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Nanocomposites consisting of SWCNTs/ DWCNTs decorated with Re nanoparticles

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ABSTRACT

Purpose: The main aim of this work is to present a method for manufacturing nanocomposite consisting of single and double-walled carbon nanotubes and rhenium nanoparticles. A decoration process was started with functionalization of CNTs, then placed CNTs in a medium containing rhenium precursors, inserted it in quartz vessel and finally heating wet material in the atmosphere of H_2 and in the shield of inert gas Ar.

Design/methodology/approach: The microscope examinations of single- and double walled carbon nanotubes decorated with Re were carried out with the TEM and STEM mode using an HAADF detector. An energy dispersive spectroscope (EDS) was employed to determine chemical composition of the material.

Findings: This paper shows the fabrications of SWCNTs/DWCNTs–Re hybrid nanostructures. The researches has found that rhenium nanocrystals are located in the outer walls and in the core of the carbon nanotubes.

Research limitations/implications: The development of CNTs decorated with metal nanoparticles has concerned intensive interest in the last decade because of their outstanding sensing properties. CNTs-based gas sensors are attractive because of their small size, low weight, low power consumption, ultra sensitivity (high and prompt response).

Originality/value: Rhenium is a heavy metals, possesses very high melting and boiling point, good electrical and thermal properties, and is used in the developing industries such as space, electrical, petrochemicals, chemicals. Searching for new uses of Re, including as a component of nanocomposites composed of CNTs is purposeful and interesting.

Keywords: Rhenium; Nanoparticles; Single wall carbon nanotubes; Double wall carbon nanotubes; Nanocomposites

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MATERIALS

1. Introduction

Nanotechnology is a rapidly developing field of science and technology these days. There are many definitions of nanotechnology, however, the overall related topic consists generally of research into the methods of producing and developing modern materials and devices using such materials. There has been considerable interest in those unusual nanomaterials since 1991 when Professor S. Iijima described in detail the structure of carbon nanotubes [1]. Carbon Nanotubes (CNTs) are materials consisting of cylindrically rolled layers of graphene with a ratio between length and diameter in extreme cases being 106. In case of a single or double sheet of graphene, a nanotube is referred to, respectively, as a single-walled (Single-Walled Carbon Nanotubes - SWCNTs) or double-walled (Double-Walled Carbon Nanotubes - DWCNTs). Three or more co-axially arranged layers, whose distance between each other is 0.34 nm, represent a Multi-Walled Carbon Nanotube (MWCNT). Carbon nanotubes are characterised by a large specific area, they are light (density of approx. 1.4 g/cm^3), and also have very good mechanical, electric, heat and magnetic properties. It was found, however, that CNTs are materials with strongly hydrophobic character, do not in polar and non-polar solvents, and exhibit small reactivity [2-4]. A number of functionalisation methods have been established to broaden application possibilities for CNTs, dissolve facilitating their manipulation, allowing their dispersion in solvents and increasing their reactivity. It is justified to use CNTs as the components of nanocomposites due to their unique physiochemical properties. The research and development works associated with the deposition of nanoparticles of metals and semi-conductors onto the surface of carbon nanotubes have enjoyed strong interest [5-7]. The ability to combine carbon nanotubes with other particles, including Pt, Pd, Rh and Re, in a planned and controlled manner, in which the authors are interested, is enhancing the application potential of the materials considerably [8-12].

An interesting issue is the method of fabricating MWCNTs-Re nanocomposites, which is new in materials engineering, mainly by using rhenium nanoparticles as a nanocomposite component. Rhenium is a platinum group noble metal resistant to high temperatures, and currently is most often used as a component of superalloys applied in the space and aviation industry, as its small addition significantly improves hardness, corrosion resistance and strength of these alloys. It is also employed as a catalyst for producing high-octane fuels. It is also used in electrical devices, in particular in electrodes, electromagnets, contacts. It is highly desired to widen application options of rhenium [13,14].

2. Experimental

2.1. Materials

Commercial single-walled and double-walled carbon nanotubes were used for the experiments (Fig. 1), whose characteristics are presented in Table 1. The presence of impurities in the form of amorphous carbon surrounding the carbon nanotubes and single triple-walled nanotubes were observed during the examinations. $HReO_4$ was used as a metal pre-cursor in the process of depositing Re nanoparticles onto carbon nanotubes.

Table 1.
Characteristics of the materials for the examinations

Rhenium		CNTs	
Group, period	7, 6	Materials	SWCNTs/DWCNTs 99%
Atomic number	75	Outher diameter	1-4 nm
Melting point	3180°C	Lenght	< 30 μm
Boiling point	5627°C	Source	Commercial (HDPlas)
Density	21.04 g/cm^3	Fabrication method	CCVD, plasma: Ar

By applying the covalent functionalisation of carbon nanotubes, this material can be decorated with rhenium nanoparticles. The function groups created on the surface of the CNTs represent the nucleus centres of Re crystals. Single- and double-walled carbon nanotubes were functionalised in HNO_3 by aiding the process with ultrasounds for 3 hours, and then the mixture was left for 24 without any interference. The mixture was then filtered with a vacuum filtration set. The carbon nanotubes were next placed in rhenium acid $HReO_4$ (VII), the process was aided with ultrasounds for 3 hours, and were put aside for 48 hours. A portion of the wet material was then placed in a quartz vessel and pre-heated at the temperature of 330°C for 15 minutes in the atmosphere of hydrogen and in an argon shield, and then for 30 minutes at 800°C. The process conditions applied are advantageous for obtaining metallic rhenium.

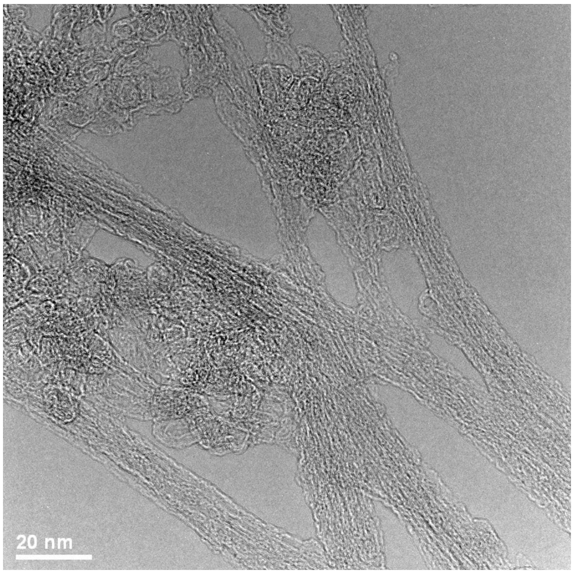

Fig. 1. Pure single- and double-walled carbon nanotubes intended for further experiments

2.2. Methodology

The observations of the structure of the nanocomposite determined as SWCNTs/DWCNTs-Re were carried out using the transmission electron microscope STEM TITAN 80-300 by FEI with the point resolution of ≤ 0.200 nm. The microscope is fitted, among others, with an electron gun with FEG field emission, a condenser spherical aberration corrector, STEM scanning system, bright and dark field detectors, HAADF (High Angle Annular Dark Field), and an EDS spectrometer. An HAADF detector running in the STEM mode was used to assess the morphology of the examined nanocomposite. A preparation for transmission electron microscopy investigations was prepared in a standard manner by applying carbon materials with droplets, previously dispergated in ethanol, onto a copper mesh designed for HRTEM tests.

2.3. Results and discussion

It was concluded that pure carbon nanotubes subjected to experiments occur as concentrated clusters (of several to more than ten nanotubes), as so-called bundles, which is visible on TEM images (Fig. 1). It was also pointed out that single-walled nanotubes after the functionalisation process, if carboxyl groups exist on their surface, exhibit even a stronger tendency to join in bundles, as reported by the literature [15]. Such a property makes it difficult to obtain a homogenous material in the form of single-walled and double-walled carbon nanotubes homogenously decorated with rhenium. During the observations of the nanocomposite in HRTEM it was observed that some nanotubes posses 3 walls.

Examinations in the bright field and in dark field of a transmission electron microscope (TEM) were undertaken to characterise the structure of the nanocomposite achieved. The outcomes show that the bonded carbon nanotubes are also the original material (Fig. 2), and it is hard to isolate single nanotubes. It was found that single- and double-walled carbon nanotubes after the decoration process are permanently coated with small rhenium nanoparticles. The morphology of the so obtained nanocomposite is very diversified and interesting. Rhenium nanoparticles are mostly spherically shaped. Disparities in the diameter of Re crystals are very high though, and their diameter is usually between 1 to 10 nm. Fig. 2 shows nanoparticles occurring as individual precipitates with the diameter of below 1 nm. Figure 3 presents a much larger oval Re nanocrystal situated inside a double-walled carbon nanotube whose diameter measured along the longer axis of symmetry is 4.5 nm, and along the shorter one is 3 nm.

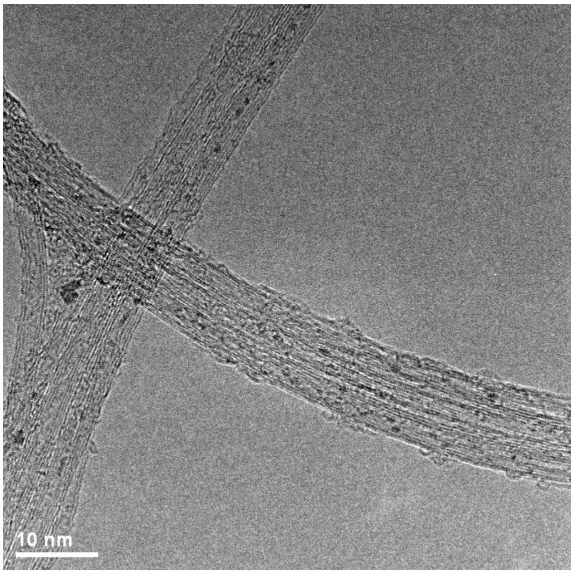

Fig. 2. SWCNTs/DWCNTs-Re nanocomposite; observation in bright field

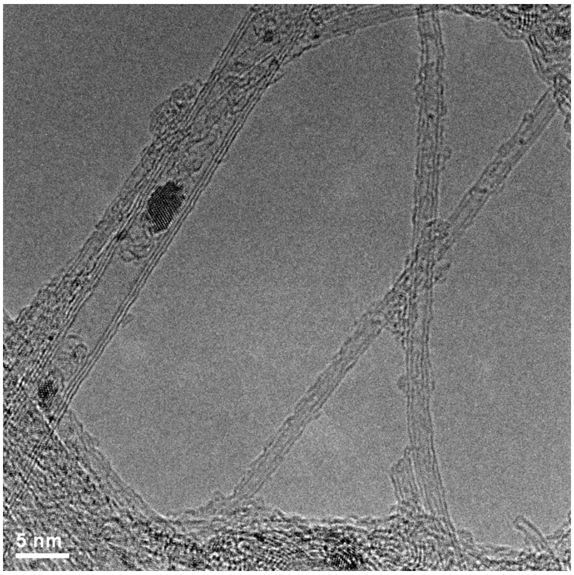

Fig. 3. Re nanoparticle inside a carbon nanotube

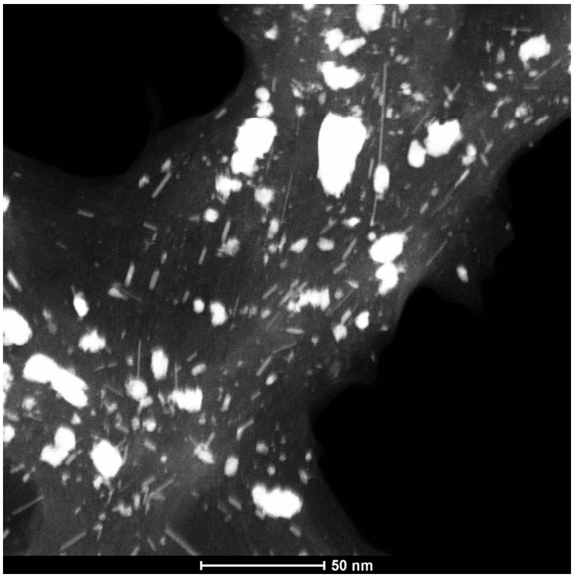

Fig. 4. Bundled SWCNTs/DWCNTs-Re nanomaterial; observation in dark field

A tendency is noticeable, however, of larger clusters of Re, which can be observed in Fig. 4. The specificity of the process prevents the use of mechanical assistance for the nanocomposite fabrication process (e.g. with ultrasounds, magnetic stirrer), hence rhenium nanoparticles tend to agglomerate. Moreover, nanotubes were also identified which were not coated with Re nanoparticles, which probably means that rhenium acid had limited access to the surface of some carbon nanotubes.

It is interesting that numerous carbon nanotubes decorated with rhenium occurring as nanowires were identified (Fig. 4). Nanowires are an interesting nanostructures [16,17]. Often, short nanowires are defined as nanorods. By terming a nanomaterial as a nanowire, the authors mean an object with the ratio of length to diameter of > 3.

The influence of functionalisation on the structure of carbon nanotubes, also in strong oxidising acids, has been already studied [19-23]. It was stated that in many cases, when single-walled nanotubes were subjected to the activity of, e.g. HNO_3, the nanotubes are opening and structural defects are formed. Conditions then exist in which a precursor (in the liquid form for the analysed process) gets inside carbon nanotubes due to the activity of capillary forces and is reduced in carbon nanotubes channels creating nanowires. An HAADF detector was used for better contrast. This type of studies is adequate for materials the components of which are strongly differing in their atomic number (so-called Z contrast), Z = 6 for carbon and Z = 75 for rhenium.

All Re precipitates are clearly visible in the dark field as light precipitates. The chemical composition of the presented SWCNTs/DWCNTs-Re nanocomposite, including the presence of rhenium in the sample, was confirmed with an Energy Dispersive Spectroscope (EDS). Figure 5 shows the results of the examination with the analysed area marked.

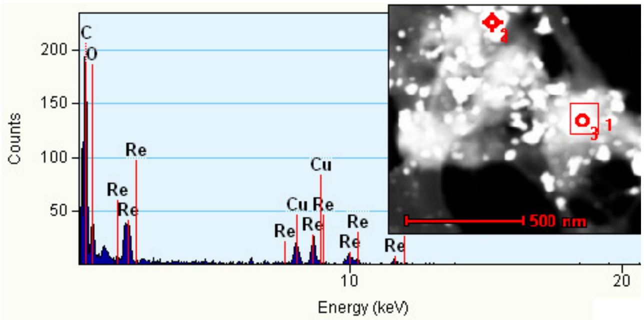

Fig. 5. Results of qualitative analysis of chemical composition of SWCNTs/DWCNTs-Re nanocomposite performed with EDS

3. Conclusions

The work presents a newly developed SWCNTs/DWCNTs-Re carbon material. Nanocomposites comprised of carbon nanotubes and rhenium nanoparticles are an interesting topic. The method of manufacturing this type of materials is simple and effective, however, the material is not homogenous within its entire volume. The last step of the manufacturing process of CNTs-Re nanocomposites provides that a wet carbon material is placed in a specially designed quartz vessel. A process of $HReO_4$ reduction with H_2 takes place in an oven then and is not assisted in any way. This leads to formation of large rhenium agglomerations and hinders to achieve a material with a homogenous structure. For this reason, research work is under way to find the optimum process parameters which will consequently allow to achieve a high-quality material homogenous within its entire volume. It was noticed on the basis of the previous works' results that nanocomposites consisting of multi-walled nanotubes covered with rhenium are easier to synthesise. This can be substantiated by the fact that multi-walled carbon nanotubes do not create so strongly connected bundles, therefore a metal precursor can freely reach the surface of nanotubes and can be reduced by creating Re nanocrystals. The area of future potential applications of the nanocomposites presented encompass, in particular, the active surface of chemical and biochemical sensors, elements of fuel cells and an application as a catalyst.

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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