PREPARATION AND STUDY OF ELECTRICALLY CONDUCTIVE CERAMIC NANOCOMPOSITES BASED ON THE AZERBAIJAN BENTONITE RAW MATERIAL AND MULTI-WALLED CARBON NANOTUBES

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This work is dedicated to the fabrication and investigation of electroconductive ceramic nanocomposite materials (based on bentonite raw materials of two Azerbaijani (Atyali, Gobu) deposits and synthesized multi-walled carbon nanotubes (MWCNTs)) by means of physicochemical (SEM, XRD, derivatography (TGA / DSC), current-voltage characteristics) methods. It was revealed that the thermal stability in the air environment for both compositions of nanocomposites reached 600 ^{0}C, and the highest electrical conductivity (111.5 S·m^{-1}) was shown by nanocarbon-ceramic samples obtained on the basis of MWCNTs (8 wt. %) and bentonite clay of the Gobu deposit.

Keywords: MWCNTs, AACVD, bentonite, electroconductive ceramic nanocomposites, SEM, XRD, TGA / DTA.

1. INTRODUCTION

The creation of composite materials with predetermined properties based on carbon nanotubes (CNTs) is one of the most important trends in modern materials science [1]. Ceramic materials, including those based on bentonite clays (BC) deposits of Azerbaijan [2, 3] are one of the promising matrices of composite materials based on nanotubes and are used in areas where high thermal and corrosion resistance is required [4]. In the scientific literature there is practically no data on ceramic nanocomposites based on BC and MWCNTs and the study of their electrophysical characteristics. In this regard, the work is devoted to the fabrication and complex study of electrically conductive composites based on the Atyaly and Gobu bentonite deposits and multi-walled carbon nanotubes synthesized from cyclohexane.

2. THE EXPERIMENTAL PROCEDURE

The synthesis of MWCNTs was performed by the AACVD method. As a carbon precursor, cyclohexane (CyH) was used, and ferrocene (Fc) – as a precursor of the catalyst. The synthesis conditions are given in [5].

Bentonite clay masses were preliminarily subjected to washing (clay was dispersed in distilled water, followed by filtration to remove large non-clay granular impurities). Dispersion of carbon nanotubes in bentonite clay was carried out using the two-factor method developed earlier by our colleagues [6]. Calcination of MWCNTs / BC nanocomposite samples was carried out in a quartz reactor in a flow of gas mixtures – argon (volumetric rate = 0.5 l / min) / hydrogen (volumetric rate = 0.025 l / min) at a temperature of 1050 ^{0}C for 120 minutes.

3. RESULTS AND DISCUSSION

Samples of synthesized MWCNTs and composite ceramic materials based on natural bentonite (Atyaly and Gobu) with nanotubes content of 4 % were selected for the study. SEM image of synthesized MWCNTs is illustrated in Figure 1.

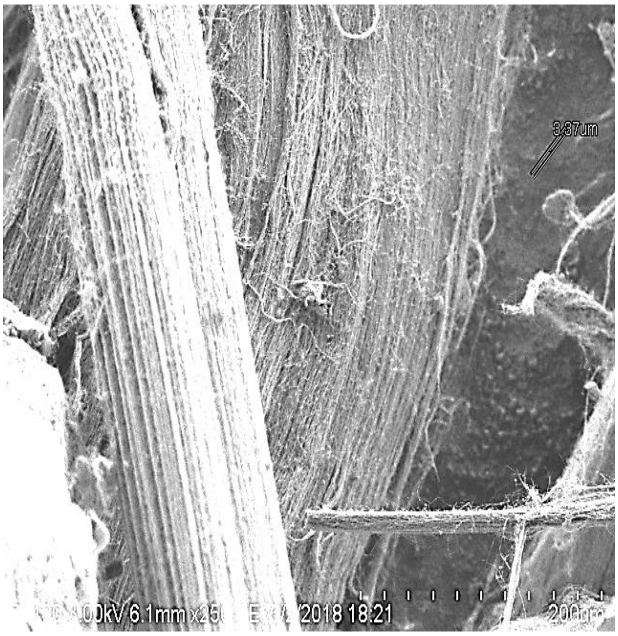

Fig. 1 – SEM image of synthesized MWNTs

From the above picture of MWCNTs (Figure. 1), it is clearly seen that nanotubes are compacted arrays of multi-walled carbon nanotubes having the shape of elongated long filaments, the so-called "carbon nanotubes forests", and the nanotubes themselves have obtained a sufficiently high degree of frequency (there are no non-tubular carbon structures).

For the nanocarbon-ceramic composites, their current-voltage (I-V) characteristics were measured (Figure. 2), and on the basis of these data, the electrical resistivity, specific resistivity, and specific conductivity of the samples were calculated.

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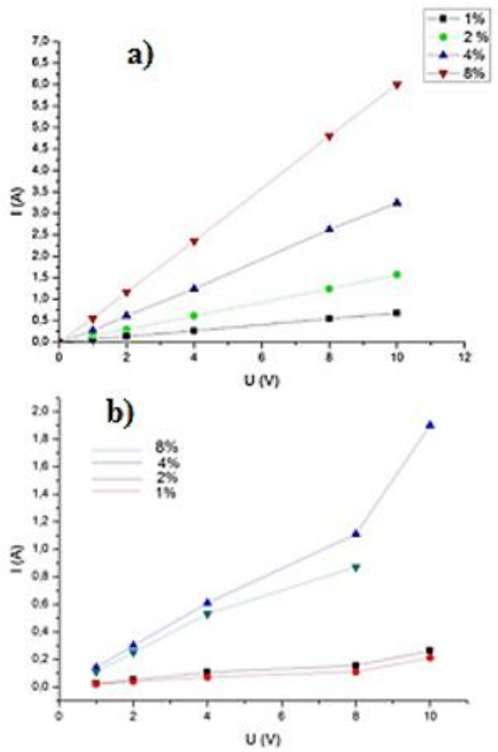

Fig. 2 Current - voltage characteristics of nanocarbon-ceramic composites based on: a) AT/MWCNTs; b) Gobu / MWCNTs.

Analyzing the data obtained, it may be deduced that, with the same MWCNTs content, the electrical conductivity of those ceramic nanocomposites is higher, which includes the clay of the Gobu deposit; this can be explained by the difference in the quantitative composition of the main components and the qualitative composition of clay impurities in two different deposits.

The thermal stability of the composites was studied by the TGA / DTA method. TGA curves of hybrid material samples have a similar character – an increase in the mass of the sample when heated in the temperature range from 80 to 605-640 ^{0}C, followed by a sharp decrease in mass with further heating. The increase in mass can be related to the process of oxidation to higher degrees of both nano-sized iron Fe and FeO (formed as a result of the reduction of iron (III) oxide by hydrogen and carbon in the calcination process of BC / MWCNTs composites) as a result of interaction with oxygen and air vapor with the formation of higher oxides (Fe_2O_3) and iron metahydroxide FeOOH. At temperatures of 605-680 ^{0}C, in the thermogravimetric curves detected an inflection characterizing sharp mass lose, which is caused by the oxidation of MWCNTs and the destruction of its carbon skeleton, with consequent release of carbon oxides (CO, CO_2). The wide pronounced exopics of oxidation on the DTA curves with a maximum at a temperature of about 700 ^{0}C also indicate that weight loss is caused by the degradation of nanotubes during combustion process.

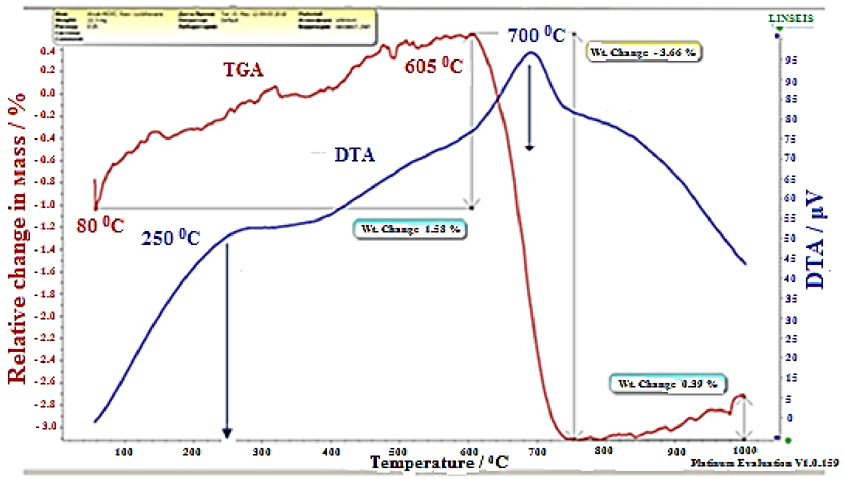

Fig. 3 Derivatogram of mass loss (TGA) and heat fluxes (DTA) curves taken from the sample AT / MWCNTs

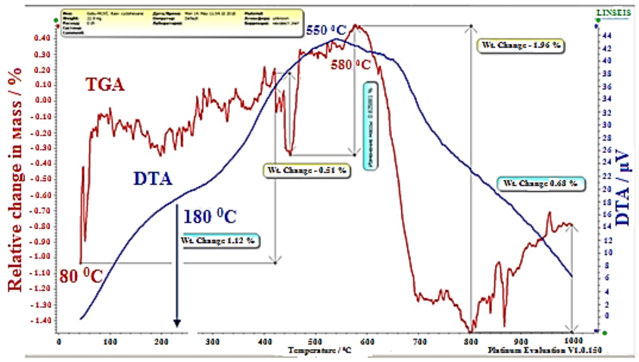

Fig. 4 Derivatogram of mass loss (TGA) and heat fluxes (DTA) curves taken from the sample Gobu / MWCNTs.

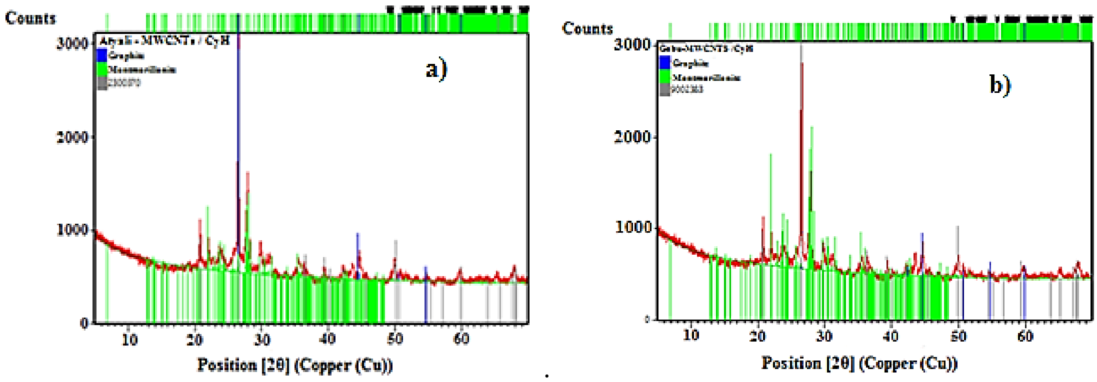

Fig. 5 X-ray diffractograms of the samples: a) AT / MWCNTs; b) Gobu / MWCNTs.

The mineralogical and phase compositions of nanoceramic composite samples were studied by X-ray diffraction analysis (Figure 5)

In the roentgenogram, the most intense peaks (marked in blue in the figure 5) indicated by (002) reflect the concentric cylindrical structure of embedded graphene sheets (hexagonal graphite structure), while the presence of reflexes $2\theta = 25.77^0$ imply multilayered nature of carbon nanotubes. The identified phase owned by bentonite is shown on the roentgenogram in green (in the range $25 < 2\theta < 47$). XRD analysis data confirm the presence in the composites of two main components – multi-walled carbon nanotubes and bentonite. Thus, the above results lead to the conclusion that hybrids, which constituted a system based on bentonite minerals and MWCNTs, are promising materials that have conductivity and withstand high temperatures, by which it is possible to develop various heating elements, electrodes, substrates for microelectronic devices and other products for use in various fields.

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