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The modern approach to manufacturing of carbon-rhenium nanocomposites

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ABSTRACT

Purpose: The aim of the paper is to present the high-temperature method of producing MWCNTs-Re nanocomposites, the selection of satisfactory production conditions and the presentation of the results of microscopic and spectroscopic studies of nanocomposites produced by this method.

Design/methodology/approach: Two methods of manufacturing carbon-rhenium nanocomposites were tested: ineffective chemical synthesis and high-temperature reduction using H_2, which was proven successful and allowed the production of nanocomposites with the expected properties. The received nanocomposites were investigated using Transmission Electron Microscope (TEM), and Scanning Electron Microscope (SEM), as well as were subjected to spectroscopic examination.

Findings: The article presents three steps of MWCNTs-Re nanocomposites fabrication using the high-temperature method, functionalization, impregnation and reduction. As part of own work, satisfactory conditions for producing those nanocomposites using a materials science and heuristic analysis were selected.

Research limitations/implications: The proposed high-temperature method allows to join rhenium nanoparticles with MWCNTs permanently. It is reasonable to test in the future whether the method is also effective for other carbon nanomaterials and/or nanoparticles of other metals.

Practical implications: MWCNTs-Re nanocomposites can be used as sensors of gases that are harmful to the environment. It was also confirmed that the MWCNTs-Re_4 nanocomposite has catalytic properties.

Originality/value: The paper presents a modern approach to the manufacturing of MWCNTs-Re nanocomposites, which assumes the use of a high-temperature furnace to heat the material in a hydrogen atmosphere.

Keywords: Rhenium, MWCNTs, Nanocomposites, High-temperature method, SEM/TEM

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MANUFACTURING AND PROCESSING

1. Introduction

Over the past decade, carbon-metallic nanocomposites have been intensively researched in many scientific centres around the world due to their possible wide application in areas such as chemical sensing, catalysis, diagnostics and medicine, energy storage as well as environmental engineering. A review of the literature shows that there are many reports on carbon-metallic nanocomposites containing nanoparticles of metals such as Au [1], Ag [2], Pt [3], Cu [4], Pd [5], Co [6], Rh [7], Ni [8], Al [9]. The literature describes examples of obtaining rhenium on a nanometric scale in such forms as nanoparticles [10,11], nanowires [12] and bimetals [13]. Like the other metals mentioned, nanocrystalline rhenium can be permanently joined with carbon nanomaterials, thus creating nanocomposites. However, the state-of-the-art indicates that until today information concerning the use of nanocrystalline rhenium as a component of carbon-metallic nanocomposites is limited to rather occasional publications. A research group headed by Zhang have been received materials consisting of single-walled carbon nanotubes (SWCNTs), the cores of which were filled with Re nanocrystals [14]. Inside the SWCNTs cores, it is also possible to place ultrathin rhenium disulfide (ReS_2) nanoribbons [15]. Interesting results of investigations concerning the fabrication of multi-walled carbon nanotubes (MWCNTs) decorated with Re using the CVD method were published by a Russian group of scientists [16]. Efforts were also made to develop berry-shaped nanoparticle clusters (NPCs) in which Re is combined with amorphous carbon (a-C) and/or MWCNTs [17]. Experiments were carried out involving the support of ultra-small rhenium clusters consisting of 2-13 Re atoms on graphene [18]. A team of scientists headed by Veerakumar developed rhenium nanoparticles decorated on activated carbon derived from the biomass raw materials cardamom pods [19].

Moreover, this research team elaborated on nanocomposites useful for diagnostic applications containing other metals besides rhenium and carbon, such as platinum [20] or ruthenium [21]. Own research in the analysed field [22,23] concerned research and description of the structure of carbon-metallic nanocomposites consisting of nanostructured rhenium permanently joined with carbon nanomaterials in the form of single-, double- or multi-walled carbon nanotubes as well as single-walled carbon nanohorns (SWCNHs). This paper presents the research results on nanocomposites consisting of MWCNTs decorated with rhenium nanoparticles selected from a wider set of our experiments.

2. Materials and research methodology

MWCNTs were produced using EasyTube®2000 system by First Nano. The device is used for Catalytic Chemical Vapor Deposition (CCVD). During the CCVD process, ethylene is thermally decomposed. It is a carbon source that ensures the growth of carbon nanotubes. The other process gases are hydrogen and argon. The EasyTube®2000 system requires using a catalyst, which is iron deposited on a silicon wafer [24,25]. $HReO_4$ and optionally NH_4HReO_4 were used as the rhenium source during the out carried experiments. The morphology of nanocomposite materials using the SEM Supra 35 Scanning Electron Microscope by Carl Zeiss was examined. High resolution during imaging of the examined specimens was obtained thanks to the use of the In-lens detector. The microscopic observations enabling the obtaining of high-resolution images of the structure of the tested materials on a nanometric scale were made using the scanning and transmission electron microscope STEM TITAN 80-300 by FEI. The microscope has Bright Field (BF) and Dark Field (DF) and the High Angle Annular Dark Field (HAADF) detector. Energy Dispersive Spectroscopy (EDS) was used to determine the qualitative chemical composition of the newly produced nanocomposites. For this purpose, the EDS analytical attachment for the STEM microscope was used.

3. Effective high-temperature method of MWCNTs-Re nanocomposites manufacturing

Initial research included an attempt to produce MWCNTs-Re nanocomposite using a two-step indirect method, including covalent functionalization of carbon nanotubes and covering them with Re nanoparticles by chemical synthesis. The conducted experiments indicate that applying the method for fabricating MWCNTs-Re nanocomposites is ineffective. Therefore, it was excluded from subsequent experiments.

MWCNTs-Re nanocomposites can be effectively manufactured using the high-temperature method, which is the subject of our own patent [26]. It assumes the use of a high-temperature furnace to heat the material in a hydrogen atmosphere. In order to select satisfactory manufacturing conditions for MWCNTs-Re nanocomposites, three series of experiments were performed. Table 1 includes ten different variants of the manufacturing conditions.

Table 1.
Optional manufacturing conditions of MWCNTs-Re nanocomposites by the high-temperature method

Material sign	Functionalization time, h	Rhenium precursor	Impregnation time, h	Material wetness
MWCNTs-Re_1	5	$HReO_4$	1	wet
MWCNTs-Re_2	5	$HReO_4$	1	dry
MWCNTs-Re_3	5	$HReO_4$	2	wet
MWCNTs-Re_4	5	$HReO_4$	2	dry
MWCNTs-Re_5	5	NH_4ReO_4	1	wet
MWCNTs-Re_6	5	NH_4ReO_4	1	dry
MWCNTs-Re_7	0	$HReO_4$	3	dry
MWCNTs-Re_8	1	$HReO_4$	3	dry
MWCNTs-Re_9	3	$HReO_4$	3	dry
MWCNTs-Re_10	5	$HReO_4$	3	dry

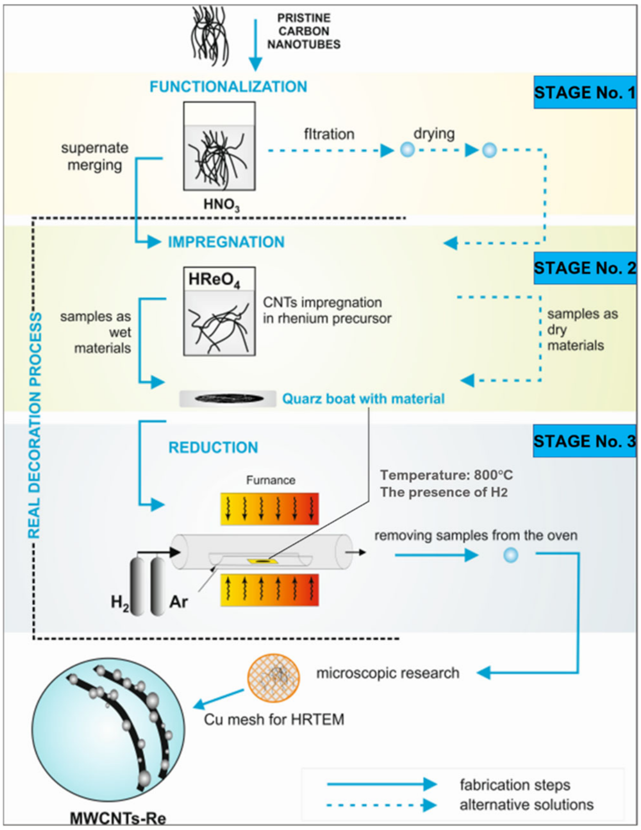

Fig. 1. The process diagram of MWCNTs-Re nanocomposites manufacturing by the high-temperature method (based on [27])

The high-temperature method includes three stages (Fig. 1). Stage No. 1 is the functionalization of pristine carbon nanotubes. Carbon nanotubes are oxidized in nitric acid 65% (V); as a result of that, functional groups – COOH, = CO and/or – OH appear on their surface. They are the sites for the nucleation of rhenium nanocrystals. Stage No. 2 is impregnation, placing the nanotubes in a medium containing rhenium precursor ($HReO_4$ or NH_4HReO_4). Stage No. 3 is a reduction leading to the permanent deposition of rhenium nanocrystals on carbon nanotubes. The material is heated in the furnace's working chamber in a special quartz boat. It ensures a proper supply of process gases and effective deposition of Re on carbon nanotubes.

4. Selection of satisfactory manufacturing conditions

In order to select satisfactory manufacturing conditions MWCNTs-Re nanocomposites, a materials science and heuristic analysis was performed. Each material fabricated under the manufacturing conditions specified in Table 1 was assessed, taking into account the obtained results of microscopic and spectroscopic examinations. During the assessment, the universal scale of relative states was used, where 1 is the minimum and 10 is the maximum.

Two groups of criteria were adopted to define the attractiveness and potential of the analysis subject. Each detailed criteria has been assigned weights that define their importance throughout the assessment process. The weights of the detailed criteria are given below in parentheses. The detailed criteria for assessing attractiveness (A) are as follows: [A1] Homogeneous dispersion of Re nanoparticles (0.4); [A2] Relatively narrow diameter distribution of Re nanoparticles (0.2); [A3] No tendency to agglomerate Re nanoparticles (0.2); [A4] Purity and slight damage of carbon nanotubes (0.2). The detailed criteria for assessing potential (P) are as follows: [P1] Short total ultrasound treatment time (0.2); [P2] Relevance of Re precursor selection (0.2); [P3] Homogeneity of the obtained microscopic results (0.2); [P4] Possibility of practical application (0.4). Each nanocomposite was assessed according to the above-mentioned criteria, giving scores from 1 (min) to 10 (max).

Table 2.
The results of a material science and heuristic analysis of the attractiveness and potential of MWCNTs-Re nanocomposites fabricated under various manufacturing conditions (based on [27])

Material sign	Attractiveness assessment				Weighted average (A)	Potential				Weighted average (P)
	A1	A2	A3	A4		P1	P2	P3	P4	
MWCNTs-Re_1	1.2	0.2	0.6	1.0	3.0	1.0	1.6	1.4	2.0	6.0
MWCNTs-Re_2	1.2	1.0	1.4	1.0	4.6	1.0	1.6	1.4	2.4	6.4
MWCNTs-Re_3	2.4	0.6	0.2	1.4	4.6	0.8	1.8	1.4	1.6	5.6
MWCNTs-Re_4	3.6	1.8	1.6	1.6	8.6	0.8	1.8	1.8	3.6	8.0
MWCNTs-Re_5	2.0	0.8	0.6	1.8	5.2	1.0	1.6	1.8	2.0	6.4
MWCNTs-Re_6	1.6	0.6	0.4	2.0	4.6	1.0	1.6	1.4	1.6	5.6
MWCNTs-Re_7	2.8	1.4	1.4	1.8	7.4	1.6	1.8	1.4	3.2	8.0
MWCNTs-Re_8	3.6	1.6	1.6	1.4	8.2	1.2	1.8	1.6	3.2	7.8
MWCNTs-Re_9	3.6	1.8	1.6	1.8	8.8	1.0	1.8	1.8	3.6	8.2
MWCNTs-Re_10	2.4	1.2	1.0	1.0	5.6	0.6	1.8	1.6	2.8	6.8

Detailed assessments were multiplied by criteria weights and summed up to obtain weighted averages reflecting the attractiveness and potential of each variant of manufacturing conditions (Tab. 2).

A dendrological matrix was used for the graphical presentation of the analysis results (Fig. 2). The matrix consists of four quarters, the names of which intuitively refer

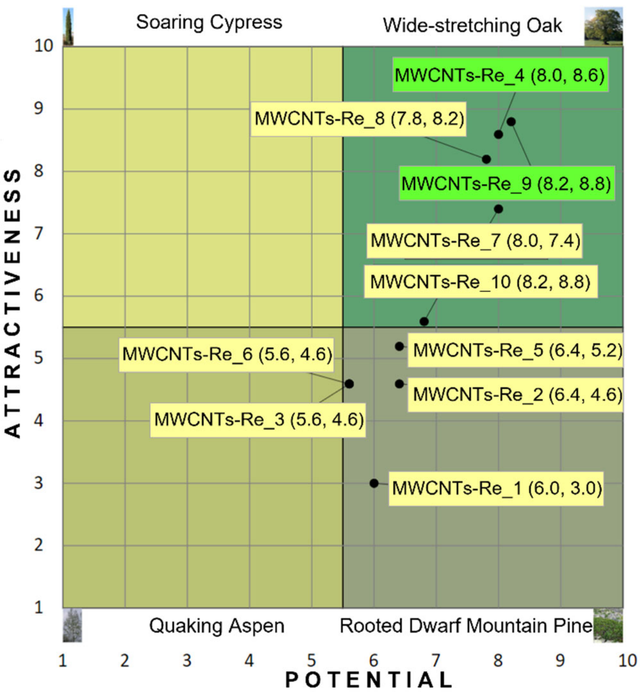

Fig. 2. Dendrological matrix. Positioning of MWCNTs-Re nanocomposites created in various manufacturing conditions (based on [27])

to the trees' specificity. The best quarter is called "Wide-stretching Oak" [28]. The best structure and morphology characterise the nanocomposites with the highest scores in the quarter. The analysis results presented graphically indicate that the production conditions corresponding to MWCNTs-Re_4 and MWCNTs-Re_9 specified in Table 1 should be ensured when using the high-temperature method. The best variants are marked in light green on the matrix.

5. Results of microscopic and spectroscopic investigations

The chapter contains representative results of MWCNTs-Re_4 nanocomposite investigations. In line with chapter 4, the nanocomposite was created under manufacturing conditions, ensuring a satisfactory morphology and structure of the analysed group of materials.

SEM studies of the morphology of MWCNTs-Re_4 nanocomposite indicate high homogeneity of the distribution of Re nanoparticles on the surface of carbon nanotubes in the entire volume of the material (Fig 3a). The structure of MWCNTs-Re_4 includes single large Re nanoparticles (above 50 nm), but the most numerous are oval particles with a diameter of 10 to 30 nm. In Figure 3b, in the central part on the right, is a visible single carbon nanotube, approx. 2 µm long, with Re nanoparticles deposited on its walls. High-resolution TEM enables the examination of the fabricated nanocomposites, revealing the graphene planes of decorated MWCNTs (Fig. 4a) and the crystal structure of Re nanoparticles deposited on their surface (Fig. 4b). Figure 5a made in the HAADF-STEM mode shows the MWCNTs-Re nanocomposite in the dark field with the area marked with a blue frame in which the EDS analysis was performed

(Fig. 5b). The EDS results confirm the presence of Re in the chemical composition of tested nanocomposites together with carbon from carbon nanotubes. Copper comes from the mesh used to make the samples for HRTEM testing.

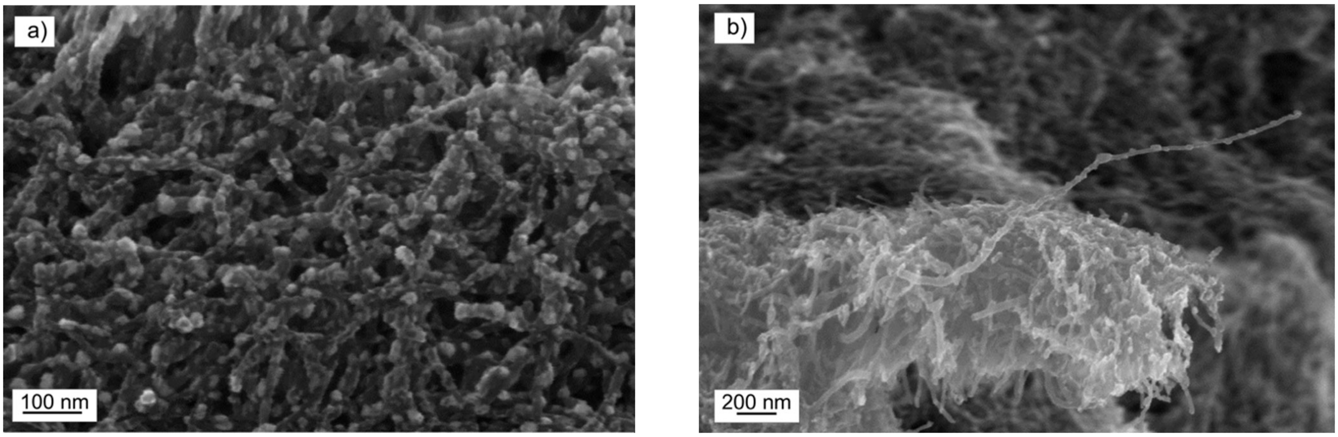

Fig.3. MWCNTs-Re_4 nanocomposite: a), b) SEM, In-lens detector

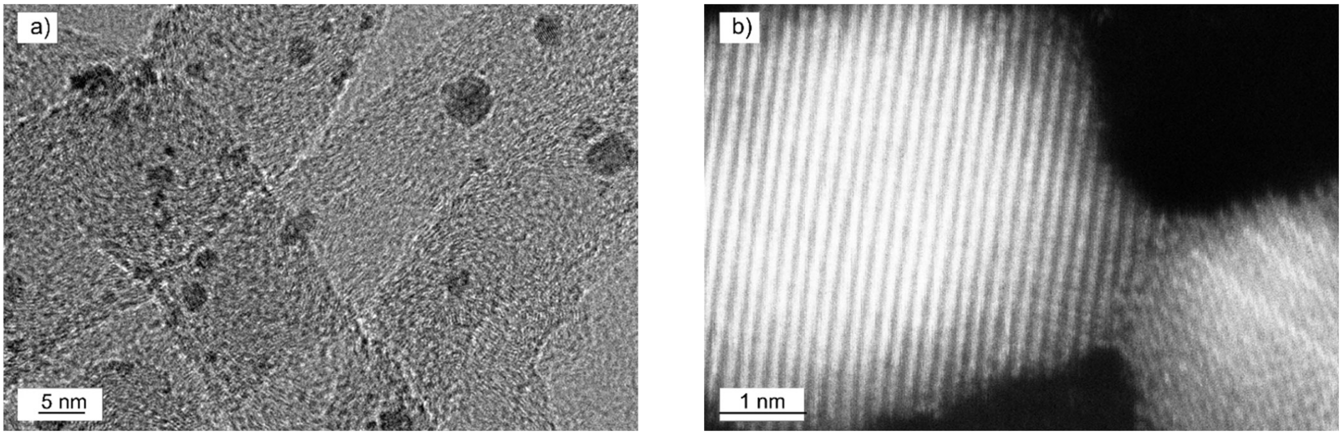

Fig.4. MWCNTs-Re_4 nanocomposite: a) MWCNTs decorated with Re nanoparticles, BF, HRTEM; b) crystal structure of Re nanoparticles, HAADF, STEM

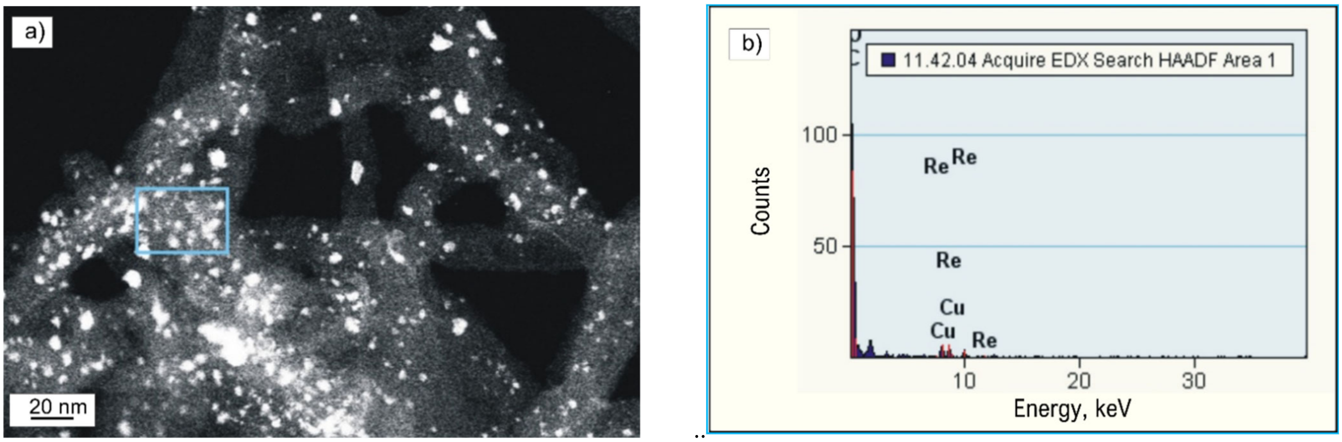

Fig. 5. Cluster of MWCNTs decorated with Re nanoparticles; HAADF, STEM (a); Qualitative analysis of the chemical composition from the area marked with a blue frame in 5a figure, EDS (b)

6. Conclusions

Like many other metals, Nanocrystalline Re can be permanently jointed with carbon nanomaterials, thus forming a carbon-metallic nanocomposite. Own experiments were carried out to achieve this goal. Two alternative methods have been tested, i.e., chemical synthesis and the high-temperature method. Chemical synthesis, despite successful applications in other own research for the fabrication of CNTs-NPs nanocomposites (with Pt, Pd, Rh), is not suitable for carbon-rhenium nanocomposites. Satisfactory results were achieved using the original high-temperature method, which is the subject of our patent [26]. The structure of MWCNTs-Re nanocomposites is influenced by the functionalization and impregnation time, Re precursor, and wetness of the heated material. Ten variants of manufacturing conditions were tested, and the best two were selected using material science and heuristic analysis. The representative example of MWCNTs-Re_4 shows the structure, morphology, and chemical composition of carbon-rhenium nanocomposites obtained by the high-temperature method. They can be used in catalysis and as sensors for harmful gases.

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