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COMPARISON OF THE MWCNTs-Rh AND MWCNTs-Re CARBON-METAL NANOCOMPOSITES OBTAINED IN HIGH-TEMPERATURE

PORÓWNANIE WĘGLOWO-METALOWYCH NANOKOMPOZYTÓW MWCNTs-Rh I WCNTs-Re OTRZYMANÝCH METODĄ WYSOKOTEMPERATUROWĄ

Carbon-metal nanocomposites consisting of multiwalled carbon nanotubes coated with rhodium or rhenium nanoparticles by the high-temperature method were fabricated during the research undertaken. Multiwalled carbon nanotubes fabricated by Catalytic-Chemical Vapour Deposition (CCVD) were used in the investigations. Multiwalled carbon nanotubes functionalisation in acid or in a mixture of acids was applied to deposit rhodium or rhenium nanoparticles onto the surface of carbon nanotubes, and then the material was placed in a solution being a precursor of metallic nanoparticles. The material prepared was next subjected to high-temperature reduction in the atmosphere of argon and/or hydrogen to deposit rhodium or rhenium nanoparticles onto the surface of multiwalled carbon nanotubes. The investigations performed include, respectively: fabrication of a CNT-NPs (Carbon NanoTube-NanoParticles) nanocomposite material; the characterisation of the material produced including examination of the structure and morphology, and the assessment of rhodium and/or rhenium nanoparticles distribution on the surface of carbon nanotubes. Micro- and spectroscopy techniques were employed to characterise the structure of the nanocomposites obtained.

Keywords: nanocomposites, carbon nanotubes, CCVD, metal nanoparticles

W ramach wykonanych badań wytworzono węglowo-metalowe nanokompozyty składające się z wielościennych nanorurek węglowych pokrytych nanocząsteczkami rodu lub renu metodą wysokotemperaturową. W badaniach wykorzystano wielościenne nanorurki węglowe wytworzone metodą katalityczno-chemicznego osadzania z fazy gazowej (ang.: Chemical Catalytic Vapor Deposition – CCVD). W celu osadzenia nanocząsteczek rodu lub renu na powierzchni nanorurek węglowych zastosowano funkcjonalizację wielościennych nanorurek węglowych w kwasie lub mieszaninach kwasów, następnie materiał umieszczono w roztworze będącym prekursorem nanocząsteczek metalicznych. Przygotowany materiał poddano następnie redukcji wysokotemperaturowej w atmosferze argonu i/lub wodoru w celu osadzenia nanocząsteczek rodu lub renu na powierzchni wielościennych nanorurek węglowych. Wykonane badania obejmują kolejno: wytworzenie materiału nanokompozytowego typu CNT-NPs (ang.: Carbon NanoTube-NanoParticles), scharakteryzowanie wytworzonego materiału obejmujące badanie jego struktury i morfologii oraz ocenę rozmieszczenia nanocząsteczek rodu i/lub renu na powierzchni nanorurek węglowych. Dla scharakteryzowania struktury otrzymanych nanokompozytów zastosowano techniki mikro- i spektroskopowe.

1. Introduction

Carbon nanotubes, composed of cylindrically rolled graphene layers, are characterised by a large specific area, they are light, and also have very good mechanical, electric, heat and magnetic properties [1-3]. By enriching nanotubes chemically, it is possible to control their properties, which enables to use nanotubes as nanocomposites components [4-6].

Numerous types of composites have been developed whose reinforcing component are various nanoparticles [7] or nanotubes [8,9], e.g. carbon nanotube metal matrix composites

(CNT-MMC) [10], and also such where carbon nanotubes represent a scaffold for metallic nanoparticles. Carbon-metal CNT-NPs (Carbon NanoTube-NanoParticles) nanocomposites are especially interesting due to improved properties resulting from synergic interaction of two special forms of carbon and metal. The authors of this article are particularly interested in the optimisation of such materials' manufacturing processes and their practical application as an active element in sensors of chemical and biological substances [4,11-17].

The undertaken state-of-the-art reveals that methods exist of obtaining a nanocomposite consisting of carbon

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nanotubes and rhodium nanoparticles using plasma [17], chemical reduction [18] and electrodesposition [19]. The fabrication of a nanocomposite consisting of carbon nanotubes joined permanently with rhenium occurring in the form of singular nanocrystals or a nanolayer has been described in few publications to date [20-21]. This article depicts a custom method of fabricating nanocomposites consisting of carbon nanotubes joined permanently with rhodium or rhenium, occurring in the form of nanocrystals. The method elaborated is based on the high-temperature reduction of a precursor of selected noble metals.

This article presents and compares high-temperature fabrication methods of MWCNTs-Rh MWCNTs-Re nanocomposites, describes the fabricated materials by examining their structure and morphology and the arrangement and size of metal nanoparticles on the surface of carbon nanotubes. The following research techniques were employed to characterise the structure of the nanocomposites obtained: Scanning Transmission Electron Microscopy (STEM), Transmission Electron Microscopy (TEM), Energy Dispersion Spectrometer (EDS) and Raman spectroscopy.

2. Experimental studies

2.1 Materials

Multiwalled carbon nanotubes fabricated by Catalytic-Chemical Vapour Deposition (CCVD) were employed in the investigations to produce MWCNTs-Rh and MWCNTs-Re nanocomposites. Pristine MWCNTs, being an input material for nanocomposite fabrication, contained few impurities in the form of metallic catalyst and amorphous carbon nanoparticles. Fig. 1 presents a TEM image of pristine multiwalled carbon nanotubes before the process of decoration with rhodium or rhenium nanoparticles. Rhodium chloride (III), RhCl_3 , and rhenium acid (VII), HReO_4 were used as precursors in the decoration process of multiwalled carbon nanotubes with such nanoparticles.

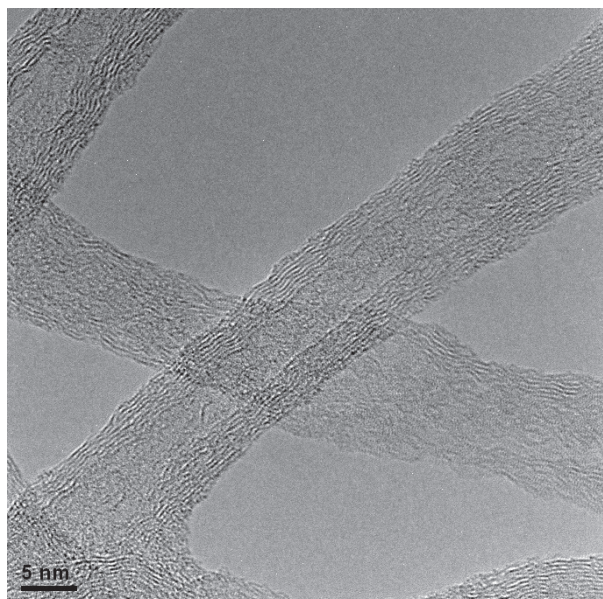


Fig. 1. TEM image of pristine MWCNTs being input material for MWCNTs-Rh and MWCNTs-Re nanocomposites fabrication

2.2 Synthesis of MWCNT-Rh and MWCNT-Re nanocomposites

In the first phase of MWCNTs-Rh nanocomposites synthesis, multiwalled carbon nanotubes were placed in a mixture of HNO_3 (concentration of 65%) and H_2SO_4 (concentration of 95%) acids at a rate of 1:3 and were subjected to a functionalisation process in order to produce function groups on the external surface of carbon nanotube, to which rhodium nanoparticles were attached in the next stage. Functionalisation was carried out using ultrasounds at an elevated temperature of 60°C for 2 hours, and the mixture was left covered without any interference for 24 hours. When the required time has lapsed, the mixture was filtered and the acid mixture was collected. In the second phase of synthesis with carbon material decoration with rhodium nanoparticles, the functionalised multiwalled carbon nanotubes were placed in an RhCl_3 solution, and the mixture was treated with ultrasounds for 2 hours and put aside without any interference for 24 hours. The actual process of carbon nanotubes decoration with rhodium nanoparticles was carried out in a high-temperature oven with a high-temperature reduction reaction of rhodium chloride solution (RhCl_3). The so prepared carbon-metallic material was placed in a quartz boat which was placed in a sample feeder. Once the temperature of the oven reached more than 800°C , a sample was introduced into the oven, and then the sample was subjected to heating at 850°C for 45 minutes in an argon atmosphere. After finishing high-temperature reduction, the sample was cooled down to room temperature, removed from the oven and subjected to microscopic and spectrometric investigations. The method of high-temperature fabrication of MWCNTs-Rh nanocomposites is subject to a patent claim [22].

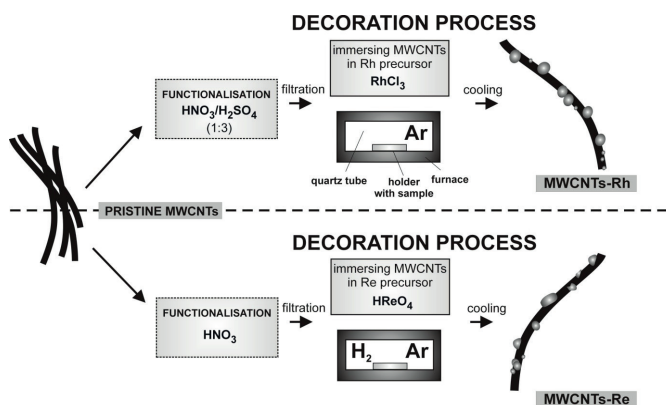


Fig. 2. Diagram of MWCNT-Rh and MWCNTs-Re fabrication process

The MWCNT-Re nanocomposite manufacturing process embraces several phases. Pristine carbon nanotubes placed in a beaker were flooded with nitric acid (V) (65%), were subjected to the activity of ultrasounds for 5 hours, and then filtered and rinsed several times with deionised water. The nanotube material was then placed in a rhenium precursor - HReO_4 (VII), aiding the process with ultrasounds for 1 hour, and then the mixture was put aside for 15 hours without any interference. Ultrasounds were again used shortly prior to the CNTs decoration process, and then a portion of the wet

material was placed in a quartz vessel. The reduction of the Re precursor with hydrogen took place in a heating oven at the temperature of 800°C. The flow of H₂ was decreased after 15 minutes of heating. The process was continued for 30 minutes, and then the sample was cooled to the ambient temperature and underwent examinations. The entire decoration process takes place in a protective atmosphere of argon. The method of high-temperature fabrication of MWCNTs-Rh nanocomposites is also subject to a patent claim [23]. The diagram presented in Fig. 2 presents the subsequent fabrication phases of MWCNTs-Rh and Re nanocomposites. Table 1 presents a comparative overview of a synthesis of MWCNTs-Rh and MWCNTs-Re nanocomposites.

2.3 Methodology

The carbon nanotubes and carbon-metal nanocomposites obtained were observed using a high-resolution electron scanning and transmission microscope. TEM images were made using an STEM TITAN 80-300 microscope by FEI fitted with an electron gun with XFEG field emission, a condenser Cs spherical aberration corrector, STEM scanning system, bright (BF) and dark field (DF) detectors, an HAADF (High Angle Annular Dark Field) detector, and an EDS spectrometer used for the determination of the chemical composition of the nanocomposites obtained. The exact imaging of the materials produced, whose constituent parts differ significantly in the atomic number *Z* (*Z* contrast), is possible by applying an HAADF detector in the examinations. The materials for transmission electron microscopy investigations are prepared by dispersing the nanocomposites obtained in ethanol using an ultrasound washer, and then by depositing them using a pipette with droplets onto a copper mesh. The material deposited as a droplet was dried with free air at the room temperature.

A level of defects of the attained carbon nanotubes' and carbon-metal nanocomposites' structure was examined using a Via Reflex Raman Spectrometer by Renishaw fitted with a confocal Research Grade microscope by Leica. Excitations were carried out with a line with the wavelength of $\lambda = 514$ nm of an ion-argon laser with the capacity of 50 mW, with a plasma filter for 514 nm. The measurements were recorded using a Long Working Distance (LWD) lens with magnification of twenty times. The materials for investigations using a Raman spectroscope were prepared by depositing the materials produced onto a glass substrate. The so prepared preparations were examined over the entire range of spectrum registration, i.e. 0 - 3500 cm⁻¹.

3. Results and discussion

3.1 Microscopic research results

As part of the undertaken microscope investigations of MWCNTs-Rh and MWCNTs-Re nanocomposites, observations were made in bright and dark field using an HAADF detector working in the STEM mode using a transmission electron microscope (TEM). When an HAADF detector is used, rhodium and rhenium nanoparticles are visible as lightly illuminating precipitates on the surface of dark grey nanotubes considering a large difference between the value of atomic numbers of elements forming part of the nanocomposite: carbon (*Z*=6), rhodium (*Z*=45), rhenium (*Z*=75).

Fig. 3 presents an MWCNTs-Rh nanotube consisting of carbon nanotubes together with rhodium nanoparticles permanently deposited on their surface, which are spherically shaped, and their diameter is between 3 and 7 nm. It was confirmed during microscope investigations of the MWCNTs-

TABLE 1
Comparative overview of functionalisation of MWCNTs-Rh and MWCNTs-Re nanocomposites obtained by the high-temperature method

| Decoration phase | Process description | MWCNTs-Rh | MWCNTs-Re |
|-------------------------------|---|--|---|
| 1. Functionalisation | Type of functionalisation | Covalent functionalisation, oxidisation | Covalent functionalisation, oxidisation |
| | Reagent type | HNO ₃ (65%)/H ₂ SO ₄ (95%) at a rate of 1:3 | HNO ₃ (65%) |
| | Duration of mechanically-assisted functionalisation | 2 hrs | 5 hrs |
| | Functionalisation aiding method | Ultrasounds | Ultrasounds |
| | Process temperature | 60°C | Room temperature |
| | Functionalisation time without interference | 24 hrs | 15 hrs |
| | Method of separation of nanotube material from medium | Vacuum filtration | Vacuum filtration |
| 2. High-temperature reduction | Time of material preheating in oven | None | 15 min. |
| | Time of proper heating of materials in oven | 45 min. | 30 min. |
| | Preheating temperature | None | 800°C |
| | Temperature of proper heating | 850°C | 800°C |
| | Gas atmosphere | Ar | H ₂ , Ar |

Re nanocomposite that the material consists of carbon nanotubes coated with Re nanoparticles. As compared to the MWCNTs-Rh nanocomposite, the shape of Re nanoparticles covering carbon nanotubes is more diverse, and the majority of nanoparticles is irregularly shaped (Fig. 4). The rhodium nanoparticles of the MWCNTs-Rh nanocomposite are irregularly distributed on the surface of carbon nanotubes, which is visible in Fig. 5, where carbon nanotubes are also observed not covered with rhodium nanoparticles and a difference in the size of the few nanoparticles (over 10 nm). Rhodium nanoparticles' agglomeration tendency was also noticed during the investigations. The clusters of nanoparticles visible during observations in the dark field as large bright fields were also identified in some areas for the MWCNTs-Re nanocomposite (Fig. 6). The size distribution of rhodium nanoparticles on the MWCNTs-Rh nanocomposite is presented in Fig. 7, and the smallest observed nanoparticle is ~ 2 nm, whilst the largest one ~ 13.5 nm. Rhodium nanoparticles sized 4 and 6 nm occur most often.

A more homogenous material was achieved as compared to the previous results of investigations [14] 20 of the MWCNTs-Re nanocomposite providing another method of MWCNTs functionalisation, and Re nanoparticles are smaller. The distribution size of the nanoparticles is shown in Fig. 8. Rhenium nanoparticles sized 4 and 6 nm occur most often.

It was also observed during a microscopic analysis of the MWCNTs-Re nanocomposite in the dark field that carbon nanotubes are covered across the entire surface with rhenium crystals with the diameter of much less than 0.5 nm, which are almost non-identifiable in the bright field (Fig. 9). It is concluded at this stage of research works that the functionalisation method is of key importance for the morphology of MWCNTs-Re nanocomposites. Good dispersion of carbon nanotubes in HNO_3 acid and in a metal precursor is achieved by employing ultrasound mixing, hence better contact of the medium with the surface of nanotubes is ensured. The relatively uniform distribution of rhenium nanocrystals is consequently seen after a reduction reaction, and precipitates are finer.

The experiments performed indicate that agglomeration, differences in the shape and size of rhodium and rhenium nanoparticles, are dependent on the following factors: the functionalisation process execution method, a concentration of a metal precursor solution, and heating time and temperature of a sample in an oven.

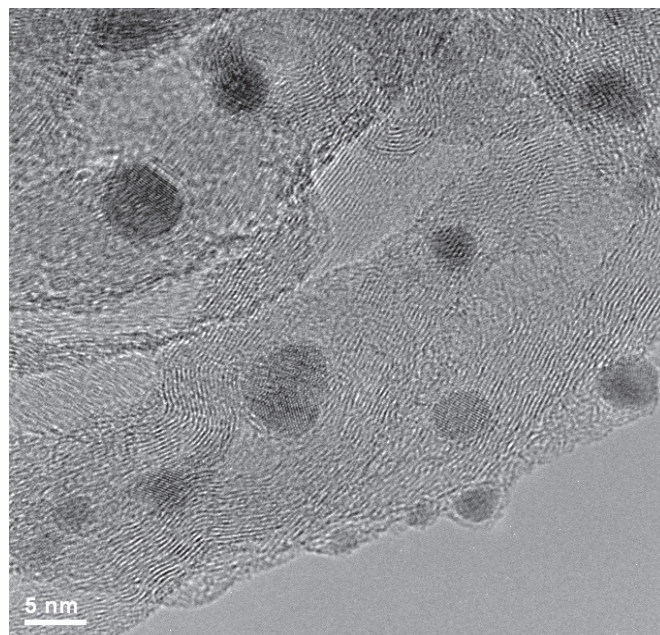


Fig.3. TEM image of MWCNTs-Rh nanocomposite

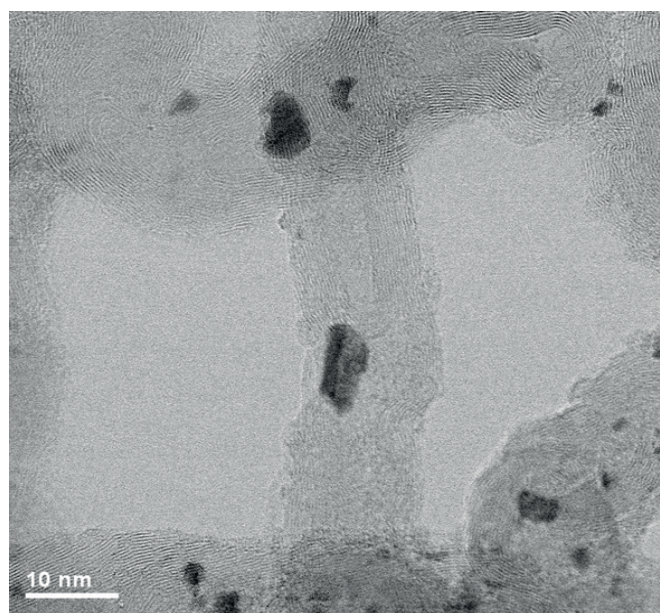


Fig.4. TEM image of MWCNTs-Re nanocomposite

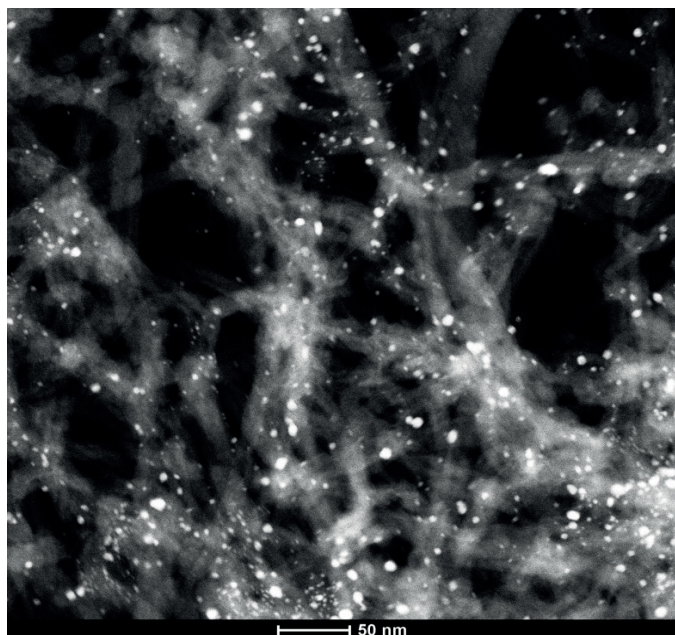


Fig. 5. STEM image of MWCNTs-Rh nanocomposite made using HAADF detector

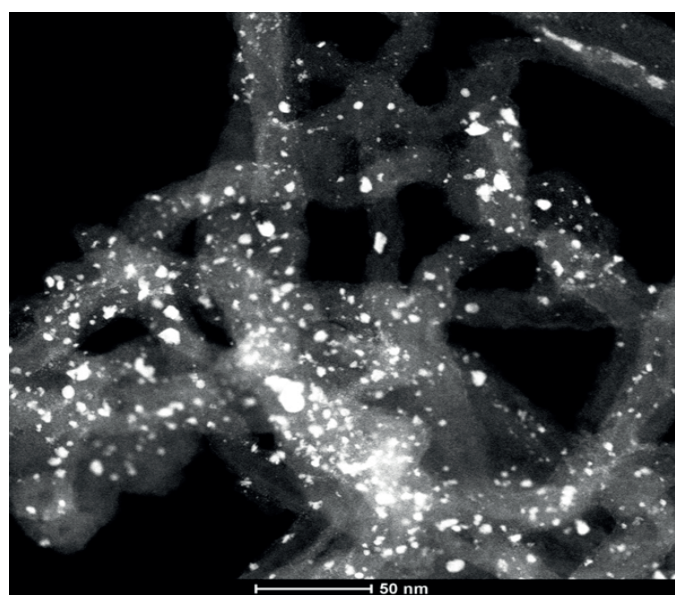


Fig. 6. STEM image of MWCNTs-Re nanocomposite made using HAADF detector

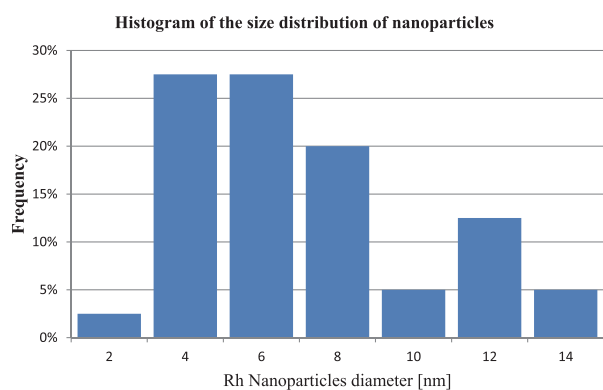


Fig. 7. Histogram of Rh nanoparticles size distribution in MWCNTs-Rh nanocomposite

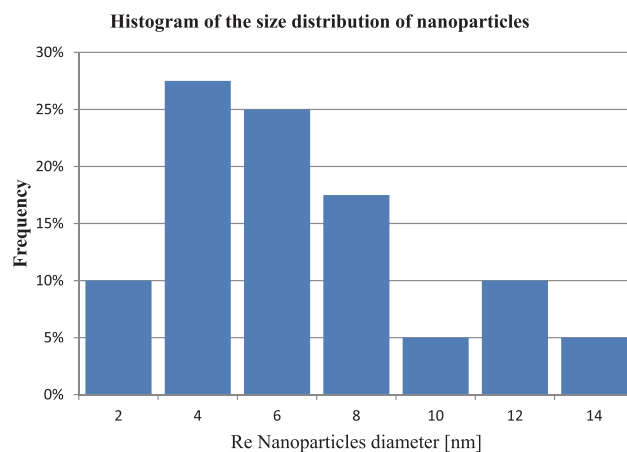


Fig. 8. Histogram of Re nanoparticles size distribution in MWCNTs-Rh nanocomposite

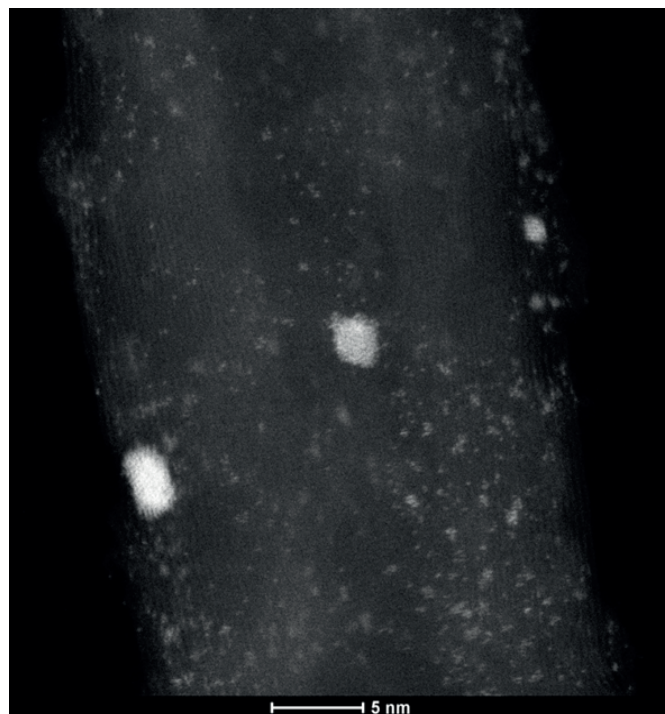


Fig. 9. HRTEM image of carbon nanotube decorated with Re, with visible particles with the diameter of several Å

3.2 Spectroscopy research results

Spectroscopy research was carried out with two specialist instruments. A qualitative analysis of chemical composition from the microarea of carbon-metal preparations was performed with Energy Dispersive Spectroscopy (EDS) by EDAX. The defects degree of the structure of carbon nanotubes decorated with rhodium and rhenium against the defects degree of pristine carbon nanotubes was determined using a Via Reflex Raman Spectrometer by Renishaw.

The elements forming the given material were identified through an EDS analysis based on a radiation energy value recorded by the instrument expressed with [keV], which is characteristic for each element. A qualitative analysis of chemical composition from the microarea for the both

nanocomposites was made as part of the experiments, the results of which are shown, respectively, in Fig. 10 and 11. A spectral qualitative analysis of chemical composition shows that the composition of the investigated preparation contains Rh, C and Cu as well as Re, C and Cu, where C is associated to the presence of carbon nanotubes, while the presence of Cu is explained by a copper mesh used at the stage of preparation, onto which the studied nanocomposites were deposited.

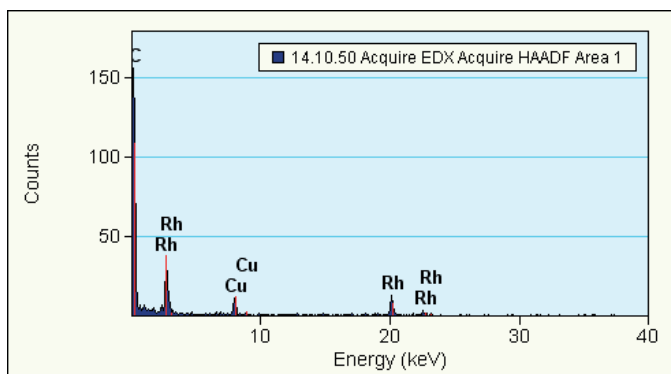


Fig. 10. Qualitative analysis of chemical composition from microarea of MWCNTs-Rh nanocomposite made with the EDS method

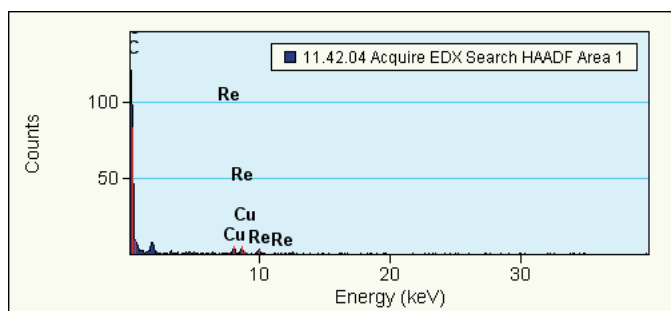
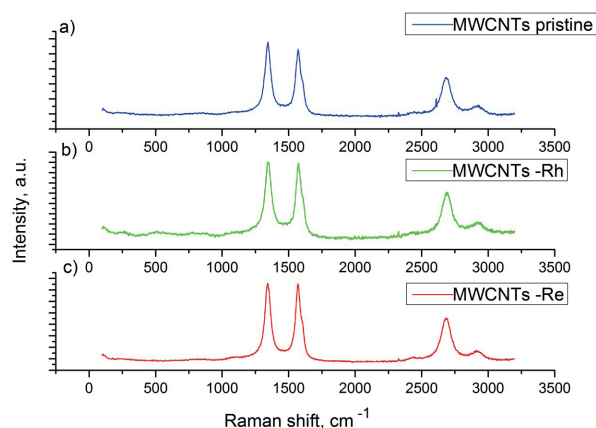


Fig. 11. Qualitative analysis of chemical composition from microarea of MWCNTs-Re nanocomposite made with the EDS method

The investigations held with a Raman spectrometer have indicated the occurrence of bands characteristic for multiwalled carbon nanotubes for nanotubes unmodified and decorated with rhodium and rhenium nanoparticles. A spectrum of pristine carbon nanotubes (Fig. 12a) is characterised by the occurrence of the following bands: *D* (1344 cm^{-1}), *G* (1570 cm^{-1}) and *G'* (2676 cm^{-1}). The following bands exist for the spectrum of nanotubes decorated with rhodium (Fig. 12b): *D* (1343 cm^{-1}), *G* (1573 cm^{-1}) and *G'* (2685 cm^{-1}). A spectrum of carbon nanotubes decorated with rhenium (Fig. 12c) is characterised by the presence of the following bands: *D* (1342 cm^{-1}),

G (1571 cm^{-1}) and *G'* (2684 cm^{-1}). Table 2 presents a summary of numerical values of all the characteristic spectrum bands recorded for the identified nanotubes and MWCNTs-Rh and MWCNTs-Re nanocomposites. The intensity value of the *D* band recorded for unmodified nanotubes is higher than the intensity of *G* band, which can be correlated with the presence of small impurities in the input material. Such a theory is confirmed in TEM observations which have revealed small amounts of amorphous carbon and/or residual catalyst particles. It was also observed that a Raman spectrum of an MWCNTs-Rh nanocomposite, in terms of the shape and location of its characteristics bands, i.e. *D*, *G* and *G'*, and also in terms of the intensity of *D* to *G* (I_D/I_G) bands, determining a change in the geometry of carbon nanotubes, is very similar to the spectrum of pristine MWCNTs, signifying a favourable effect of high temperature (over 800°C) and the improved quality of the material during a nanotubes decoration process in an oven. Functionalisation, starting a synthesis of CNTs-NPs nanocomposites, results in a decreased quality of the material, as described in the authors' earlier work [24].

It was found based on a comparative analysis of the spectra recorded for the unmodified MWCNTs and for the MWCNTs-Re nanocomposite that the presented nanocomposite is characterised by a higher intensity of *D*, *G* and *G'* bands. The data presented in table 2 for the MWCNTs nanocomposite show that the I_D/I_G 0.1 indicator is decreasing. Heating at an elevated temperature (800-1600°C) is directly influencing the order of carbon nanotubes' graphene structure and removes carbon contaminants formed at the stage of synthesis. Considering that heating time was only 45 minutes, the decrease of the intensity rate of *D* to *G* by 0.1 is considered a positive result.



Rys.10. Raman spectra: a) for pristine multi-walled carbon nanotubes, b) of multi-walled carbon nanotubes with rhodium nanoparticles, c) of multi-walled carbon nanotubes with rhenium nanoparticles.

TABLE 2

Comparative analysis of relative intensities of *D*, *G*, *G'* bands and their position on Raman spectra of unmodified carbon nanotubes and carbon nanotubes containing rhodium and rhenium nanoparticles.

| Materials | Ramanshift [cm^{-1}] | | | Intensity | | | ID/IG |
|-------------------------|---------------------------------|------|------|-----------|------|------|-------|
| | D | G | G' | D | G | G' | |
| Pristine MWCNTs | 1344 | 1570 | 2676 | 2382 | 2149 | 1201 | 1,11 |
| MWCNTs-Rh nanocomposite | 1343 | 1573 | 2685 | 1406 | 1378 | 807 | 1,02 |
| MWCNTs-Re nanocomposite | 1342 | 1571 | 2684 | 3285 | 3259 | 1758 | 1,01 |

4. Conclusions

The intensive development of nanotechnology is mainly caused by the demand for new materials with excellent properties. The article presents a comparative analysis of microscope and spectroscopy examinations of two types of carbon-metal nanocomposites. The specificity of the two elements, i.e. rhodium and rhenium, was decisive for selecting a method of manufacturing the presented nanocomposites. It was found, based on a comparative analysis of the structure of MWCNTs-Rh and MWCNTs-Re nanocomposites, that despite applying the same start material and similar manufacturing methods - the nanocomposites have a different morphology. Such characteristics as size, disparities in the particles size, their dimensions and arrangement method on the surface of carbon nanotubes, differ. It is therefore concluded that CNTs' functionalisation method, a reduction method of precursors of the selected noble elements have a significant effect on the morphology of the compared carbon-metal nanocomposites. The authors of the article are planning next research tasks serving to optimise a fabrication process of MWCNTs-Rh and MWCNTs-Re nanocomposites. It is necessary to substantiate the effect of parameters of the manufacturing process for such a type of nanostructural materials to achieve results repeatability and to fabricate a material with a homogenous structure within the whole volume. The principal objective of the authors is to examine relationships between the structure and properties of the fabricated engineering materials. CNTs' functionalisation is leading to the creation of completely new nanostructural composites combining unique properties of carbon nanotubes with other materials, including nanoparticles of noble metals. Investigations into the nanocomposites described will contribute to designing innovative sensors in which the newly created nanocomposites constitute an active element of sensors. The literature review undertaken allows to conclude that currently there is a high interest in such materials and chemical sensors and biosensors, for this reason it is appropriate to pursue new research in this field and to create innovative solutions.

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