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Original Research Article

Microscopic and spectroscopic investigation of carbon nanotubes-rhenium nanocomposites fabricated in different conditions

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ABSTRACT

The article describes the morphology of carbon-metal nanocomposites consisting of nanostructured rhenium permanently attached to carbon nanomaterials, in the form of single-walled (SWCNTs), double-walled (DWCNTs) or multi-walled carbon nanotubes (MWCNTs). Such nanocomposites are produced as a result of the high-temperature reduction of a rhenium precursor, including $HReO_4$ or NH_4ReO_4, to metallic rhenium, deposited on the previously functionalised carbon nanomaterials in the form of nanoparticles whose size and dispersion are dependent upon the conditions of a technological process. Microscopic examinations carried out with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed a differentiated structure of the presented nanocomposites depending on impregnation time in a rhenium precursor, which is one of the manufacturing steps of such materials. It has been demonstrated that longer impregnation time brings favourable results for material homogeneity in the whole volume. Moreover, the Raman spectroscopy results of functionalised carbon nanotubes and carbon nanotubes decorated with rhenium also has been presented.

1. Introduction

The outcomes of materials science research [1–4] and foresight research [5,6] indicate that nanocomposites consisting of carbon nanomaterials and nanoparticles of other materials are considered to be the most prospective groups of materials. The nanocomposites fabricated by intentionally attaching the nanoparticles of, e.g. transition metals to the surface of carbon nanomaterials, have unique physiochemical properties occurring due to the synergy effect. The principal characteristic feature is an expanded, chemically active specific surface area [7–9]. The type of the nanoparticles attached has large influence on the properties of this type of carbon-metal nanocomposites. Rhenium is a rare chemical element which is used at the same time in (i) space and aviation industry as a

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component of superalloys [10,11]; (ii) shipyard industry for parts of sea ships [12–14]; (iii) chemical industry as a catalyst of many chemical reactions, also in petrochemical industry [15,16]; (iv) medical industry which uses radioactive isotopes ^{186}Re and ^{188}Re [17,18]. Owing to its very high thermal resistance it is also applied for incandescent parts, fibres and cathodes [19]. Considering the nanocomposites whose component are carbon nanotubes, the numerous nanoparticles deposited on their surface are acting as active centres. Nanotubes or other carbon materials are, however, a carrier whose role is to expand an active area of a catalyst and to additionally stiffen and increase the resistance of the catalyst. It was found based on extensive research and literature reports that rhenium is an irreplaceable catalyst in many chemical reactions [20–23]. Rhenium nanoparticles deposited on carbon nanotubes, carbon nanohorns, graphene or other forms of combinations of rhenium with carbon nanomaterials, have been intensively researched in the recent years [24–29]. The fabrication of such materials, especially when carried out in satisfactory fabrication conditions [30,31], is an interesting alternative for the existing fabrication technologies of Re-based catalysts. This is due to a highly expanded, porous material surface and the presence of rhenium nanoparticles with high dispersion.

2. Materials and methodology

A material fabricated in catalytic chemical vapour deposition (CVD) was employed for experiments serving to manufacture the nanocomposite materials consisting of multi-walled carbon nanotubes decorated with rhenium nanoparticles [4]. The following process gases were used in the process: H_2 (300 SCCM), C_2H_4 (300 SCCM) and Ar (1 SLPM), the process time was 45 min, and temperature was 750 °C. An SWCNTs/DWCNTs-Re nanocomposite consisting of single- and double-walled carbon nanotubes was fabricated using a commercial carbon material. The following are the chemical substances used in the experiment: HNO_3, C_2H_5OH, $HReO_4$, NH_4ReO_4. The following procedures are applied in the synthesis of the presented nanocomposites [26]: (1) functionalisation, (2) impregnation in a rhenium precursor and (3) heating in an oven in the atmosphere of hydrogen. Carbon nanotubes are first placed in a beaker, flooded with HNO_3 acid and the mixture is treated for 5 h with ultrasounds. In the next step, called impregnation, carbon nanotubes are flooded with $HReO_4$ or NH_4ReO_4 and ethanol solution and the mixture is treated for specific time with ultrasounds. After such operations, the rhenium precursor is reduced to metallic rhenium in the form of nanoparticles in an oven in the presence of hydrogen. The dried material is placed in a quartz vessel and pre-heated in the atmosphere of hydrogen and in an argon shield for 45 min. A diagram of the manufacturing process of nanocomposites of the carbon nanotubes-rhenium nanoparticles-type are presented in Fig. 1. The use of a material in the dried form is technologically substantiated because the device does not become dirty, part of the material is not lost, and the process is carried out in a controlled manner. Other experiments were also conducted in which a material in the form of wet paste was introduced into the oven, however, with unsatisfactory results [26].

The carbon-metal nanocomposites presented in this article (Table 1) were synthesised in a CCVD EasyTube®2000 device at the temperature of 800 °C and with a flow rate of H_2 of 400 cm^3/min. The flow rate of hydrogen was decreased twice after 15 min of the process and heating was continued for 30 min. The morphology and structure of the newly produced nanocomposites was examined by scanning electron microscopy. The SEM Supra 35 microscope was used equipped with a GEMINI electrical and optical column, an electron backscatter diffraction camera, an energy dispersive spectroscope (EDS) by EDAX. The high resolution of viewing the examined carbon preparations was achieved by applying an In-lens detector. Microscope observations, which assumed to obtain high-resolution photographs of the structure of the fabricated nanocomposites, were carried out using a high-resolution STEM TITAN 80-300 electron scanning and transmission microscope by FEI equipped with bright field (BF) and dark field (DF) detectors and a high angle annular dark field (HAADF) detector. The Raman spectroscopy method was applied to characterise nanocomposites and to confirm changes in carbon nanotubes' structure after a decoration process. The investigations were performed with an inVia Reflex Raman Spectrometer device by Renishaw, fitted with a confocal

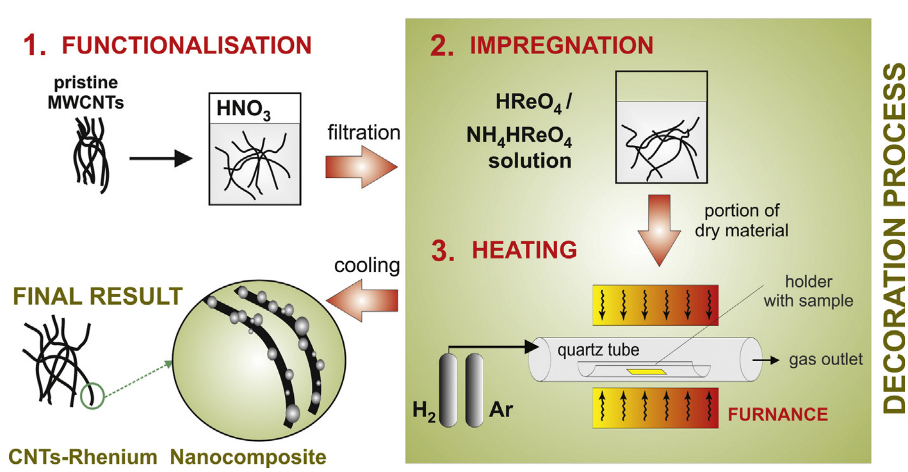

Fig. 1 – The process diagram of manufacturing the nanocomposites of the carbon nanotubes-rhenium type.