

A.D. DOBRZAŃSKA-DANIKIEWICZ*[#], W. WOLANY*, D. CICHOCKI*, D. ŁUKOWIEC*

MICROSCOPIC AND SPECTROSCOPIC RESEARCH OF THE MWCNTs-Re NANOCOMPOSITES

BADANIA MIKROSKOPOWE I SPEKTROSKOPOWE NANOKOMPOZYTÓW TYPU MWCNTs-Re

The combination of TEM research and Raman spectroscopy to characterization of MWNTs-Re nanocomposites gives a new notion about the structure and quality of materials obtained. TEM studies indicate that the functionalization method significantly influences the morphology of obtained MWCNTs-Re nanocomposites. Due to the specific spectrum recorded for the MWCNTs they can be distinguished from other forms of carbon, furthermore comparative analysis of the results at different stages of the manufacturing process confirms the covalent modification of the MWCNTs structure.

The D-band intensity compared to the G-band intensity provides valuable information about the quality of the sample, in particular indicates the existence of contamination and/or the presence of structural defects. Preliminary results suggest that the high-temperature manufacturing process of MWCNTs-Re nanocomposite improves the quality of the carbon material intended for the experiment.

Wykorzystanie transmisyjnej mikroskopii elektronowej oraz spektroskopii ramanowskiej, zastosowanych do scharakteryzowania nanokompozytów typu MWCNTs-Re, umożliwia określenie struktury i jakości uzyskanego materiału. Badania TEM wskazują, że sposób funkcjonalizacji znacząco wpływa na morfologię otrzymanych nanokompozytów typu MWCNTs-Re. Charakterystyczne widmo ramanowskie uzyskane dla nanorurek wielościennych umożliwia ich identyfikację, ponadto analiza porównawcza uzyskanych wyników na różnych etapach procesu wytwórczego potwierdza kowalencyjną modyfikację struktury MWCNTs. Stosunek intensywności pasma D do intensywności pasma G informuje o jakości badanych próbek, w szczególności wskazuje na występowanie ewentualnych zanieczyszczeń i/lub obecność defektów strukturalnych. Wstępne wyniki badań wskazują, że proces wytwarzania nanokompozytu typu MWCNTs-Re z zastosowaniem wysokiej temperatury wpływa na poprawę jakości wyjściowego materiału nanorurkowego.

1. Introduction

The intensive development of nanotechnology is mainly caused by a demand for new materials with excellent properties and also by an effort to miniaturise electronic circuits and other devices. Carbon nanostructures have attracted scientists' attention since being discovered, and special attention was paid to Carbon Nanotubes (CNTs) possessing, among others, excellent mechanical and electrical properties. Since Iijam's publication in 1991 [1], regarded to be one of breakthroughs in nanotechnology, numerous research institutions have undertaken investigations associated with carbon nanotubes [2-5]. The surface functionalisation of CNTs is substantially enhancing potential applications of the material. Many types of composites have been developed whose reinforcing component are carbon nanotubes, e.g. carbon nanotube metal matrix composites (CNT-MMC) [6], and also such where carbon nanotubes represent a scaffold for nanoparticles, e.g.

metallic nanoparticles, by forming a Carbon Nanotubes-Nanoparticles (CNTs-NPs) nanocomposite [7,8].

It has been proven many times that electrical conductivity of carbon nanotubes changes as a result of interaction with other chemical substances [9-11]. This effect of changes in conductivity may also be enhanced if carbon nanotubes are deposited with other particles. Modern chemical sensors often contain an active element in the form of a nanocomposite consisting of carbon nanotubes coated with the nanocrystals of, e.g. precious metals. This interesting aspect represented an incentive for creating a new nanocomposite consisting of carbon nanotubes and nanoparticles of a high-melting precious metal – rhenium [12,13]. There are numerous examples in the literature of nanocomposites based on nanotubes decorated with nanoparticles of, e.g. Ag, Au, Pt, Pd, Rh, Cu [14-18]. A less popular precious element is rhenium possessing very interesting properties. Poland is one of the leading manufacturers of this element which persuades to regularly

* FACULTY OF MECHANICAL ENGINEERING, SILESIAN UNIVERSITY OF TECHNOLOGY, 18 A KONARSKIEGO STR., 44-100 GLIWICE, POLAND

[#] Corresponding author: anna.dobrzanska-danikiewicz@polsl.pl

broaden the range of its industrial applications. Until now, rhenium, having a high melting point, small addition of which significantly improves mechanical properties of alloys, is used in the aviation and space industry for parts of rocket engines, in heating elements and power devices, in thermocouples and electromagnets, and also in production of high-octane fuels due to its catalytic properties.

The primary aim of the article is to characterise, using microscope and spectroscopy techniques, a structure of the Multiwall Carbon Nanotubes-Rhenium (MWCNTs-Re) nanocomposite and the degree of this nanocomposite's structural defects.

2. Materials and methodology

Commercial multiwalled carbon nanotubes with the diameter of 10 to 20 nm and the length of 10 to 30 μm have been used for the experiment. The manufacturer's specifications provide that the material was produced with the Chemical Catalytic Vapour Deposition (CCVD) method and its purity, declared by the manufacture, is over 98%.

The elaborated method of manufacturing the MWCNT-Re nanocomposite comprises the three key phases: (1) carbon nanotubes' surface is prepared for further procedures, (2) MWCNTs are placed in a medium being a source of rhenium, and (3) a rhenium precursor is reduced to metallic rhenium. A functionalisation process of carbon nanotubes, intended for further experiments, carried out in nitric acid (V) is very important for the entire fabrication process. Functional groups ($-\text{COOH}$, $-\text{OH}$, $=\text{O}$), representing subsequently the nucleus place of Rhenium nanocrystals, are obtained on the surface of the input material as a result of the acting oxidising acids. The uniform distribution of nanotubes on the surface of carbon nanotubes is achieved through correctly conducted functionalisation in relation to the fabrication of CNT-NPs nanocomposites. It is one of the important elements of fabrication process optimisation. The article presents research outcomes for two functionalisation variants. *The first variant* includes the following procedures: MWCNTs are placed in a beaker, are filled with HNO_3 acid, the mixture is treated with ultrasounds (for 3 hrs), put aside for 24 hours without any interference, the material is filtered, MWCNTs are filled with HReO_4 acid, the mixture is treated with ultrasounds (for 3 hrs) and put aside for 24 hours without any interference. *The second variant* provides to extend the time of treating the mixture (MWCNTs+ HNO_3) with ultrasound to 5 hours, the time of keeping MWCNTs in acids without any interference is shortened to 15 hours, the material is filtered, MWCNTs are filled with HReO_4 acid and again mixing with ultrasounds for 1 hour just before the relevant decoration process with rhenium nanocrystals.

An MWCNTs-Re nanocomposite synthesis process is an *in situ* process. This means that the reduction of the rhenium precursor (HReO_4) leads to formation of metallic Re nanoparticles directly on carbon nanotubes. After the both described functionalisation variants, a portion of the wet material is placed in a quartz vessel designed for the purpose of the experiment (Fig. 1) and pre-heated in the atmosphere of hydrogen and argon shield in a CVD device at the process

temperature of 800°C and with H_2 flow rate of 400 SCCM. The flow rate of hydrogen was decreased twice after 15 minutes of the process and heating was continued for 30 minutes.



Fig. 1. Quartz holder for heating the material in a CVD oven designed for the purpose of the experiment

The essential task of the publication's author, i.e. to confirm the occurrence of rhenium nanocrystals on the surface of carbon nanotubes, was carried out using a Zeiss Supra 35 scanning electron microscope (SEM) equipped with an X radiation energy dispersive spectroscopy (EDS) and a TITAN 80-300 transmission electron microscope (TEM) by FEI equipped, in particular, with a STEM scanning system, light and dark field detectors, High Angle Annular Dark Field (HAADF) and EDS. The properties of the input material, i.e. unmodified carbon nanotubes, the material after functionalisation (acc. to the two variants) and the output material in the form of an MWCNTs-Re nanocomposite, were compared with the Raman spectroscopy method. The examinations were performed with a Raman spectrometer in Via Reflex by Renishaw fitted with a confocal and laser argon microscope with the wavelength of $\lambda = 514 \text{ nm}$.

3. Results and discussion

A thermogravimetry analysis of the input material was carried out to identify the purity of the material intended for further experiments and this confirmed that the purity of MWCNTs is approx. 98% (Fig. 2). A result of an experiment carried out with the Raman spectroscopy method shows that the investigated carbon nanotubes have structural defects as observed also during examinations with a transmission electron microscope.

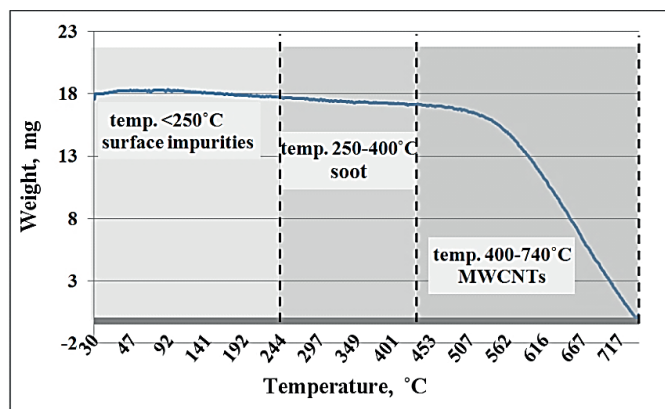


Fig. 2. Results of the thermogravimetry analysis of MWCNTs undergoing subsequently further stages of the experiment

The rhenium nanoparticles deposited on the surface of nanotubes, with the diameter of 3 to 12 nm, are spherically shaped and are seen as dark points on TEM images in the light field (Fig. 3a and 3b). Re nanoparticles have a crystalline structure, as confirmed by crystalline planes clearly discernible on the images (Fig. 4). The chemical composition of the newly fabricated nanocomposite, including the presence of rhenium, was confirmed with an Energy Dispersive Spectroscopy (EDS), also shown in Fig. 4.

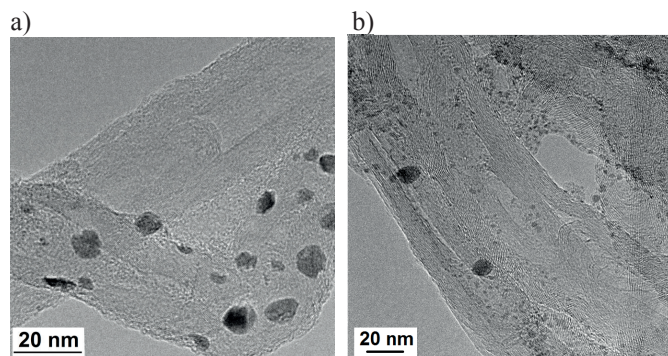


Fig. 3. MWCNT-Re nanocomposite formed through carbon nanotubes' functionalisation according to: a) the first variant, b) the second variant

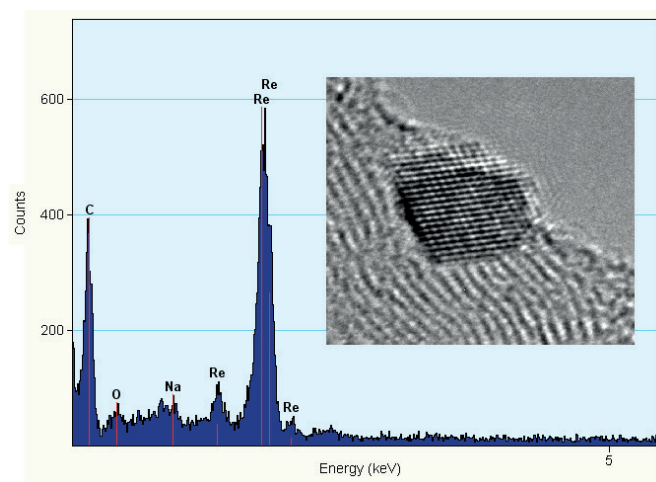


Fig. 4. EDS diagram and rhenium nanocrystal deposited on carbon nanotube (right-hand top corner of the figure)

Examinations with a STEM using High Angle Annular Dark Field (HAADF) have shown that the material fabricated according to the first functionalisation variant tends to create larger agglomerates of rhenium and bigger nanoparticles. The carbon nanotubes not coated with rhenium are also observed (it's visible in Fig. 5a), which most probably signifies unevenly dispersed nanotubes in the medium containing the deposited element. The material obtained with the second functionalisation variant is a little different (Fig. 5b). Rhenium nanoparticles in this case are smaller (even below 1 nm), there are more of them and are evenly spread across the nanotubes surface. During the microscopic investigation was observed some places where there were unattached nanoparticles located on a copper grid (on carbon film).

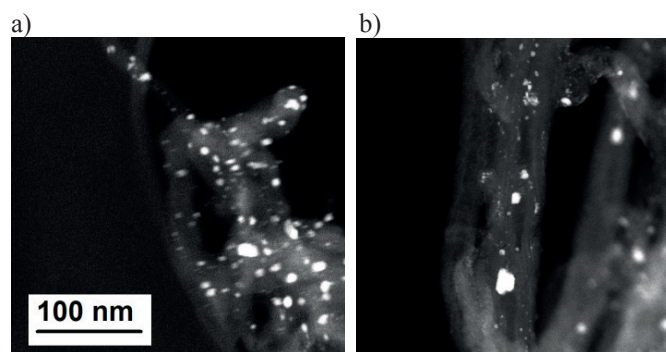


Fig. 5. Carbon nanotube functionalised according to: a) the first variant, b) the second, covered with fine rhenium nanoparticles

Raman spectroscopy was used for identifying the type of the investigated carbon (single- or multiwalled) nanotubes and identify the degree of their structural defects. The presence of multiwalled carbon nanotubes in the preparation can be determined according to distinctive bands on the chart: (i) D bands informing about the presence of impurities in the specimen and the presence of structural defects; (ii) G band indicating the degree of order for graphene structure in nanotubes and (iii) G' band being the derivative of D peak (2D) [19-21]. The results of spectroscopy examinations show the absence of Radial Breathing Mode (RBM) distinctive for singlewalled nanotubes, which also clearly shows the presence of MWCNTs only in the studied preparation.

Studies with the Raman spectroscopy method were made to identify the degree of structural defects of the studied material at different stages of the fabrication process. The following was examined, in particular: unmodified MWCNTs for further studies (type A specimens); MWCNTs functionalised according to two variants (B type specimens) and the newly developed MWCNT-Re nanocomposite (C type specimen). A comparative analysis of the results of spectroscopy examinations for particular types of specimens according to two variants of their functionalisation are presented in table 1. Fig. 6 shows graphically Raman spectra characterising the degree of structural defects of specimens of the A, B and C type corresponding to the second variant of functionalization with the peak value presented in table 1.

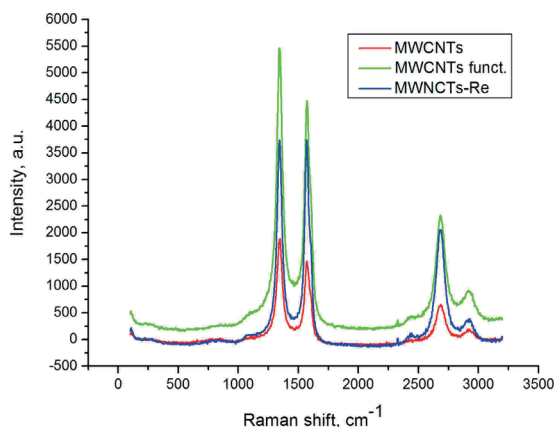


Fig. 6. Raman spectrum of MWCNT-Re carbon materials at different stages of fabrication, functionalised acc. to the second variant

TABLE 1

Intensity of the bands recorded with the Raman spectroscopy method having a degree of structural defects of the studied material acc. to two variants differing in the method of carbon nanotubes functionalisation

Specimen	VARIANT 1			VARIANT 2		
	D	G	I _D /I _G	D	G	I _D /I _G
A	2353	1876	1,254	2353	1876	1,254
B	4588	3620	1,268	5468	4474	1,222
C	4060	3233	1,256	3739	3747	0,998

A - pristine MWCNT's; B- MWCNTS after functionalisation; C- MWCNT's-Re nanocomposite

It can be concluded based on the initial outcomes of the investigations that the intensity rate of D/G peak for the investigated specimens is falling after the process of decoration with rhenium nanoparticles.

The treatment of the material containing CNTs in aggressive oxidising mediums may affect the value of the D/G intensity rate in two ways. First of all, carbon impurities are removed such as amorphous carbon leading to a smaller degree of material defects. On the other hand, intensive oxidation of nanotubes' surface causes the formation of new functional groups and, consequently, the ID/IG rate is increased. According to the data presented in table 1, obtained after functionalisation in HNO₃ for the first variant, the ID/IG indicator is rising slightly by 0.014, while decline by 0.032 is seen for the other variant. The investigations' results presented in table 1 do not indicate clearly, therefore, the dominant impact of a given factor as it differs for each variant. The results of measurements performed for specimens containing carbon nanotubes

decorated with Re nanoparticles indicate an improving structure of the carbon material. The intensity rate of D and G peaks for the output material compared to pure MWNCTs is lower (for the more advantageous second variant – by 0.256). In this case, the number of defects created during functionalisation in acids was most probably compensated due to high-temperature heating leading to specimen homogenisation by homogenising the graphene structure and removing other impurities.

4. Conclusions

It is a requirement in the present times to design and deliver materials on demand. Alignment with market requirements determines a need to design new or improved products meeting customer requirements. Much attention in material engineering is devoted to usable functions of materials, in particular by designing new nanocomposites with the desired structure and expected physiochemical properties. At present the different nanocomposites reinforced with various nanoparticles or other nanostructures [22-26] are very popular because of the enhanced mechanical, magnetic, optical or other properties. Furthermore, it was also prepared a variety of composites in which all the components are in nano-scale, as it is set forth in the article. A newly developed MWCNT-Re nanocomposite [12] was created in response to a demand for materials being active parts of various chemical and biological sensors.

The presented results of research show that carbon nanotubes were coated with rhenium nanoparticles by applying a high-temperature reduction reaction in the hydrogen atmosphere of HReO₄ acid and in an inert gas shield. The investigations performed are classified as basic investigations and serve to recognise thoroughly the physiochemical phenomena conditioning the potential modification of CNTs' surface with Re nanoparticles. The authors of the article are planning next research tasks serving to optimise the fabrication process and determine the effect of process parameters on the ultimate structure of the MWCNTs-Re nanocomposite. A series of investigations is also planned to recognise the electrical properties of newly created MWCNT-Re-type materials in the gas and liquid environment.

Acknowledgements

The works have been implemented within the framework of the ELCONANO project headed by Prof. A.D. Dobrzańska-Danikiewicz, funded by the Polish National Science Centre in the framework of the "OPUS" competitions. The project was awarded a subsidy under the decision DEC-2011/03/B/ST8/06070. Weronika Wolany and Dawid Cichocki are holders of scholarship from project "Scholarship and Internship Fund for the development of knowledge transfer in the region" co-financed by the European Union under the European Fund.

REFERENCES

- [1] S. Iijima, *Nature* 354, 56 (1991). DOI:10.1038/354056a0.
- [2] A. D. Dobrzańska-Danikiewicz, D. Cichocki, M. Pawlyta, D. Łukowiec, W. Wolany, *Phys. Status Solidi B* 251/12, 2420 (2014), DOI:10.1002/pssb.201451178.
- [3] J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adamc, *J. Mater. Chem.* 21, 15872 (2011). DOI:10.1039/C1JM12254A.
- [4] Y. Chen, Y. Zhang, Y. Hu, L. Kang, S. Zhang, H. Xie, D. Liu, Q. Zhao, Q. Li, J. Zhang, *Advanced Materials* 26/34, 5898 (2014). DOI: 10.1002/adma.201400431.
- [5] G. Trykowski, S. Biniak, L. Stobinski, B. Lesiak, *Acta Physica Polonica A* 118/3, 515 (2010).
- [6] S.R. Bakshi, D. Lahiri, A. Agarwal, *International Materials Reviews* 55/1, 41 (2010). DOI:10.1179/095066009X12572530170543.
- [7] A. D. Dobrzańska-Danikiewicz, D. Łukowiec, D. Cichocki, and W. Wolany, *Arch. Mater. Sci. Eng.* 61(2), 53 (2013).
- [8] V. Georgakilas, D. Gournis, V. Tzitzios, L. Pasquato, D. M. Guldie, M. Prato, *J. Mater. Chem.* 17, 2679 (2007). DOI: 10.1039/b700857k.
- [9] W. D. Zhang, W. H. Zhang, *J. Sens.* 2009, 160698 (2009). DOI: 10.1155/2009/160698.
- [10] Y. Wang, J.T.W. Yeow, *Journal of Sensors* 2009, 1 (2009). DOI:10.1155/2009/493904.
- [11] A.D Dobrzańska-Danikiewicz, D. Łukowiec, M. Pawlyta, T. Gawel, M. Procek, *Phys. Status Solidi B* 251/12, 2426 (2014). DOI: 10.1002/pssb.201451179.
- [12] Patent application no.407887, Polish Patent Office.
- [13] A.D Dobrzańska-Danikiewicz, W. Wolany, G. Benke,
- [14] Z. Rdzawski, *Phys. Status Solidi B* 251/12, 2485 (2014). DOI: 10.1002/pssb.201451360.
- [15] N. Claessens, F. Demoisson, T. Dufour, A. Mansour, A. Felten, J. Guillot, J.J. Pireaux, F. Reniers, *Nanotechnology* 21/38, 385603 (2010). DOI:10.1088/0957-4484/21/38/385603.
- [16] R. Mohan, A.M. Shanmugaraj, R. Sung Hun, *J Biomed Mater Res B Appl Biomater.* 96/1, 119-126 (2011). DOI:10.1002/jbm.b.31747.
- [17] A. D. Dobrzańska-Danikiewicz, D. Łukowiec, *Phys. Status Solidi B* 250/12, 2569 (2013). DOI:10.1002/pssb.201300083.
- [18] A.D Dobrzańska-Danikiewicz, M. Pawlyta, D. Łukowiec, *Advanced Materials Research* 939, 3 (2014). DOI: 10.4028/www.scientific.net/AMR.939.3.
- [19] L.A. Dobrzański, M. Pawlyta, A. Krztoń, B. Liszka, C.W. Tai, W. Kwaśny, *Acta Physica Polonica A* 118, 483 (2010).
- [20] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, *Carbon* 43, 1731 (2005). DOI:10.1016/j.carbon.2005.02.018.
- [21] S. Costa, E. Borowiak-Palen, M. Kruszyńska, A. Bachmatiuk, R. J. Kaleńczuk, *Materials Science-Poland* 26/2, 433 (2008).
- [22] M. Zdrojek, W. Gębicki, C. Jastrzębski, T. Melin, A. Huczko, *Solide State Phenomena* 99, 265 (2004). DOI: 10.4028/www.scientific.net/SSP.99-100.265.
- [23] M. Szutkowska, L. Jaworska, M. Rozmus, P. Klimczyk, M. Bucko, *Diamond composites with nanoceramic boride bonding phases, Archives of Materials Science and Engineering* 53/2, 85-91 (2012).
- [24] M. Szutkowska, M. Leonowicz, L.A. Ivanchenko, *Microstructure and Properties of Biogenic Hydroxyapatite Doped with Magnetite, Advances in Science and Technology* 49, 51-55 (2006).
- [25] L.A. Dobrzański, A. Mucha, *The influence of carbon nanotubes on the mechanical properties of nanocomposites, Materials Processing* 3/147, 179-183 (2012).
- [26] A. Kaczmarek-Pawelska, T. Klekiel, E. Krasicka-Cydzik, *Fluoride concentration effect on the anodic growth of self-aligned oxide nanotube array on Ti6Al7Nb alloy, Surface and Interface Analysis* 42/6-7, 510-514 (2010).

Received: 20 March 2015.

