Carbon-Carbon Composition "Expanded Graphite – Multiwalled Carbon Nanotubes"

Sementsov Yurii[1, 2], Grebel'na Yulia[2], Strelchuk Victor[3], Dovbeshko Galyna[4], Zhuravskyi Serhii[2], Makhno Stanislav[2], Wang Bo[1], Kartel Mykola[1, 2]

[1]Technology and Business Department, Ningbo University of Technology, Ningbo, China

[2]Department of Carbon Nanomaterials, O. Chuiko Institute of Surface Chemistry, NAS of Ukraine, Kyiv, Ukraine

[3]Department of Photonic Crystals, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, Kyiv, Ukraine

[4]Department of Physics of Biomaterials, Institute of Physics, NAS of Ukraine, Kyiv, Ukraine

Email address:

ysementsov@ukr.net (S. Yurii), nikar@kartel.kiev.ua (K. Mykola)

Abstract: It is given the description of expanded graphite (EG) as a cluster-assembled nanoscale system. It is shown that in the structure of EG there are both extended defects formed by the convolution of one or more graphene layers and orientation defects - disclination. The strength characteristics of EG compacted materials can be controlled by changing the parameters of the production process in a limited interval (the ratio of the amount of oxidizing agent, intercalant, with natural dispersed graphite, its particle size). The procedure for treating multiwalled carbon nanotubes (MW CNTs) with a solution of potassium dichromate in sulfuric acid was carried out according to the known technology of oxidation of natural graphite in order to obtain expandable graphite. It provides for the use of sulfuric acid as an intercalating agent and potassium dichromate ($K_2Cr_2O_7$) as an oxidizing agent. The aqueous dispersion of oxidized MW CNTs is stable over time: the average particle size is 50 nm; two fractions - from 20 to 100 nm, amount - 99.9%, mass - 10%; from 250 to 500 nm and amount of 0.1%, mass - 90%; high polydispersity ranges from 0.35-0.4, that is, the particles are quite close to the spherical shape. Modification of CNTs by oxygen simultaneously with anodic oxidation of natural dispersed graphite allowed for the first time to create a carbon-carbon composite "EG – MW CNTs" with enhanced physical and mechanical characteristics without additional use of binders.

Keywords: Expanded Graphite, Multi-walled Carbon Nanotubes, Carbon-Carbon Composite, Oxidative Intercalation, Declination

1. Introduction

Exfoliated (expanded) graphite (EG) is a group of materials with a graphite-like structure, which is obtained by rapid heating (thermal shock) of graphite intercalation compounds and their hydrolyzed forms. Decomposition and evaporation of the intercalant leads to a strong expansion of the particles along the axis perpendicular to the graphene plane. The EGs are characterized by a complex structure with developed surface and a presence of extended slit-like and cylindrical defects with a cross-sectional diameters of 0.7 to 20 nm which occur due to the coagulation and bending of several layers of graphene (Figure 1a, b) [1].

These defects manifest themselves in the Raman spectra, positron annihilation, low-temperature nitrogen adsorption-desorption experiments which all confirms a nanoscale structure of the EG [1, 2]. The presence of such defects is confirmed by the type of particles obtained by anodic oxidation of the EG-derived dense materials (Figure 2a, b) [3]. Moreover, the thinnest particles (multilayer graphene's of about 5...7 layers thick) are exfoliated by the mechanism of "secondary intercalation" (diffusion via defects) and aggregate in 3D structures on conductive substrates.
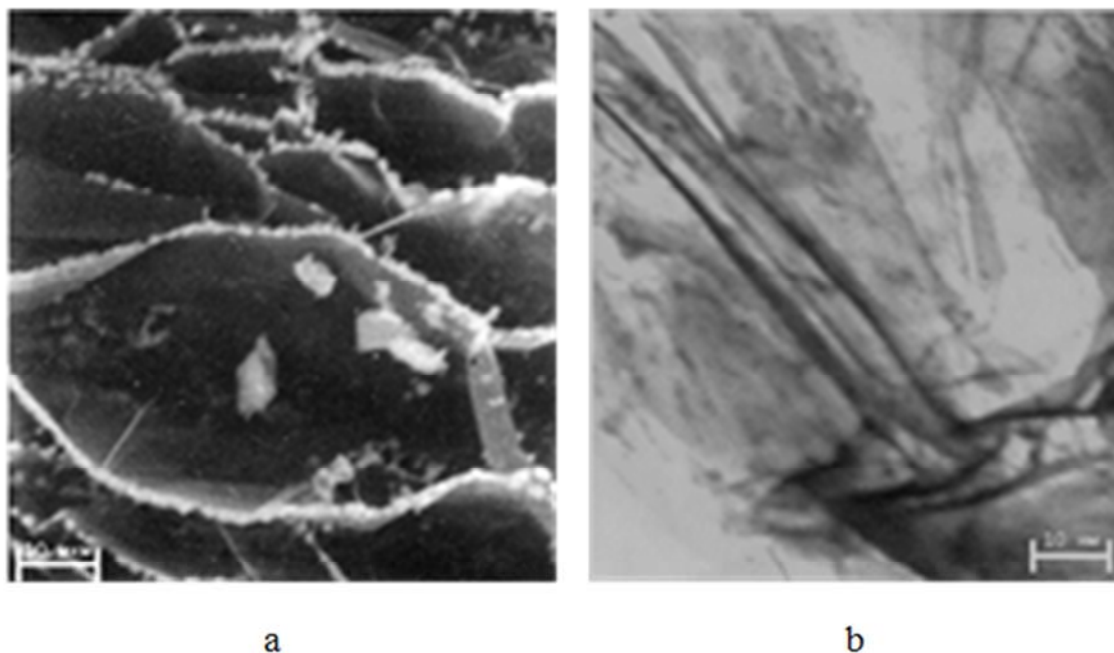
Figure 1. *Electron microscopic images of EG particles: a – SEM; b – TEM.*
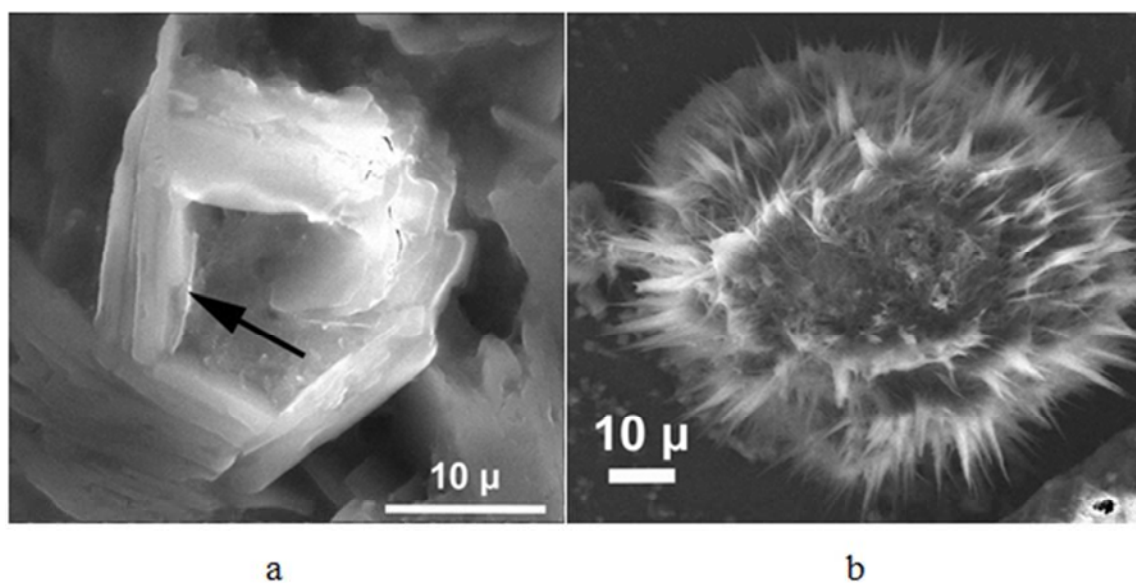

Figure 2. *SEM images of the two types of carbon particles obtained by the anodic oxidation of the EG-derived dense materials: a - pentagonal, b - flat flower –like.*

Larger, micron-sized particles, having the form of a pentagonal prism in the cross-section (Figure 2a) appear to have a declinational mechanism of formation [4-6]. The formation of microcrystals of pentagonal symmetry is typical for almost all metals with a face-centered cubic lattice for all types of crystallization with suggested declination mechanism of their origin is discussed [6].

The EG retains all properties of natural graphite and acquires the ability to pressing and rolling without any binders. The materials rolled and pressed from the EG with a density of 1.0-1.8 g/cm^3 і, in addition, have a unique set of elastic-plastic properties (Figure 3). Therefore, they are widely used as sealing materials in modern engineering. The increase of wear resistance and elastic component of deformation provides the increase of reliability and service life of such seals. Within some limits, the strength characteristics of the EG materials can be adjusted by changing the conditions of oxidative intercalation in the EG preparation route.
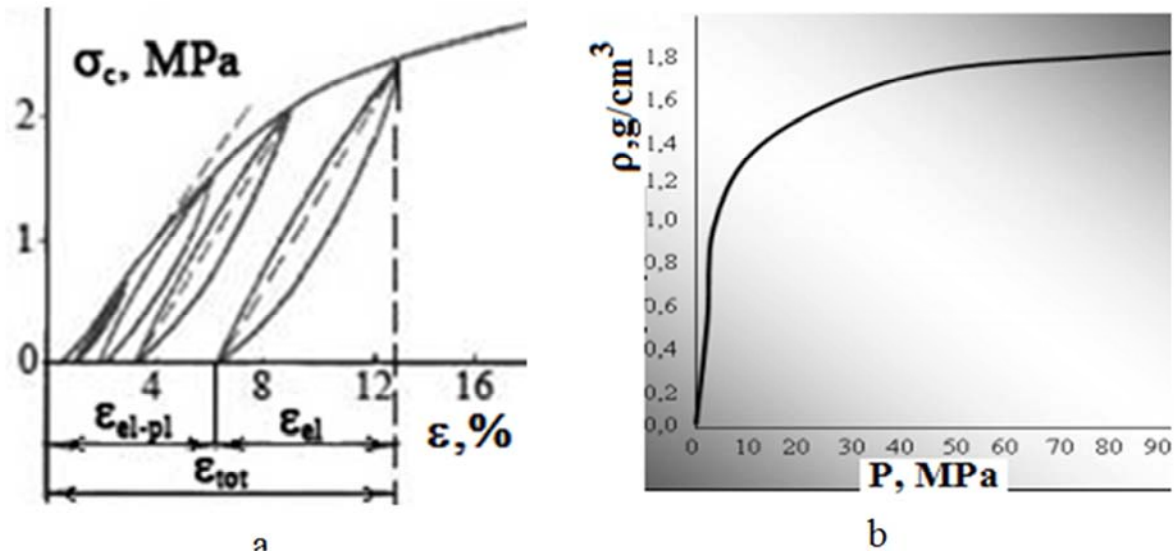
Figure 3. *a - Diagram of compression re-static loads for the EG; b – EG density dependence on compaction pressure.*
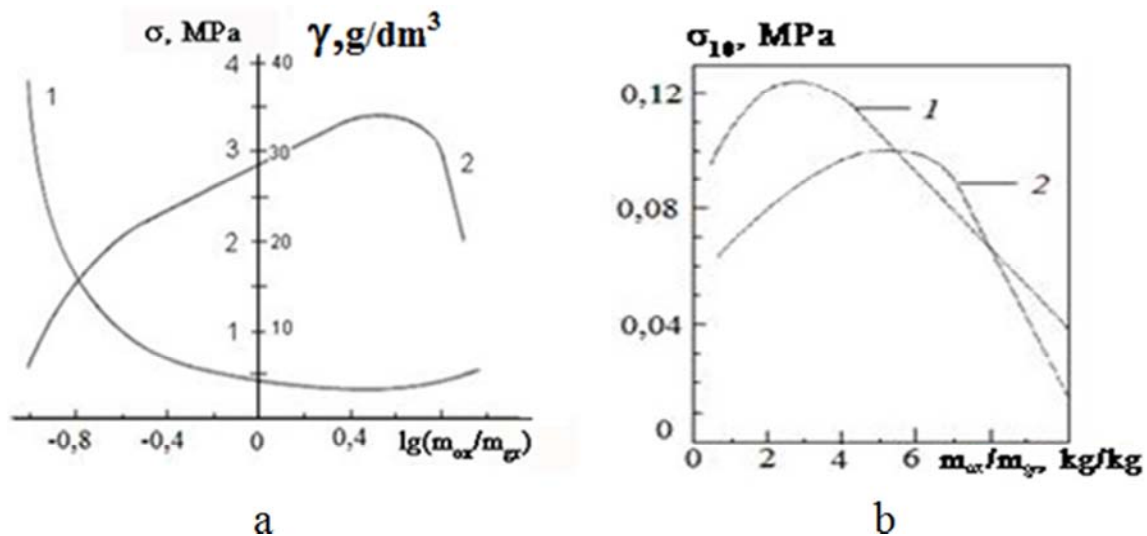

Figure 4. *EG characteristics: a - the dependence of the bulk density (γ) – (1), and tensile strength (σ) – (2), on the mass ratio of oxidant and graphite (ρ= 0.9 g/cm^3, m_{ox}/m_{gr} = 2); b – the dependence of the tensile strength on the mass ratio of graphite - oxidant at a constant weight ratio of acid to graphite: 1 – m_{acid}/m_{gr} = 2; 2 – m_{acid}/m_{gr} = 4.*

Another possibility of increasing the elasticity of materials derived from EG is the introduction of a high-modulus component into the material, which can be carbon nanotubes (CNTs). In [7], CNTs are introduced into the system "water-soluble polymer (WP)/surfactant/CNTs" in a rotating homogenizer, where WP is an acrylic copolymer, surfactant is an isodecyl alcohol ethoxylate. This system is used as a "permanent stickiness" adhesive in the production of EG gaskets reinforced with various filaments. The introduction of ~0.1 wt%. CNTs led to an increase in the recoverability of the foil by 17% and the packing - by 39%. However, the thermal resistance of the composite material is lost. Seals made of EG can be used in air up to 450°C, and the acrylic system burns up at 350°C.

The aim of this work is to obtain a carbon-carbon composition of EG-CNTs without the use of binders.

2. Materials and Methods

The methods of obtaining multi-walled carbon nanotubes (MW CNTs, Figure 5) and their characterization are described in [8]. The average diameter of the CNT was 10–20 nm, specific surface area determined by argon desorption was 200–400 m^2/g, and bulk density was within 20–40 g/dm^3. According to TEM, X-ray diffraction, and Raman spectroscopy data, the noticeable amount of amorphous carbon was not detected. Large-scale production of MW CNTs, as a rule, is a chemical vapor deposition (CVD) method, which gives CNT agglomerates in the form of tubes entangled with each other, with the size of 20–500 μm in diameter. We investigated a possibility of deagglomeration of MWCNT in an ultrasonic disperser UZDN-2 and universal homogenizer using shear deformation together with the effect of cavitation in an aqueous dispersion in the presence of surfactants. The

analysis of the agglomerates was carried out by means of laser correlation spectroscopy. The particle size distribution

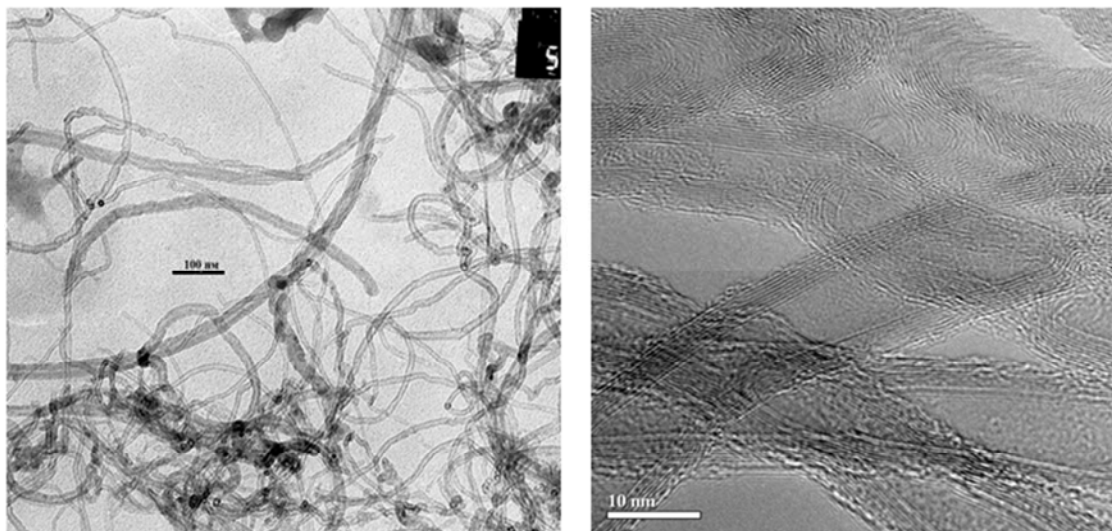function was determined with laser photon correlation spectrometer «Zetasizer-3» (Malvern Instrument, UK).

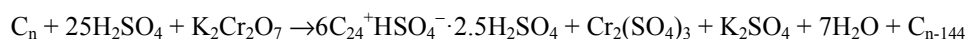**Figure 5.** *TEM images of MWCNTs.*

Effective deagglomeration agent for CNTs are strong acids and oxidizing agents, as reported e.g. in [9]. Therefore, our idea was, to use a simultaneous process of deagglomeration CNTs and intercalation of natural graphite. This procedure was performed in two ways: the first way- chemical oxidation in solutions of strong oxidants as described in [2]; the second way is electrochemical (anodic) oxidation as in [10]. The first option was carried out as follows. Sulfuric acid was mixed with an oxidizer and CNTs in proportion: per 1 dm^3 of sulfuric acid, 0.5–10 g of CNTs and 55–80 g of potassium permanganate or 85–125 g of potassium bichromate. Then, in a mixture of sulfuric acid with CNTs and oxides, graphite is added with stirring in the ratio of 1.6–2.2 dm^3 of sulfuric acid-CNTs-oxide mixture per 1 kg of graphite. Stirring continued for 5–20 min. The resulting product was washed with a water filter to pH = 6–7 and dried. The dried product was heated in the heat stroke mode to a temperature of 850–1250°C. After cooling, the product was rolled into a foil. Then the recoverability, compressibility, and tensile strength were measured. The mechanical tensile and compression tests of the prepared composites were carried out on a 2167 P 50 breaking machine with continuous automatic recording of the load-strain diagram on the PC.

The essence of the second option is as follows. The concentrated sulfuric acid is mixed with CNTs and graphite in proportion: per 1 dm^3 of sulfuric acid, 1–30 g of CNTs and 0.8–1.1 kg of graphite. This mixture was subjected to anodic oxidation at a current density of 5–35 mA/cm^2 and an electric

power consumption of 80–120 A·h/kg. The obtained product was washed with water to a pH value is of ≈ 6–7 and dried. The dried product is heated to a temperature of 850–1250°C in the thermal shock mode. A composite carbon material was obtained with composition, wt%: CNTs 0.1–3.0; expanded graphite the rest. After cooling, the composite carbon material was rolled into a foil and characterized for compressibility, recoverability and tensile. The chemical used for this synthesis procedure were as follows: carbon nanotubes at TU 24.1032911669–009, graphite brand GSM-2, GOST 17022-81; sulfuric acid according to GOST 4204. Changes in the structural state of CNTs under the influence of their oxidation, as well as the composite materials "EG-CNTs" structure were investigated using Raman spectroscopy. Raman spectra of CNTs were recorded using the T-64000 Horiba Jobin-Yvon spectrometer in the backscattering geometry at room temperature when excited by an argon laser (λ = 514.5 nm, 1 mV).

3. Results and Discussion

The procedure of MW CNTs treatment with a solution of potassium bichromate in sulfuric acid according to known technology natural graphite oxidation aiming at obtaining expandable graphite, is based on the following scheme, which involves the use of sulfuric acid as an intercalating agent and potassium dichromate ($K_2Cr_2O_7$) as oxidizer [2]:

$$C_n + 25H_2SO_4 + K_2Cr_2O_7 \rightarrow 6C_{24}^+HSO_4^- \cdot 2.5H_2SO_4 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O + C_{n-144}$$
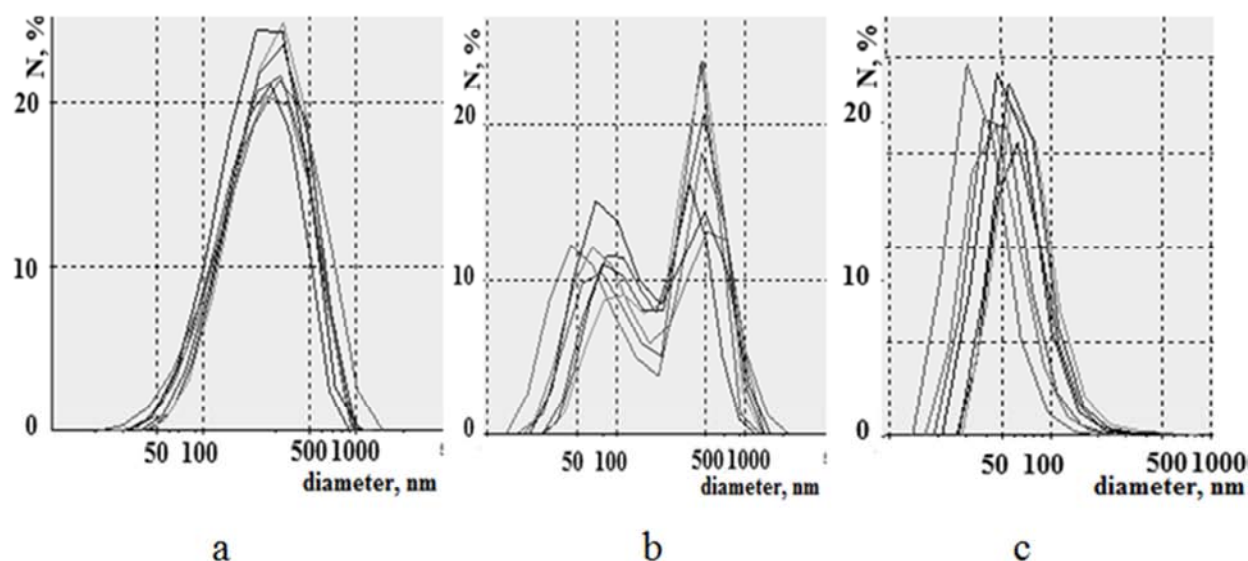
Figure 6. *Particle size distribution in the CNT suspension: a - "mono-modal" mode; b -"poly-modal" mode, particle volume distribution (mass if density is constant); c - "poly-modal" mode, particle distribution by number.*

The dependencies of particle size distributions were recorded in the so-called "mono-modal" and "poly-modal" modes. In Figure 6 the particles distribution for the composition obtained by oxidation of CNTs is shown. Water dispersion of the composition is stable over time: the average particle size is 50 nm; two fractions – from 20 to 100 nm, the amount - 99.9%, weight - 10%; from 250 to 500 nm, the amount of 0.1%, weight - 90%; high polydispersity ranges from 0.35-0.4, that is, the particles are close enough to spherical shape. It should be noted that the suspension when diluted 10 times is incredibly stable and did not require additional shaking throughout the study period and the next day the data from polydispersity did not differ from the previous ones. Thus, the results of laser correlation spectroscopy (LCS) indicate that after the chemical treatment of CNTs with powerful oxides, such as potassium in the presence of concentrated sulfuric acid, CNTs are crushed and form a stable suspension of spherical particles of almost the same size.

Anodic oxidation of CNTs in 94% sulfuric acid gives a similar particle size distribution as shown in Figure 6. The specific surface area is monotonous, slightly declining from 293 to 256 m^2/g with an electric power consumption rising up to 120 A·h/kg. According to the analysis of the XPS (X-ray photoelectron spectroscopy) of high resolution spectra, it follows [7] that the outputs of CNT's have 0.75 at% after oxidized under 120 A·h/kg with 3.62 at% of oxygen. The relative concentrations of oxygen-containing centers are given in Table 1. Thus, the anode treatment of CNT's under 120 A·h/kg significantly (4.8 times) increases the amount of oxygen on the surface of CNTs.

Table 1. *Relative concentrations of oxygen-containing centers of CNT's and corresponding binding energy.*

Samples of CNT's	Relative concentration of oxygen-containing groups, %			
	E_b= 286.1-1286.3 eV (C-OH)	E_b = 287.3–287.6 eV (C=O)	E_b = 288.4–288.9 eV (C-OOH)	E_b = 290.4–290.8 eV (CO, CO_2)
Initial	49.1	17.2	17.2	16.5
120 A·h/kg	53.8	53.8	13.6	12.8

In Figure 7 the Raman spectra of the initial CNTs and CNTs obtained after transmission of 120 A·h/kg of electricity are presented. The obtained Raman spectra are typical for MW CNTs. The G-band (the so-called "graphite" symmetry mode E_{1g} at the point G of the Brillouin zone) was recorded at 1573 cm^{-1} for the initial CNTs, which corresponds to the tangential oscillations of carbon atoms in the rings of the graphene layer [11]. The so-called d-band for the initial CNTs was also detected at 1348 cm^{-1} which characterizes a disordering in multilayer graphene structures and absence of ideal hexagonal graphite lattice [12].

This feature corresponds to breathing vibrations of rings of graphene layer in the K point of the Brillouin zone. The ratio of the intensities of D and G bands, and half-width (FWHM) values represent the degree of ordering of the graphite-like structure (the bands broadening and shifting to a higher frequency region corresponds to a greater degree of disorder). As shown in Figure 7 and Table 2, for the initial CNTs the intensity of the G-mode is a little higher than that of D-band. Typically, this intensity ratio indicates a slight disordering of the structure caused by defects. With a low concentration of defects, including the presence of an ideal packing of layers in highly oriented graphite, the D-band is not observed. The action of 120 A·h/kg of electric power leads to an increase of the intensity ratio of the D-band, while the G-band shifts towards higher frequencies and becomes wider, so the CNT defectiveness increases. The Raman spectra of the EG-CNT composite materials are shown in Figure 8. The main

parameters of the characteristic bands observed in the micro-Raman spectra of EG of different origin and EG-CNT composites are shown in Table. 1. From the comparison of Raman spectra of the EG samples obtained under different conditions, it can be concluded that the most defective structure is the EG synthesized by chemical oxidation in a

solution of potassium bichromate in sulfuric acid with their ratio significantly exceeding the stoichiometric value. The result is so-called peroxidation graphite, as well as a significant defectiveness of the EG prepared after the hydrolysis, drying, and heat treatment.
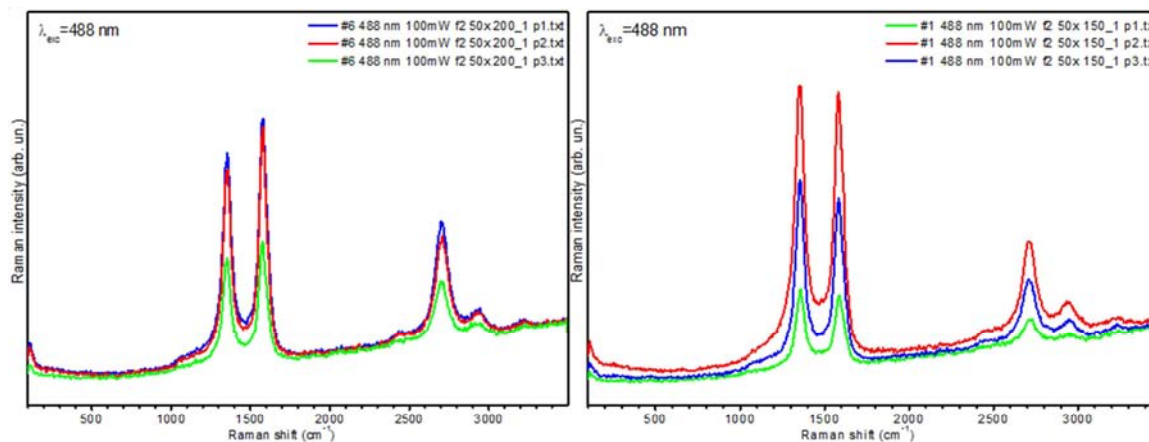

Figure 7. The Raman spectra of the initial CNTs - (a) and CNTs obtained after transmission of 120 A·h/kg of electricity – (b).
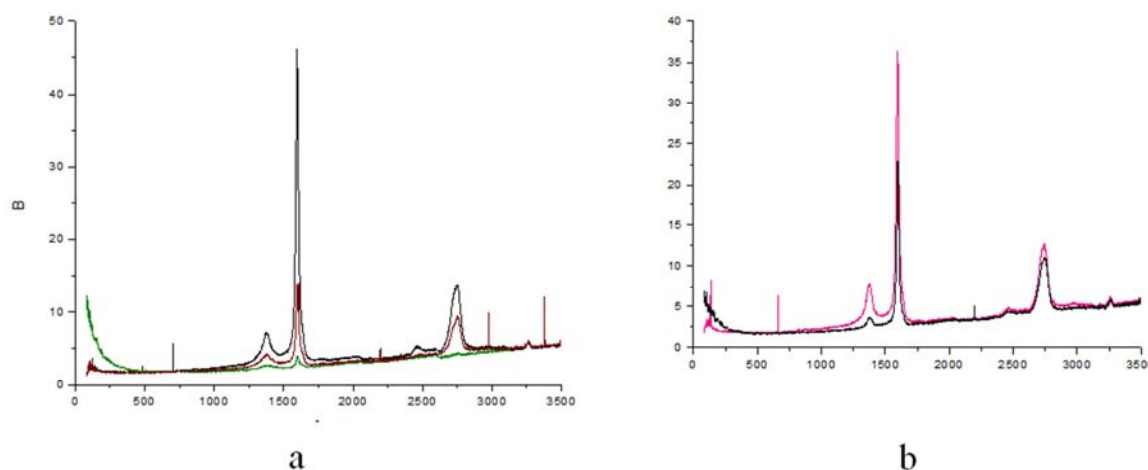

Figure 8. Raman spectra of the EG-CNT compositions: a – after chemical oxidation; b – after anodic oxidation.

The G-band of initial CNT is shifted under action 120 A·h/kg towards high frequencies, its half-width increases, the I_D/I_G ratio acquires the maximum value in comparison with the EG samples of other origin. As can be seen from the Table

2, the EG samples obtained from anodically oxidized graphite have the least amount of defects. CNTs not significantly change the Raman spectra of the composite material EG-CNT, which can be explained by the low CNTs content of ~1 wt%.

Table 2. The basic parameters of the characteristic Raman bands of CNTs of different oxidation degrees, EG and EG-CNT compositions.

Samples	D, cm⁻¹	G, cm⁻¹	2D, cm⁻¹	D_{FWHM}, cm⁻¹	G_{FWHM}, cm⁻¹	I_D, a.u.	I_G, a.u.	I_D/I_G
CNTs-in*	1348	1573	2706	51	53	9.0	10.4	0.86
CNTs-AO	1352	1583	2711	55	59	11.78	11.34	1.04
EG-CO	1378	1602	2794	89	53	8.1	11.1	0.73
EG-AO	1374	1598	2752	-	18	3	117	0.03
COMP-CO	1377	1598	2748	-	22	14	126	0.11
COMP-AO	1375	1597	2737	51	23	5	33.6	0.13

*In – initial; AO – anodic oxidation at 120 A·h/kg; CO – chemical oxidation; COMP – composite EG+CNTs.

TEM images of the EG samples and EG-CNT compositions are shown in Figure 9.

The images show that EG-CNT samples have a folded

structure, with clearly visible CNTs "embedded" in the body of EG (shown by arrows).

As can be seen from the Tables 3, 4 the introduction of

CNTs into the EG matrix under combined chemical anodic oxidation of CNT and natural graphite allows you to create the carbon-carbon composition containing EG and CNT. Such a composite has an increased the recoverability (by 15...18 %), the decreased compressibility and a small increase in the tensile strength.
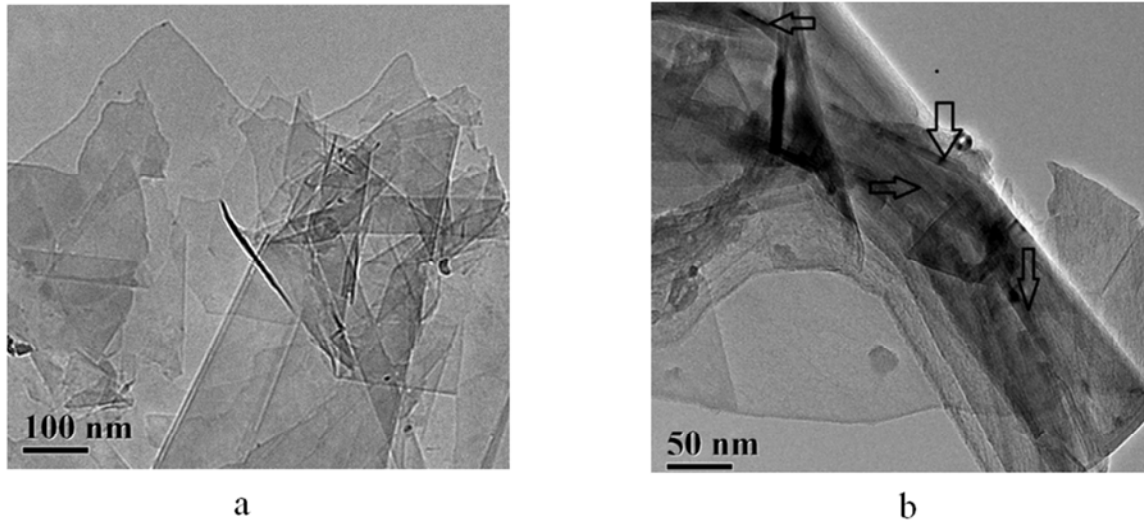

Figure 9. TEM images of (a) EG samples and (b) EG-CNT compositions (CNTs are shown by arrows).

Table 3. Recoverability, compressibility and tensile strength for the EG sample and EG-CNT compositions obtained by combined chemical oxidation of CNTs and natural graphite depending on the process parameters.

Example	CNT mass	Volume of the solution of oxidizer	Mass $K_2Cr_2O_7$. g per 1 dm^3 of H_2SO_4	The mass of $KMnO_4$. g per 1 dm3 of H_2SO_4	Mixing time. minutes	Recoverability. %	Compressibility. %	Tensile strength. MPa
1	1.0	2	171	–	5	53±2	64±2	3.4±0.5
2	0.2	2	–	130	10	47±2	81±2	2.8±0.5
3	0.8	2	180		10	50±2	69±2	3.0±0.5
4	2.0	2.2	–	110	20	52±2	63±2	3.2±0.5
5	1.0	2	250	–	6	52±2	63±2	3.3±0.5
6	1.0	1.6	0.6	–	15	50±2	64±2	3.0±0.5
7	1.0	2	200	–	10	51±2	65±2	3.1±0.5
8	1.0	3	–	160	18	53±2	65±2	3.4±0.5
9	1.0	2	–	140	8	51±2	65±2	3.2±0.5
10	0	2	200		20	46±2	83±2	2.6±0.5

Table 4. Recoverability, compressibility and tensile strength for the EG sample and EG-CNT compositions obtained by combined chemical anodic oxidation of CNT and natural graphite depending on the process parameters.

Example	CNT mass, g	Graphite weight, kg	Current density, mA/cm^2	Amount of electricity, A·h/kg	Recoverability, %	Compressibility, %	Tensile strength, MPa
1	10	1,0	25	90	52±2	63±2	3,3±0,5
2	1	0,8	25	80	48±2	80±2	2,7±0,5
3	8	0,9	25	90	51±2	70±2	3,1±0,5
4	20	1,1	25	100	53±2	64±2	3,3±0,5
5	30	1,1	25	90	53±2	64±2	3,2±0,5
6	10	1,0	5	90	52±2	63±2	3,2±0,5
7	10	1,0	25	90	51±2	64±2	3,2±0,5
8	10	1,0	35	90	52±2	64±2	3,3±0,5
9	0	1,0	25	90	45±2	84±2	2,5±0,5

4. Conclusion

Natural graphite in the "expanded state" (the EG) is a nanoscale cluster vibrate system, which is characterized by the presence of extended cylindrical, conical and slit-like defects with average cross-section diameters of 0.7–20 nm, due to the coagulation and bending of several layers of graphene, possibly associated with disclination defects. They manifest themselves in the spectra of Raman scattering, electron-positron annihilation, the structural parameters defined by X-ray diffraction, isotherms of adsorption-desorption of nitrogen and the images of transmission electron microscopy. These defects determine the density and elastic-plastic characteristics of the compression deformation of dense materials based on EG. EG physical and mechanical characteristics can be adjusted in a certain interval by changing the process parameters of its production. Effectively,

you can influence the elastic properties of carbon dense materials based on the EG and CNTs. Treatment of CNTs with solutions of strong oxidizers in sulfuric acid and anodic oxidation in concentrated sulfuric acid disperses CNTs agglomerates, and oxygen modification provides the possibility of creating stable CNTs dispersions. Modification of multi-walled carbon nanotubes by oxygen simultaneously with anodic oxidation of natural dispersed graphite, made it possible for the first time to create a carbon-carbon composite "EG - MW CNTs" with enhanced physical and mechanical characteristics without additional use of binders.

References

[1] G. I. Dovbeshko, V. S. Kopan, S. L. Revo, M. M. Nishchenko, G. P. Prikhod'ko, M. L. Pyatkovsky, Yu. I. Sementsov, and M. Vestermayer, "Nanostructure of expanded graphite", Metal Physics and Novel Technologies, 2005, vol. 27, pp. 1001-1010.

[2] Yu. I. Sementsov, S. L. Revo, and K. O. Ivanenko, Expanded Graphite, Kiev: Interservis, 2016, p. 241 [In Russian].

[3] M. Kartel, Yu. Sementsov, G. Dovbeshko, L. Karachevtseva, S. Makhno, T. Aleksyeyeva, Yu. Grebel'na, V. Styopkin, Wang Bo, and Yu. Stubrov, "Lamellar structures from graphene nanoparticles produced by anode oxidation", Advanced Materials Letters, 2017, vol. 8 (3), pp. 212-216.

[4] A. E. Romanov, M. A. Rozhkov, and A. L. Kolesnikova, "Disclinations in polycrystalline graphene and pseudo-graphenes", Review Letters on Materials, 2018, vol. 8, pp. 384-400.

[5] I. S. Yasnikov, A. L. Kolesnikova, and A. E. Romanov, "Multi-destination configuration in pentagonal microcrystals and two-dimensional carbon structures", Solid State Physics, 2016, vol. 58, pp. 1147-1152.

[6] A. A. Vikarchuk, I. S. Yasnikov, O. Dovzhenko, E. A. Talalova, and M. N. Turkov, "Pentagonal crystals of electrolytic copper origin: structure, models and mechanisms of their formation and growth", Bulletin of Samara State University, Natural Science Series, 2006, N3 (43), pp. 51-64 [In Russian].

[7] Yu. I. Sementsov, and S. L. Revo, "Expanded graphite, carbon nanotubes and its composites", In: First Intern. Conf. on Renewable Energies and Nanotechnology Impact on Medicine and Ecology (ICREN 2013), 2013, February 16-17, Algeria-Constantine, pp. 1-3.

[8] Yu. Sementsov, G. Prikhod'ko, M. Kartel et al., "Carbon Nanotubes Filled Composite Materials", In: Carbon Nanomaterials in Clean Energy Hydrogen Systems – II. NATO Science for Peace and Security Series C: Environmental Security 2, 2011, Springer Science + Business Media B. V., pp. 183-195.

[9] Z. Wang, M. D. Shirley, S. T. Meikle, R. L. D. Whitby, and S. V. Mikhalovsky, "The surface acidity of acid oxidised multi-walled carbon nanotubes and the influence of in-situ generated fulvic acids on their stability in aqueous dispersions," Carbon, 2009, vol. 47, pp. 73–79.

[10] M. Kartel, Yu. Sementsov, S. Makhno, Weijun Zhang, Xiaochen Zhang, Li Vei Gen, and Bo Wang, "Electrochemical reactor and process conditions for the continuous oxidation of natural graphite with a capacity of 10 kg/hour", Intern. Journal of Innovative Science, Engineering & Technology, 2017, vol. 4, pp. 203-209.

[11] R. J. Nemanich, and S. A. Solin, "First- and second-order Raman scattering from finite-size crystals of graphite", Phys. Rev. B., 1979, vol. 20, pp. 392-401.

[12] G. I. Dovbeshko, O. P. Gnatyuk, A. A. Nazarova, Yu. I. Sementsov, and E. D. Obraztsova, "Vibrational spectra of carbonaceous materials: a SEIRA spectroscopy versus FTIR and Raman", Fullerenes, Nanotubes and Carbon Nanostructures, 2005, vol. 13, pp. 393-400.

[13] Raman Spectroscopy for Nanomaterials Characterization, Ed. C. S. S. R. Kumar, 2012, Berlin-Heidelberg: Springer-Verlag. DOI: 10.1007/978-3-642-20620-7.