left[ C_8H_{10}\right] \) in the presence of the volatile catalyst - ferrocene \( \left[ \text{Fe}(C_5H_5)_2 \right] \) at atmospheric pressure. Ar was used as a gas-career. CNTs were deposited on the walls of tubular-type quartz chamber of
specially constructed equipment [4] and after mechanically removed from the walls for the investigations.

The regime of preferable CNTs growth on Si surfaces has been realized [5]: concentration of ferrocene in p-xylole was 10%, hydrocarbon solution injection rate – 1 ml·min$^{-1}$, temperature – 870 °C, Ar flow – 100 cm$^3$·min$^{-1}$, synthesis duration – 5 min. In this regime the vertically aligned tightly packed CNT arrays have been obtained on the walls of tubular-type quartz chamber. After removal from the walls they became powder-like.

### 3. X-ray diffraction analysis

X-ray diffraction analysis of CNT arrays was carried out at room temperature in Cu K$_\alpha$-irradiation in the regime information compiling of X-ray diffraction scattering point by point [6]. The step on angle was $\Delta 2\theta=0.03^\circ$. The information compiling time in the point of each angle position is $\Delta t=5$ sec.

X-ray diffraction pattern of powder-like CNTs is demonstrated in figure 1.

![Figure 1: X-ray diffraction pattern of powder-like nanotubes collected from the walls of tubular quartz chamber.](image)

In figure 1 at small angles 2$\theta$ is containing a halo of carbon in amorphous state and clearly exposes (111) reflex of graphite with rhombohedral structure [7]. This structure is typical for CNTs. X-ray diffraction analysis of the pattern reveals an evident domination of cementite Fe$_3$C with orthorhombic structure over the other components of the sample.

Comparing the areas of the reflexes (taking into account the crossed ones) it was established that more than 90% of nanocomposite represents Fe$_3$C relative to Fe and Fe$_5$C$_2$. Using decoding technique of orthorhombic structure and its quadratic form [6]:

$$
\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2}h^2 + \frac{\lambda^2}{4b^2}k^2 + \frac{\lambda^2}{4c^2}l^2
$$

the parameters of the unit cell of Fe$_3$C inside CNTs have been determined. The diffraction reflexes of Fe$_3$C are enough for this goal. The calculation gives the following values: $a = 0.452$ nm, $b = 0.508$ nm, $c = 0.672$ nm, what is in a good agreement with the corresponding values of parameters: $a = 4.518$ Å, $b = 5.069$ Å, $c = 6.736$ Å of the PCPDFWIN data base (cards 76-1877 and 75-0910) [7] for polycrystalline Fe$_3$C.

Since CNTs contain mainly Fe$_3$C, it is evident that Fe nanoparticles not just are incorporated into the nanotubes, but also react chemically with CNTs forming stable compound Fe$_3$C, which being in a polycristalline state possesses pronounced ferromagnetic properties.

### 4. Transmission electron microscopy investigations

The results of the transmission electron microscopy (TEM) investigations of the obtained CNTs are presented in figure 2. It is well known that the interpretation of electron diffraction patterns are fairly complicated, especially when they are obtained on the multi-wall nanotubes [2]. Nevertheless,
qualitative analysis of electron diffraction patterns of samples (figure 2a) is in a good agreement with the results of X-ray diffraction analysis.

Figure 2. TEM investigations of CNTs: (a) electron diffraction pattern, (b) typical view of CNTs filled by nanocomposite.

A halo of amorphous carbon can be clearly distinguished. There are also reflections corresponding to (002) and (004) of graphite. Possibly, these reflections contain reflexes (002) and (004) of cementite (PDF Number: 76-1877). This is the most real situation because by contrast all the inclusions in nanotubes are nanocrystals, and correspondingly must give also point picture. Moreover, it is obvious that between graphite and carbide must be coherent boundary (002)Graphite II (002)Fe$_3$C. As regards to circular reflexes, it might be reflexes of graphite. Weak reflections (110) and (211) from iron particles are also observed.

The typical view of CNTs filled by Fe$_3$C nanocomposite is shown in figure 2b. It is seen that nanotubes are multi-wall and have the outer diameters of 20-40 nm. Filling nanoparticles have a diameter approximately 5÷20 nm.

Thus, using TEM investigations of CNT arrays gave the possibility to determine the dimensions range both of nanotubes and the filler particles. There have been assigned that filler inclusions in CNTs have different configurations, dimensions and the ways they are incorporated into nanotubes. TEM analysis of the images revealed significant dimensional dispersion of the outer diameters both of multi-wall CNTs and filler.

5. Temperature Dependences of the Specific Magnetization

The specific magnetization of CNTs has been measured by static ponderomotive method [8]. The temperature range of the dependence $\sigma=f(T)$ was within 78≤$T$≤1100 K; magnetic field - $H=0.86T$; gradient of magnetic field in the sample area - $dH/dx=0.16T$ sm$^{-1}$ in the interval of $\Delta Z=3.0$ sm. Temperature dependences $\sigma=f(T)$ were obtained both in the heating mode starting from temperature of liquid nitrogen, and cooling mode - from $T_{max}$ to room temperature. The dependences $\sigma=f(T)$ of powder CNTs from the walls of tubular quartz camber for the whole temperature range are shown in figure 3. In the heating mode the temperature dependence $\sigma=f(T)$ clearly demonstrates the sequence of all magnetic phases of the CNTs filler and variation of their specific magnetization with the temperature rise. The first anomalous point on $\sigma=f(T)$ corresponds to Curie point of Fe$_3$C and is equal to $T_c$=480 K [9]. Specific magnetization in the temperature range of 500-750 K is conditioned by the total contribution of nanostructured carbide Fe$_5$C$_2$ and Fe. Comparing the specific magnetization values of Fe$_3$C at 78 K and lower of its Curie point, the cementite contribution to total magnetization from all iron-containing phases can be estimated.
From \( \sigma = f(T) \) measurements it was revealed that the cementite amount is more than 90% of the whole mass of the sample. The temperature interval of 850 to 940 K on the \( \sigma = f(T) \) dependence under the heating reflects the process of specific magnetization growth due to aggregation of the iron particles. By using the observed values of specific magnetization the magnetic moments of the composites for different temperature intervals have been calculated. The value of magnetic moment \( \mu \) depends on specific magnetization as following:

\[
\mu = \left( \frac{\sigma \cdot M}{N_A} \right) \mu_B
\]  

(2)

where \( M \) – molar weight, \( N_A \) - Avogadro constant, \( \mu_B \) - Bohr magneton value.

The calculation results show that at 78 K magnetic moment \( \mu \) of Fe in the cementite is equal to \( \mu = 0.64 \mu_B \). Nonsignificant value of magnetic moment of Fe in the cementite might be as a consequence of the Fe\(_3\)C inclusions in nanotubes with the particle size less than one domain. In the temperature range 500÷750 K the magnetic moment reaches \(-0.12 \mu_B\) characterizing the composite - metastable carbide Fe\(_5\)C\(_2\)-Fe. Iron inside of the nanotubes has at 850 K has \( \mu = 0.008 \mu_B \). Such a small value of magnetic moment for Fe at this temperature might be attributed to predominating particle sizes smaller than 14 nm [10]. Further heating gives a sharp increase of \( \mu \) by the order of magnitude, most likely due to the enlargement of Fe particles during agglomeration process. At 940 K the magnetic moment \( \mu = 0.086 \mu_B \). The heating of the specimen to the temperatures higher than 940 K results in decreasing of \( \mu \) down to zero at the Curie point of Fe at 1060 K. Since the iron-particle enlargement process is irreversible as the temperature increases, the specific magnetization behavior does not replicate \( \sigma = f(T) \) curve as the temperature of the sample is decreasing. Figure 3 demonstrates such \( \sigma = f(T) \) dependence in the cooling mode.

6. Conclusions

The vertically aligned tightly packed multi-wall carbon nanotubes arrays have been synthesized by the high temperature pyrolysis of \( p \)-xylole [C\(_6\)H\(_{10}\)] mixed with ferrocene [Fe(C\(_5\)H\(_5\))\(_2\)] on the walls of tubular quartz chamber. Using different experimental methods the composition of the synthesized CNT arrays, representing C-Fe\(_3\)C-Fe\(_5\)C\(_2\)-Fe nanocomposite, has been obtained. X-ray diffraction analysis and specific magnetization measurements revealed that the filler of CNTs are mostly composed of Fe\(_3\)C (~90%). The unit cell parameters of Fe\(_3\)C inside nanotubes are: \( a = 0.452 \) nm; \( b = 0.508 \) nm; \( c = 0.672 \) nm.

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