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Synthesis of Carbon Nanostructures on Iron Nanopowders Obtained by Electrical Explosion of Wires

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Abstract

This work presents the results of experiments on synthesis of carbon nanostructures by the method of thermal chemical vapor deposition using iron nanopowders obtained by the method of electrical explosion of wires as catalysts. To study the process of nucleation and growth of individual carbon nanostructures, experiments were conducted not only on nanopowders, but also on the separated clusters. To determine the optimum conditions of the carbon nanostructures synthesis and lower temperature limit, experiments were performed at different temperatures (300–700 °C) and pressures (100–400 mbar). The experiments have shown that the lower temperature limit for carbon nanostructures synthesis on the iron nanopowders is 350 °C and in this process the growth of carbon nanostructures is not so massive. Stable growth of carbon nanostructures for nanopowders as well as for the separated clusters began from 400 °C during the entire range of pressures. In contrast to the carbon nanostructures on nanopowders, in the case of the separated clusters a strong dependence of their nucleation and growth on temperature and pressure was traced.

1. Introduction

Carbon nanosized structures (CNs), such as nanotubes, fullerenes, graphene, and others are one of the most important objects of study in the field of nanotechnology. Since their discovery carbon nanotubes became the target of numerous experimental and theoretical researches for production and analysis of their unique mechanical, chemical and electrical properties.

Today, there are many techniques for synthesis of CNs such as laser ablation, arc discharge and various types of chemical vapor deposition.

Thermal chemical vapor deposition (TCVD) unlike other methods of CNs synthesis does not require high energy and complicated equipment. TCVD based on pyrolysis of hydrocarbons such as acetylene, ethylene, methane or ethanol and transition metals Ni, Co, Fe, Cu and others are used as catalysts [1–6].

Prospects of using fine metal powders are related to the possibility of using them as catalysts for synthesis of CNs. One of the methods for production of superfine metal powders is electrical explosion of wires (EEW). EEW nanopowders (NPs) have a number of advantages compared to NPs obtained by other ways: they are resistant to oxidation and sintering at room temperature and show high chemical and diffusion activity during heating [7].

2. Experimental

NP obtained in Tomsk Polytechnical University (Russia) by the group of Prof. A.P. Ilyin by the method of electroexplosive evaporation of metal wire in argon atmosphere. The joint researches of the catalytic activity of iron nanopowders obtained by EEW and the possibility of synthesis of carbon nanostructures on them by thermal CVD were carried out at the Institute of Materials Science, University of Siegen (Germany).

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The growth of CNs was carried out in a volume of horizontal three zone tube furnace (Carbolite Limited) (inner diameter – 90 mm, length – 1150 mm). The catalyst was loaded into a ceramic boat and after placing the sample in the reactor, the volume is pumped by mechanical forepump to achieve the operating pressure. The reactor was heated to desired temperature at a controlled rate (rate of heating of 5–10 °C/min.). After reaching the desired temperature the working gas – acetylene was fed to the reactor. After completion of synthesis (the time of experiments was 1 to 3 h), pumping of residual gases and cooling the reactor to room temperature were fulfilled. Fe NP were used as catalysts. The setup scheme for synthesis of CNs is shown in Fig. 1.

To study the process of nucleation and growth of individual CNs experiments were performed not only on iron nanopowders, but also on the separated clusters. The samples of nanopowders were suspended in chemical solutions (hexane, isopropanol) for separation. Further, ultrasonic treatment of solution was performed (suspension volume – 30 ml, frequency of ultrasound – 27 kHz, power of generator – 120 W, the operation was carried out for 30 min) and then drops of suspension with metal particles were deposited on silicon substrate.

3. Results and Discussion

3.1. Results of investigation of NP

3.1.1. Scanning electron microscopy

To study the morphology and elemental analysis of the samples, a field emission ultra-high resolution scanning electron microscope (SEM) of model Gemini Ultra 55 of the company Zeiss with a device for X-ray microanalysis of the company «Thermo Scientific» was used. The experiments were conducted at the Institute of Materials Science, University of Siegen (Germany).

Figure 2 shows SEM images of iron NP and separated samples.

SEM images of Fe powder shows agglomeration of powders with the sizes from 10 to 50 nm around the clusters with sizes from 100 to 200 nm. Thus, formation of chain-like structures of fine particles (10 to 30 nm) was observed. The shape of Fe particles is close to spherical. The particles with a large diameter usually coagulated with smaller clusters in agglomerates. In Fig. 2b and 2c it can be seen that hexane allows to separate individual iron nanoclusters. The diameter of the cluster ranges from 50 to 100 nm.

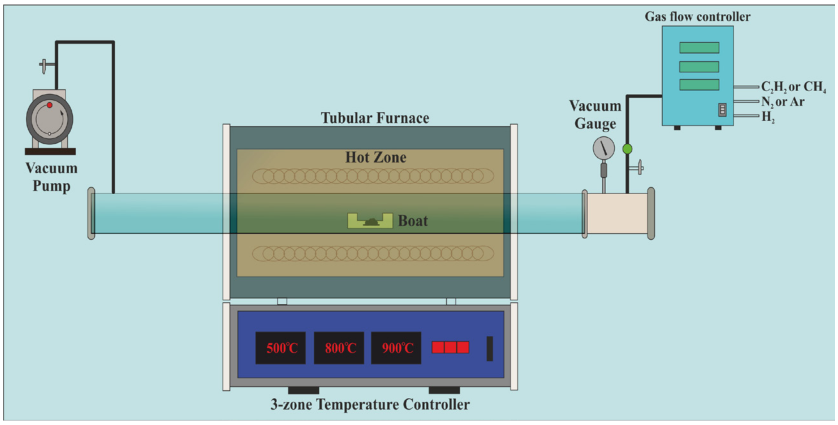

Fig. 1. The general scheme of the setup used in the method of TCVD.

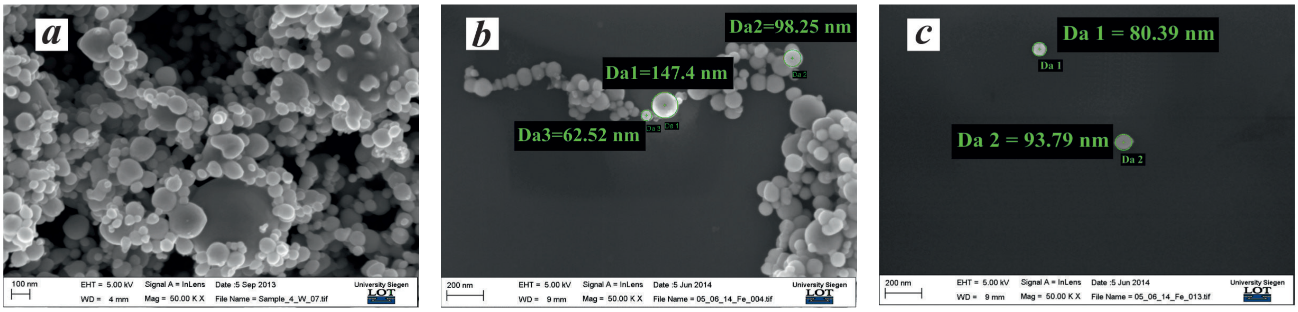

Fig. 2. SEM images of iron NP (a), agglomerates of nanoclusters (b) and individual nanoclusters (c) after separation in hexane.

3.1.2. Transmission electron microscopy

The iron NPs were studied by means of transmission electron microscope (TEM) JEM-2100 JEOL at the Institute of Nuclear Physics (Almaty, Kazakhstan). To prepare the samples, iron NPs were suspended in ethanol of 99.9% purity. Further, ultrasonic treatment of the solution was carried out for 5 minutes, after which the suspension droplets with NP were deposited on a copper grid. Sampling from 400–500 particles was used for charting the distribution of particles by sizes.

Figure 3 shows the TEM image and a histogram of the size distribution of iron NP.

The results of TEM studies of iron NPs are consistent with the results obtained by SEM. Figure 3a shows that iron NPs particles are spherical. The histogram data show that particles with the diameter of 40–70 nm predominate in the sample, the average diameter of which is equal to 65.5 nm. Histogram analysis shows that the distribution of iron nanoparticles by sizes is Gaussian with a value of the standard deviation $\sigma = 30$ nm.

3.2. Results of investigation of CNs

3.2.1. Scanning electron microscopy

To determine the optimum conditions for synthesis of CNs and lower temperature limit, experiments were conducted at different temperatures (300–700 °C) and pressures (100–400 mbar). Experiments have shown that the lower temperature limit is 350 °C for NPs and the growth of CNs is not so massive. However, only carbonization of clusters was observed on the separated particles at this temperature (Fig. 4). Similar results were obtained for synthesis temperature of 375 °C and pressure of 100–500 mbar (100 mbar increments).

Further experiments showed that a massive growth of CNs began for NP from 400 °C during the entire range of pressures. The stable growth of CNs with a large spread diameter from 40 to 100 nm and with different morphology (from helix to straight) was observed in the range of temperature 400–450 °C determined in the course of experiments. Iron catalysts are both at the tip and inside of CNs. SEM images of CNs on iron nanopowders obtained at different value, of temperature and pressure are shown in Fig. 5.

For separated powders, like for NPs, a stable growth of CNs was observed at 400 °C, but at a pressure of 100–300 mbar. Figure 6 shows SEM images of CNs on separated iron NP obtained under different experimental conditions.

SEM-images show that CNs grown on the separated NPs also have various diameter (40–100 nm) and morphology. In contrast to the CNs on NPs, in the case of the separated clusters a strong dependence of their nucleation and growth on temperature and pressure was traced.

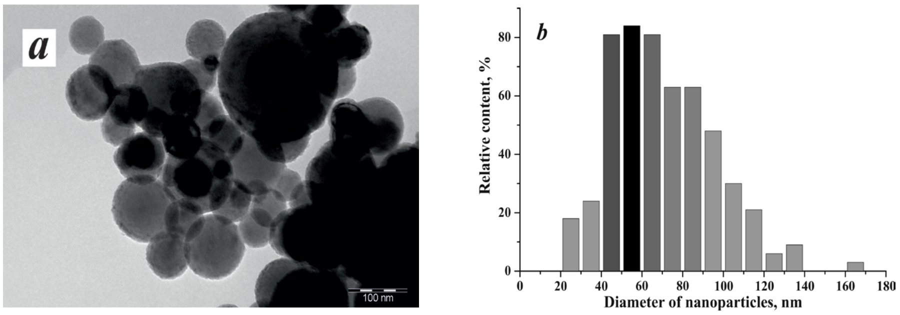

Fig. 3. TEM images of iron NPs (a) and histogram of size distribution of iron NPs (b).

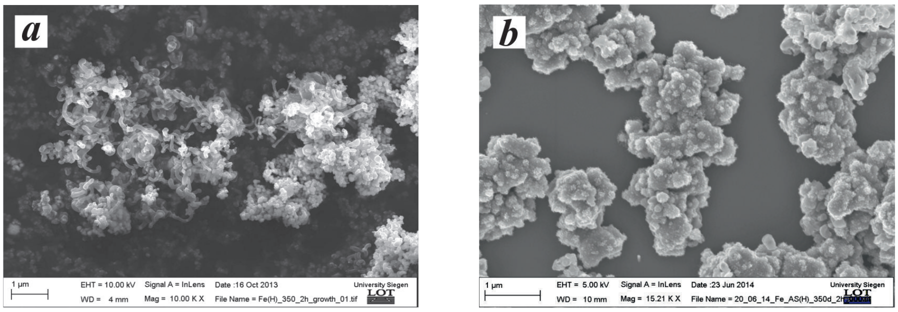

Fig. 4. SEM images of CNs on iron NP (a) and carbonated agglomerates of nanoclusters (b). Synthesis conditions: temperature – 350 ºC, pressure – 500 mbar.

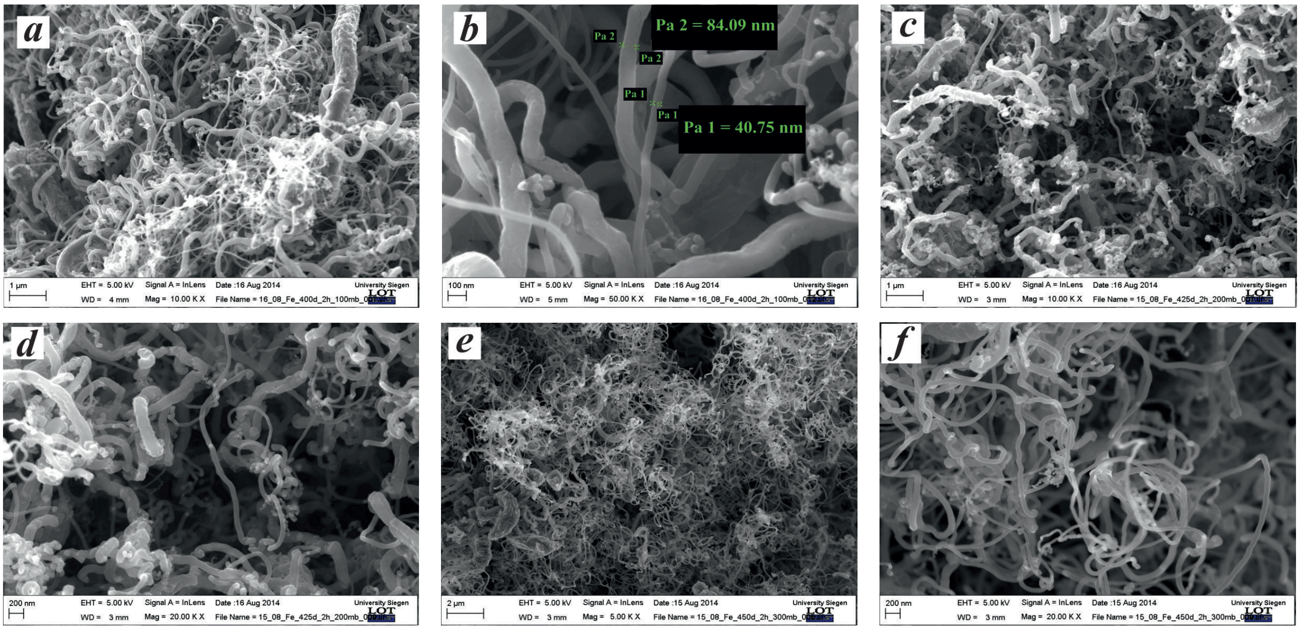

Fig. 5. SEM images of CNs on iron NP: a, b – 400 °C, 100 mbar; c, d – 425 °C, 200 mbar; e, f – 450 °C, 300 mbar.

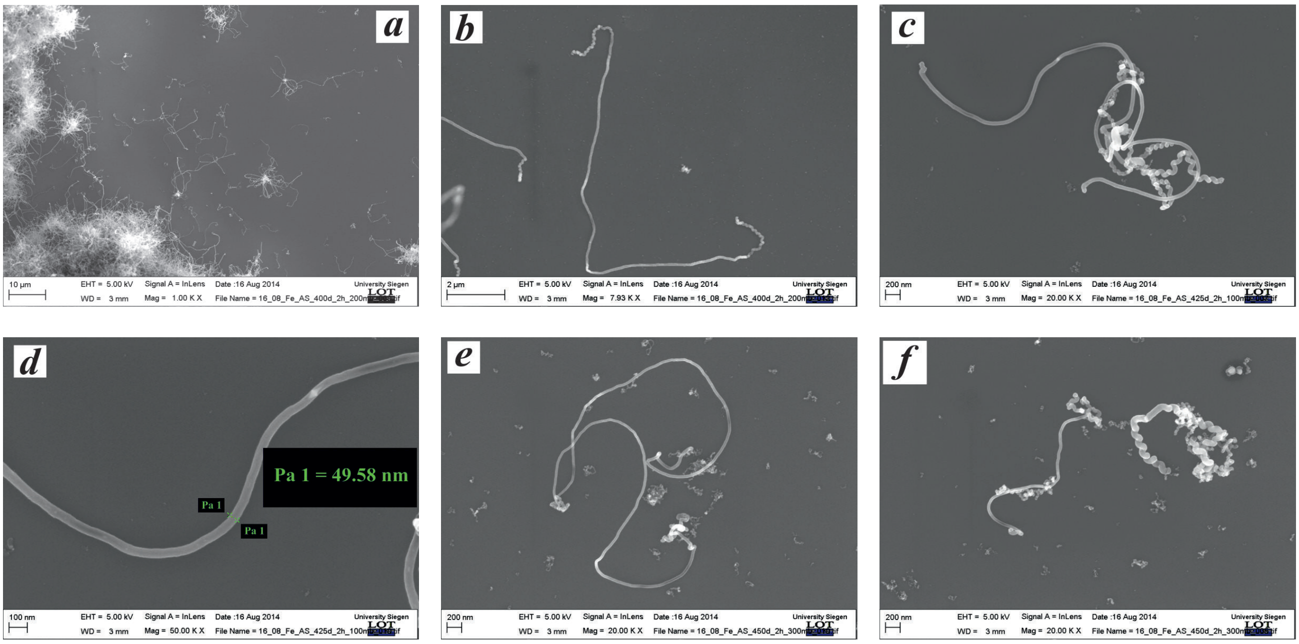

Fig. 6. SEM images of CNs on the separated iron NP: a, b – 400 °C, 100 mbar; c, d – 425 °C, 200 mbar; e, f – 450 °C, 300 mbar.

3.2.2. Investigation of CNs by X-ray analysis

Study of samples by X-ray diffraction (XRD) was conducted in Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences. XRD patterns of samples were obtained on diffractometer Rigaku D/max/2400 X-ray diffractometer using copper radiation (λ = 1.5406 Å) in digital form. Shooting modes of samples are as follows: X-ray tube voltage of 30 kV, tube current 30 mA, step movement of goniometer 0.05° 2θ and time of measuring of intensity at the point – 1.0 sec. During recording, the sample was rotated in its own plane at a rate of 60 rot/min. Processing of the X-ray patterns in order to determine the angular position and intensity of reflexes was conducted in the program Origin Pro 8.1. During the phase analysis, program PCPDFWIN with a base of diffractometric data PDF-2 was used.

Figure 7 shows the X-ray patterns of CNs on iron NP obtained at different temperatures 400–450 °C and pressures 100–300 mbar.

X-ray qualitative analysis of phase composition of the sample indicates that it contains α-Fe, Fe_3C and C. The diffraction patterns of all samples present the most characteristic reflection of graphite from the plane (002) ($2\theta \approx 26.38°$, PDF # 41-1487) [8]. Figure 7 show that temperature decreases the intensity of graphite peak increases with the decrease of temperature. The presence of significant amounts of Fe_3C reflections may indicate that the growth of CNs takes place by the vapor-liquid-solid mechanism.

3.2.3 Investigation of CNs by Raman spectroscopy

Investigation of samples by Raman spectroscopy was carried out in the National Nanotechnological laboratory of open type (Almaty, Kazakhstan) using spectrometer NT-MDT NTegra Spectra (laser wavelength $\lambda = 473$ nm).

The spectra of the samples obtained at different temperatures and pressures are presented in Fig. 8.

For samples grown at 400 and 425 °C, 100 mbar, *D* peak is located in the region of 1323.5 cm^{-1}, and *G* peak at 1576.8 cm^{-1} and 1570.2 cm^{-1}, respectively. The second order peaks 2D are also present in both spectra at 2648.1 cm^{-1} and 2653.7 cm^{-1}, respectively. Judging by the width and intensity of peaks as well as the presence of second order peak we can speak about high crystallinity of samples. For the sample grown at 425 °C, it can be noted that the intensity of *D* peak is less than that of *G* peak, also indicating a good quality of CNs. The sample grown at 450 °C shows a rather diffuse spectrum indicating a defective structure. Because of the large amount of noise, smoothing of spectrum in the program Origin Pro 8.5.1 was produced. Furthermore, a shift of *D* peak (it is observed within 1340.7 cm^{-1}) and *G* peak within the 1575.2 cm^{-1} are observed. The width at half-maximum of *D* peak is much greater than that of the first two samples, indicating a large number of defects and low crystallinity [7].

For samples grown at 200 mbar, all spectra contain main carbon *D* and *G* peaks at 1321.8–1323.9 cm^{-1} and 1580.4–1583.5 cm^{-1}, respectively. A poorly defined second order peak at 2662 cm^{-1} is present in the spectrum of the sample synthesized at 425 °C. The second order peak 2D for samples with synthesis temperature of 400 °C is observed at 2648 cm^{-1} and has the highest intensity, indicating a high concentration of CNs.

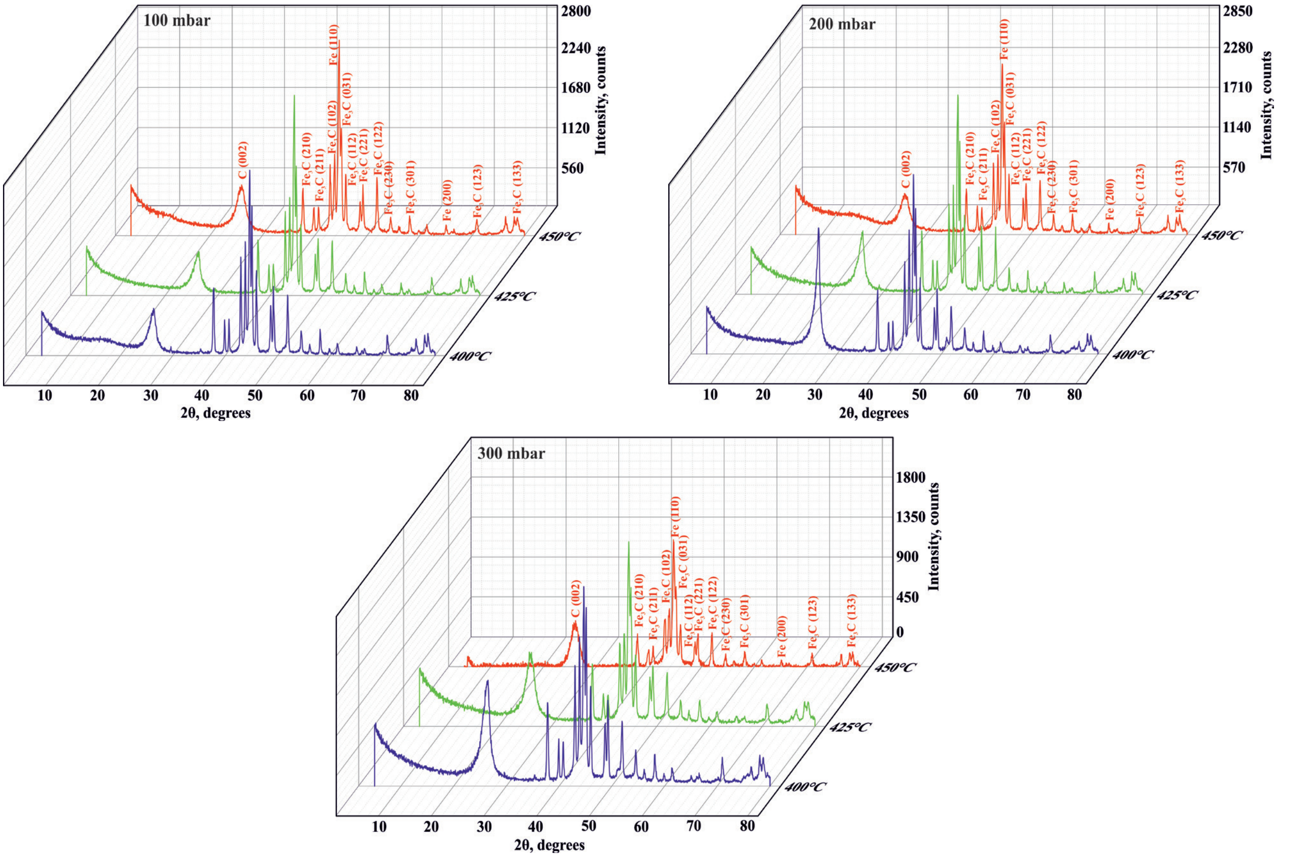

Fig. 7. X-Ray patterns of CNs on Fe NP obtained at different temperatures and pressures.

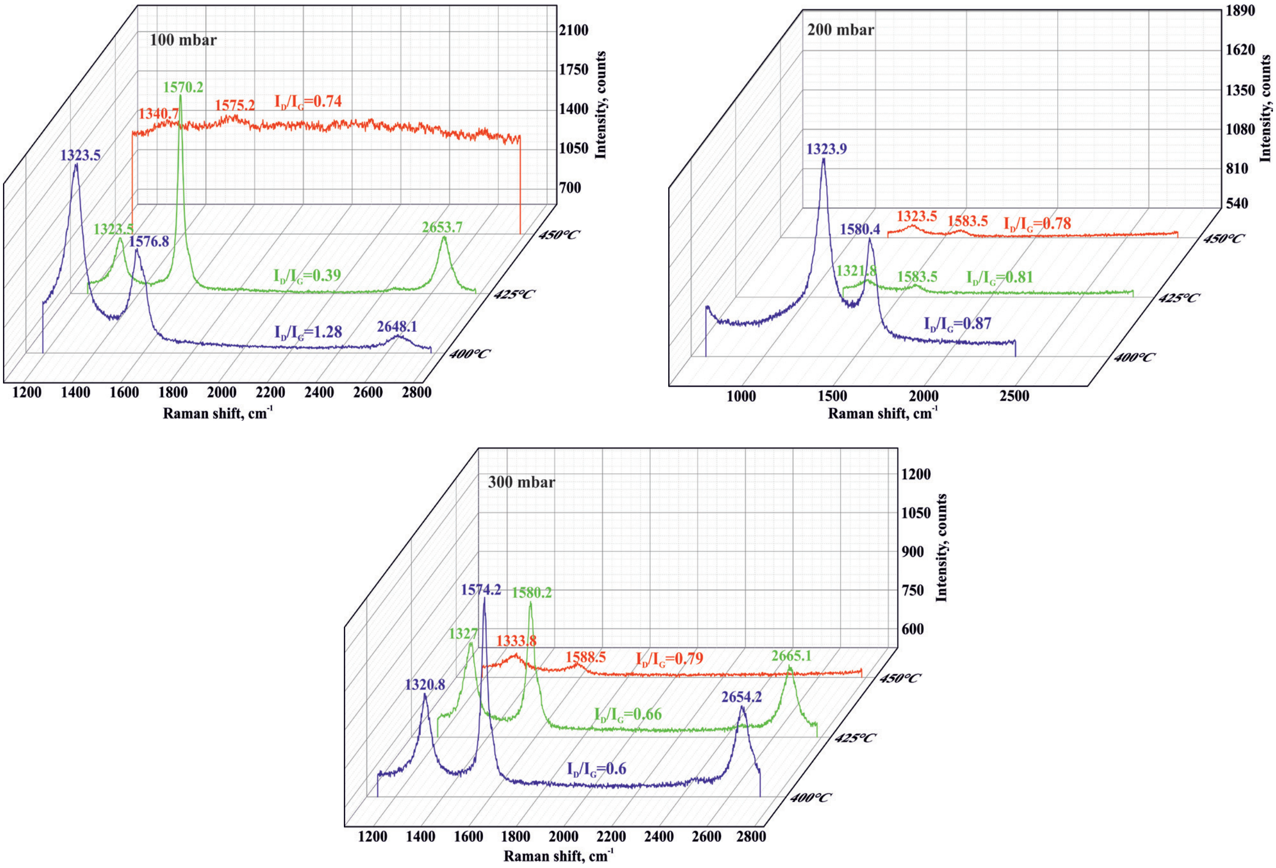

Fig. 8. Raman spectra of CNs grown on iron nanopowders at pressure of 100 mbar and different temperatures: a – 400 °C and 425 °C, b – 450 °C.

Table 1

The intensity ratio I_D/I_G of Raman spectra of CNs depending on the experimental conditions

Pressure, mbar	100			200			300		
Temperature, °C	400	425	450	400	425	450	400	425	450
I_D/I_G	1.28	0.39	0.74	0.87	0.81	0.78	0.60	0.66	0.79

The spectra show that the intensity of *D* peak is higher than that of *G* peak. This suggests that CNs have a defective structure.

For samples grown at 200 mbar, the intensity of *D* peak of the samples obtained at 400 °C and 425 °C is lower than that of *G* peak. Judging by the intensity of 2D peak, the samples obtained at 400 °C and 425 °C show high crystallinity. According to the intensity of D peak (it is located within 1320.8 and 1327 cm^{-1}, respectively) it can be assumed that CNs are rather ordered. The *G* band is observed at 1574.2 and 1580.2 cm^{-1}. The sample grown at 450 °C did not show a smooth spectrum like that of the sample obtained at 400 °C and 425 °C. The intensity of *D* peak is higher than that of *G* peak and is shifted to 1588.5 cm^{-1}. This sample does not have long-range order, because of the absence of 2D peak.

The intensity ratio of *D* and *G* groups allows to evaluate the presence of defects and purity of CNs, i.e. to assess their quality directly [10, 11]. These values have been considered for all samples and are presented in Table 1.

According to Table 1, we can say that CNs grown at 425 °C and 100 mbar have the highest purity. CNs obtained at a temperature of 450 °C and a pressure of 300 mbar, according to [10, 11], show the worst crystallinity.

4. Conclusions

The experiments demonstrated the possibility of using iron NPs obtained by EEW as catalysts for growing CNs. Optimal conditions and lower temperature limits for synthesis of both NP and separated powders were determined. According to the analysis of samples by SEM, XRD and Raman spectroscopy, obtained CNs have different morphology and structure. A stable growth of CNs is carried out at temperatures significantly lower than those usually used in TCVD.

For details of morphology and structure of the obtained samples of CNs it is necessary to carry out additional investigations by atomic force and transmission electron microscopy and electron diffraction.

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