Synthesis of carbon nanostructures on iron nanopowders

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Abstract. This work presents the results of experiments on synthesis of carbon nanostructures (CNs) 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 began from 400°C during the entire range of pressures. The analysis of Raman spectroscopy showed that the most optimum conditions for obtaining nanotubes of high quality are P = 100 mbar and T = 425°C.

1. Introduction

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 [1-5]. 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 [6].

The aims of the study were determination of the lower temperature limit of the growth of carbon nanostructures on EEW Fe NP and search for optimal conditions of low temperature (energetically favorable) synthesis using the most accessible hydrocarbons without expensive additives of inert and other gases.

2. Experimental

NPs were purchased in Tomsk Polytechnic University to be used as catalysts for the synthesis of carbon nanostructures. The procedure of obtaining NPs, experimental details and the results of studies on their morphology and structure are described in detail in works [7-9].

The joint studies on the structure and morphology of EEW NPs, their catalytic activity and the possibility of synthesis of CNs on them by thermal CVD were carried out at The Department of surface and technology of new materials at the Institute of Materials Science of the University of Siegen (Germany) [9, 10].

Experiments were carried out not only on the NPs, but also on the separated clusters to study the process of nucleation and growth of individual CNs. NPs samples were suspended in hexane for separation. Further sonication of solution was carried out (volume of suspension was 30 ml, frequency of ultrasound was 27 kHz, power of generator was 120 W, exposure was conducted for 30 minutes), after which the droplets of suspension with iron particles were deposited on a silicon substrate.

The scheme of technological equipment for synthesis of carbon materials by method of thermal CVD and the procedure of conduction of experiments were described in detail in work [9, 10].

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

The samples were investigated by Raman spectroscopy using spectrometer NT-MDT NTegra Spectra (laser wavelength λ = 473 nm) at The National Nanotechnology Laboratory of open type (Almaty, Kazakhstan).

3. Results and discussion

SEM studies

The experiments were performed at different temperatures (200-700°C) and pressures (100-400 mbar) to determine the optimal conditions for CNs synthesis and lower temperature limit. Studies have shown that the lower temperature limit for Fe NPs is 400°C. Only carbonization of clusters is observed for the separated powders at temperatures below 400°C throughout the investigated range of pressure. Thus the results of experiments made it possible to allocate the optimum range for the low-temperature synthesis: temperature is 400-450°C, pressure is mbar 100-300 [11-13].

Further, more detailed studies were carried out in these experimental ranges. Figures 1-3 show SEM images of CNs on EEW Fe NPs obtained at temperatures of 400-450°C and pressures of 100-300 mbar.

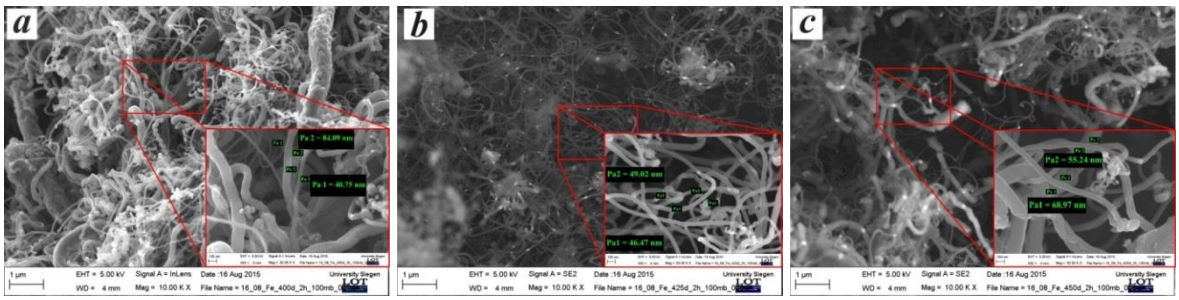

Figure 1(a,b,c). SEM images of CNs on EEW Fe NPs (pressure is 100 mbar): **(a)** – 400°C, **(b)** – 425°C, **(c)** – 450°C.

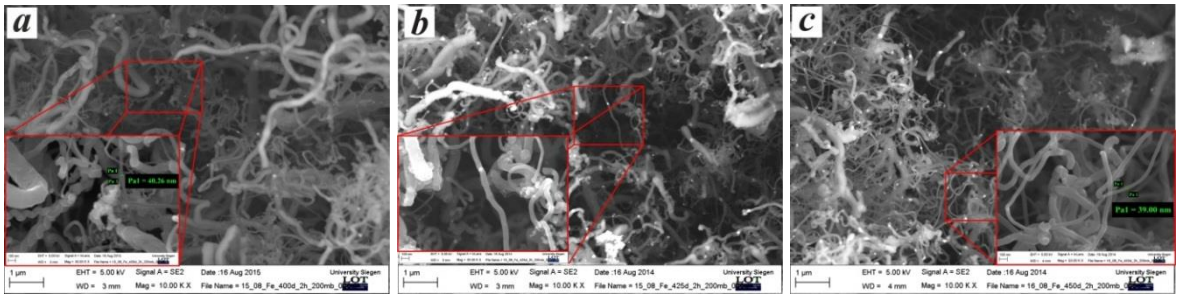

Figure 2(a,b,c). SEM images of CNs on EEW Fe NPs (pressure is 200 mbar): **(a)** – 400°C, **(b)** – 425°C, **(c)** – 450°C.

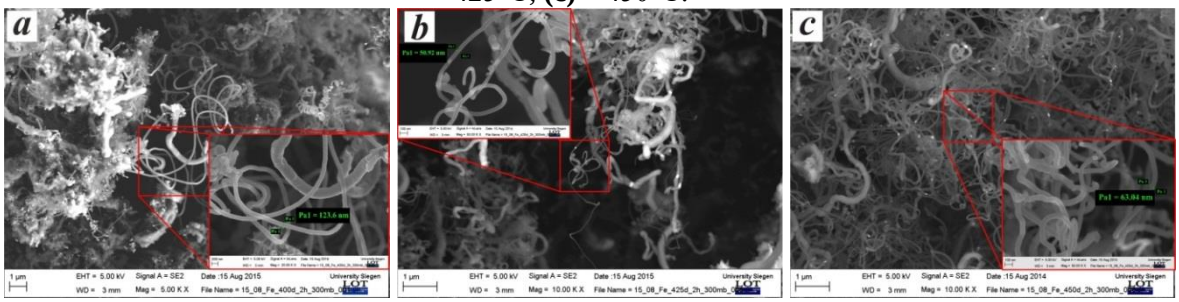

Figure 3(a,b,c). SEM images of CNs on EEW Fe NPs (pressure is 300 mbar): **(a)** – 400°C, **(b)** – 425°C, **(c)** – 450°C.

As seen from SEM images the massive growth of CNs starts for NPs at 400°C during the entire investigated range of pressures. The steady growth of CNs with a fairly large dispersion of diameter from 40 to 100 nm and a different morphology (from spiral to direct) is observed in certain experiments in the temperature range of 400-450°C. Iron clusters are found both on tips and inside of CNs.

Investigation of CNs on the EEW Fe NPs by Raman scattering

Figure 4 presents the Raman spectra of CNs on Fe NPs obtained under optimum temperature and pressure.

All Raman spectra of CNs on Fe NPs grown at 100 mbar predominantly show two groups of first order *D* and *G*. These groups are located in the region of 1330 cm^{-1} and 1576 cm^{-1} for the samples obtained at 400°C, their width at half maximum are 66 cm^{-1} and 77 cm^{-1}, respectively. But intensity of *D* peak is higher compared to the *G* peak, which is a sign of high degree of crystalline disorder of the sample.

Group *G* appears due to interplanar fluctuations of C–C bonds. Also, there is a second order group 2*D* at 2648 cm^{-1}, which is an overtone of group *D* [14]. This group is an indicator of the presence of long-range order in the sample and appears due to two-phonon secondary scattering, leading to the formation of inelastic phonon [15]. It may be associated with a level of crystallinity of the carbon nanotubes [16].

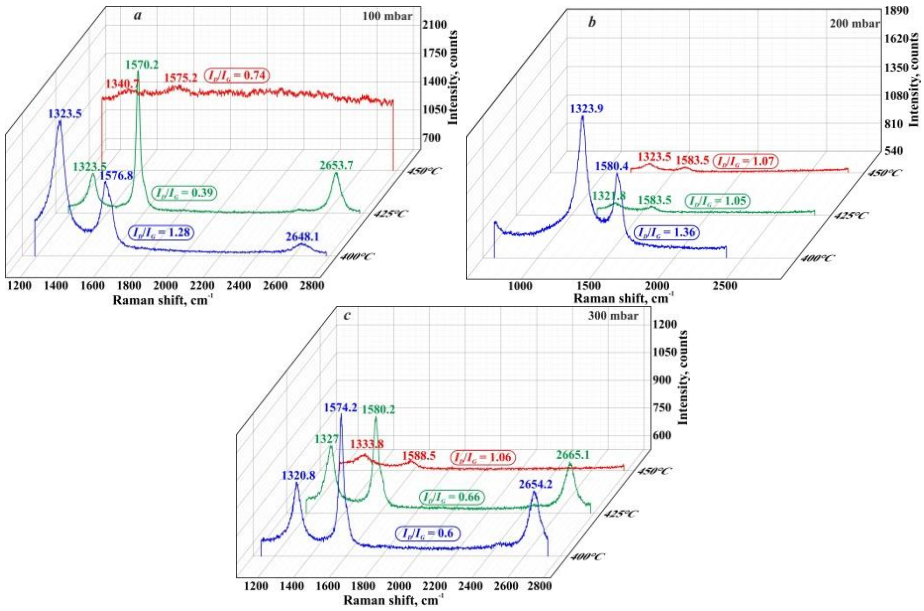

Figure 4(a,b,c). RS spectra of CNs on Fe NPs: **(a)** – 100 mbar; **(b)** – 200 mbar; **(c)** – 300 mbar.

Nanotubes grown at a temperature of 425°C show the good spectra. *D* and *G* peaks are observed at 1323 cm^{-1} and 1570 cm^{-1}, respectively. One can speak about high crystallinity of the sample judging from the width and intensity of the peaks and the presence of second order in the area of 2653 cm^{-1}. In addition, it can be seen that the intensity of *D* peak is quite small, which is also indicative of good quality of nanotubes. Full width at half-maximum (FWHM) of samples are 77 and 34.6 cm^{-1}, respectively. The sample synthesized at 450°C shows a rather blurred spectrum, indicating a defect structure. The shift of group *D* is also observed in the range of 1318 cm^{-1}, and group *G* is located in the range of 1587 cm^{-1}. FWHM of group *D* is much greater than that of the first two samples, indicating the presence of large number of defects and low crystallinity [17].

It can be said that multiwall nanotubes of good quality can be obtained at a pressure of 100 mbar and temperature of 425°C based on the RS results for this series of samples.

The spectra of CNS obtained at 200 mbar show that the intensity of *D* peak is higher than that of *G* peak. This suggests that the nanotubes have a defective structure. Group *G* in the first two samples (400°C and 425°C) is in the range of 1578.5 and 1577 cm^{-1}, but shifted to the high frequency region 1592 cm^{-1} in the sample synthesized at 450°C, indicating a significant graphitisation of sample [15]. Also, this may be indicated by the absence of 2*D* peak, while for the first two samples, it is observed within 2650 and 2662 cm^{-1}, respectively.

The samples obtained at a pressure of 200 mbar and temperatures of 400°C and 425°C show high crystallinity judging from the intensity of 2*D* peak. It can be assumed that they are quite ordered according to the intensity of *D* peak. It is located at 1329 and 1327 cm^{-1}, respectively. Group *G* is observed at 1575 and 1580 cm^{-1}. The third sample shows not smooth spectrum as previous. *D* peak intensity is higher than that of *G* peak, the latter is shifted to 1590 cm^{-1}. This sample otstutstvuet range order as *2D* peak is not observed.

The lowest value of the ratio of the intensities of *D* and *G* peaks corresponds to nanotubes obtained under the conditions of 100 mbar and 425°C. Also good results were obtained for nanotube grown at 300 mbar and 425°C, 450°C. The samples obtained under the conditions of 100 mbar and 400°C, 200 mbar and 400°C show the lowest quality. One can conclude that the most optimal conditions for obtaining nanotubes are 100 mbar and 425°C after analyzing the Raman spectra. Judging by the width and intensity of the peaks in the Raman spectra, as well as the presence of a second order peak one can talk about the high crystallinity of these samples.

4. Conclusion

The conducted experiments demonstrated the possibility of using Fe NPs, obtained by the EEW as catalysts for growth of CNs. Stable growth of CNs is carried out at temperatures significantly lower than commonly used by thermal CVD on iron catalysts. Studies have shown that the lower temperature limit is 400°C. The massive growth of CNs is observed in the entire investigated range of pressures at the same temperature. SEM studies clearly indicate the existence of a temperature range between the low temperature and high temperature (standard) mode of synthesis in which the growth of CNs occurs.

Raman spectroscopy showed that nanostructures grown on NPs at 100 mbar and 425°C have the highest crystallinity according to intensities of the groups *D* and *G*. The findings of the research results have a high potential for the development of efficient, low-energy, low-cost technology for obtaining CNTs and CNFs, without the use of expensive gas and the ability to control the structure and properties of macroscopic parameters of CNs.

Acknowledgements

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References

[1] Hafner J H, Bronikowski M J, Azamian B R, Nikolaev P, Rinzler A G, Colbert D T, Smith K A, Smalley R E 1998 *Chem. Phys. Lett*. **296** 195–202
[2] Jourdain M, Bichara Ch 2013 *Carbon* **58** 2–39
[3] Wang H, Yuan Y, Wei L, Goh K, Yu D, Chen Y 2015 *Carbon* **81** 1–19
[4] Yan Y, Miao J, Yang Zh, Xiao F, Yang HB, Liu B, Yang Y 2015 *Chem. Soc. Rev.* **44** 3295-3346
[5] Partizan G, Mansurov B Z, Aliyev B, Medyanova B, Tolegen A, Kenzhegulov A, Jiang X, Mansurov Z A 2015 *Proc. World Conf. on Carbon (Dresden)* p 231
[6] Lerner M I, Svarovskaya N V, Psakhie S G, Bakina O V 2009 *Russian Nanotechnologies* **4 (11-12)** 56-68 (in Russian)
[7] Lerner M I 2007 *Doc. Diss. (Tomsk)* 325 p (in Russian)
[8] lyin A P 2003 *Bulletin of the Tomsk Polytechnic University* **306** 133-139 (in Russian)
[9] Partizan G, Mansurov B Z, Medyanova B S, Koshanova A B, Aliyev B A 2016 *Combustion and plasmochemistry* **14** in print (in russian)
[10] Partizan G, Mansurov B Z, Medyanova B S, Aliev B A, Jiang Xin 2015 *Journal of Engineering Physics and Thermophysics* **88** 1151-1158
[11] Partizan G, Yao Ma, Mansurov B Z, Medyanova B S, Xin Jiang, 2014 *Proc. World Conf. on Carbon (Jeju island)* POT2-01
[12] Partizan G, Mansurov B Z, Aliev B A, Xin Jiang 2014 Int. Symp. "Physics and chemistry of carbon materials / nanoengineering (Almaty) p 303-307
[13] Partizan G, Mansurov B Z, Aliyev B A, Medyanova B S, Xin Jiang, Mansurov Z A 2015 *Proc. Annual Int. World Conf. on Carbon* (Dresden) p 232
[14] Xia J H, Jiang X, Jia C L 2009 *Applied Physics Letters* **95** 223110-1-223110-3
[15] Merchan-Merchan W, Saveliev A V, Kennedy L, Jimenez W C 2010 *Progress in Energy and Combustion Science* **36** 696-727
[16] Buranova Yu S 2011 *Proceedings of MIPT* **3** 30-41
[17] Dinadayalane T C, Leszczynski J 2012 Fundamental Structural, Electronic, and Chemical Properties of Carbon Nanostructures: Graphene, Fullerenes, Carbon Nanotubes, and Their Derivatives *Handbook of Computational Chemistry* (vol 2) (London, Springer) pp 793–867