ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 23, No. 2. 2017

Thermal and Electrical Characterization of the Carbon Nanofibers Based Cement Composites

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crossref http://dx.doi.org/10.5755/j01.ms.23.2.14993

Received 16 May 2016; accepted 02 September 2016

The paper describes the influence of chemical modification of vapor grown carbon nanofibers (VGCnFs) on the thermal and electrical properties of the cement composites. The surface modification of nanofibers was performed by means of ozone and nitric acid treatments. It was shown that the oxidized carbon nanofibers surface plays an important role in shaping the mechanical and especially electrical properties of cement composite. For cement matrix modified with carbon nanofibers subjected to oxidized treatment, the slightly increase of cement paste resistivity was observed. It confirms the better adhesion of carbon nanofibers to cement paste. However, independently of carbon nanofibers modification, the occurrence of VGCnFs in cement paste increased the electrical conductivity of the composite in comparison to the cement paste without fibers. The obtained values of electrical resistivity were comparable with values of cement composites modified with 4 mm long carbon fibers. Moreover, it was shown that the chemical modification of carbon nanofibers surface does not influence on the thermal properties of cement composites. In case of cement paste with unmodified and modified carbon nanofibers, the Seebeck voltage was proportional to the temperature difference and was independent of the oxidation degree of carbon nanofibers.

Keywords: thermal and electrical properties, cement paste, surface treatment, carbon nanofibers.

1. INTRODUCTION

The cement composites, except the basic features like good flexural strength and toughness, can exhibit extra multifunctional properties, which allow their wider applications. For instance, the electric conducting particles or fibers added to cement matrix in the amount corresponding to percolation threshold show the increase of electrical properties of composite and can be used, e.g. as self-sensing sensors [1 – 3]. The self-sensing determines the ability of a structural materials to sense its strain, stress, damage and/or temperature. Due to above properties there is possible to control the structure vibration, load and durability. In such materials the additives, which can change the electrical or thermal properties of cement matrix and which enable the testing of electrical resistance or thermocouples of cement composite, are applied. Among the all conducting additives used in cement composites, the short and very short carbon fibers are very interesting material because of low percentage content required to reach the percolation threshold. Authors of paper [4] achieved the value of Seebeck coefficient ranged from 3.0 to 5.5 μV/K for cement composites with carbon fibers (5 mm length, 15 μm diameter) at the percolation threshold between 0.5 – 1 wt.%. In [5] it was shown that the percolation threshold was attained at carbon fibers content varied between 0.4 and 0.6 wt.%. In this case carbon fibers with much lower diameter were used (5 mm length and 7 μm diameter). The occurrence of carbon fibers in cement paste leads to the increase of electrical conductivity of composite. This increase depends on the type of precursor, amount and length of carbon fibers [6 – 8]. The results presented in [7] show that the conductivity of cement paste increases with increasing volume fraction and carbon fiber length. The values of electrical conductivity vary from 10^{-2} Ω·cm to 10^{-1} Ω·cm for 2 mm and 8 mm length carbon fibers, respectively.

Although the thermal and electrical properties of cement composites modified with untreated carbon fibers were investigated by many researchers giving the variety of results, relatively little attention has been paid to the carbon nanofibers and the role of surface properties of carbon fibres in thermal and electrical behaviour of cement composites. Therefore, the following article presents the results of the research on the influence of chemical modification of carbon nanofiber surface on the thermal and electrical properties of the cement composite. As the fiber extender the carbon nanofibers received from the gas phase of the hydrocarbons were used (VGCnFs). The oxidizing modification of the nanofibers was conducted in the gas phase, in the ozone atmosphere, and in the liquid phase, in concentrated nitric acid. The evaluation of the oxidation of the fiber surface was made by means of cyclic voltammetry method. While for cement composites the electrical, thermal, structural and mechanical properties were tested.

2. EXPERIMENTAL

Portland cement CEM I 42.5 and distilled water in water to cement ratio (w/c) equaled 0.50 were used to prepare cement-carbon nanofibers composites. Three types of cement pastes: with the addition of unmodified,

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modified in ozone and nitric acid carbon fibers in the amount of 3 wt.% were prepared. As carbon fibers additive the vapor grown carbon nanofibers VGCnFs supplied by ShowaDenco company were used. VGCnFs are received in a one stage process of catalytic decomposition of hydrocarbons [9 – 11]. As a result of this process fibers with a specific structure are created (Fig. 1), consisting of centrally located microfibril with a high graphitization level, surrounded by cylindrical pyrolytic graphite layers (the so-called concentric structure).

VGCnFs exhibit a very small diameter (about 0.2 µm; diameters in fibers from PAN and coal-tar pitch are in range from 5 µm to 15 µm) and high level of graphitization. Those fibers are characterized by very good mechanical properties, especially in relation to production costs, and much better, in comparison with other carbon fibers, heat and electric conductivity. The basic structural parameters of as-received carbon fibers were presented in Table 1.

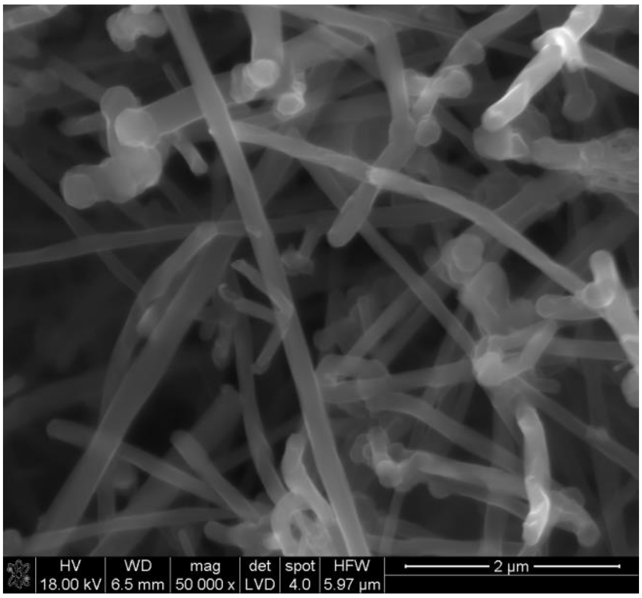


Fig. 1. Specific structure of vapor grown carbon nanofibers

Table 1. Basic structural parameters of as-received VGCnFs

Parameter	Unit	Value
Fibre diameter	nm	150
Fibre length	µm	10 ~ 20
Real density	g/cm^3	2.0
Bulk density	g/cm^3	0.04
Specific surface area	m^2/g	13
Electrical resistivity	Ω·cm	1 × 10^{-4}
Thermal conductivity	W/mK	1200

The chemical oxidation of VGCnFs was performed in concentrated nitric acid in 120 °C and by means of gaseous ozone in 160 °C. In case of oxidation in nitric acid carbon fibers were placed in a three-neck flask, poured by concentrated nitric acid and then heated gradually to 120 °C using the reflux condenser by three hours. After the oxidative treatments carbons were washed out with water and dried at 110 °C in air for 5 h. The process of carbon fibers oxidation in ozone was performed in a glass reactor under a continuous flow of gaseous ozone at a constant flow rate of 2 dm^{3}min^{-1}. Ozone was produced from air in an ozone generator. The oxidative treatment of fibers were carried out at temperature of 160 °C by 20 minutes.

In presented research the method of unmodified and chemically treated carbon fibers surface evaluation was the cyclic voltammetry CV. Cyclic voltammetry is a very valuable analytical method, enabling the estimation of electrode process kinetics, taking into consideration the inevitability of reactions related to charge transfer on the verge of electrode/electrolyte. The advantage of cyclic voltammetry application is also the possibility to conduct electrochemical research on very small carbon material samples with low level of surface development. Moreover, when in the electrolyte solution there is no depolarizer, the cyclic voltammetry enables the analysis of chemical character of the carbon material surface. The presence of electrochemically active oxygen groups on the carbon material surface is indicated by a current peak on the voltamperometric curve. Many researchers attribute this current peak to electrochemical reaction of surface functional groups in the quinone/hydroquinone arrangement [12, 13]. This arrangement can be also created by carbonyl and hydroxyl (phenolic) groups and carboxyl and anhydride or lactone groups on the verges of aromatic surfaces.

The 15 × 15 × 75 mm plate-like test specimens were made to measure the Seebeck coefficient and electrical resistivity of cement-carbon fibers composites. The samples were stored in water during 28 days. The electrical resistivity and Seebeck effect were measured on the prototype test device, in which the specimen was installed between the two plates having controlled temperatures (Fig. 2). The temperature of each plate was stabilized by an independent thermostat. On the ends of specimen there were the electric contacts from thin sheet copper [14]. The Seebeck coefficient (relating to copper) was determined every time after the stabilization of temperature measured in the contact of specimen with heating plates. The difference of temperature during the measurements was 20, 40 and 60 °C respectively, in relation to the 10 °C fit as reference temperature on the one side of sample.

The flexural strength was determined on the 15 × 15 × 75 mm plate-like test specimens by the three-point bending test, at the deformation rate of 1.0 mm/min using the universal machine type QC-508.

SEM analysis of carbon fibers and cement-carbon fibers composites was performed by the use of scanning electron microscope Nova NanoSEM, model 200 (FEI).

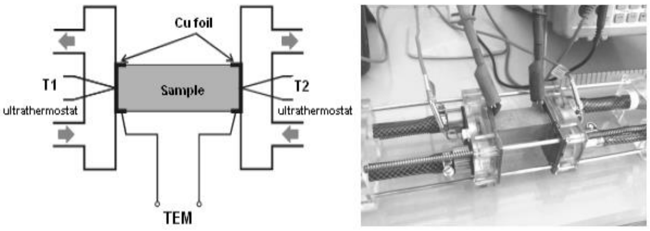


Fig. 2. Electrical and thermal testing device used in the project

3. RESULTS AND DISCUSSION

Chemical oxidation of carbon materials in liquid or gas phase leads to the creation of different acidic functional groups as: carboxyl, lactone, phenolic or anhydride ones on their surface [15 – 17]. The cyclic voltammetry curves presented in Fig. 3 clearly indicate the influence of the chemical treatment on the electrochemical character of fiber surface.

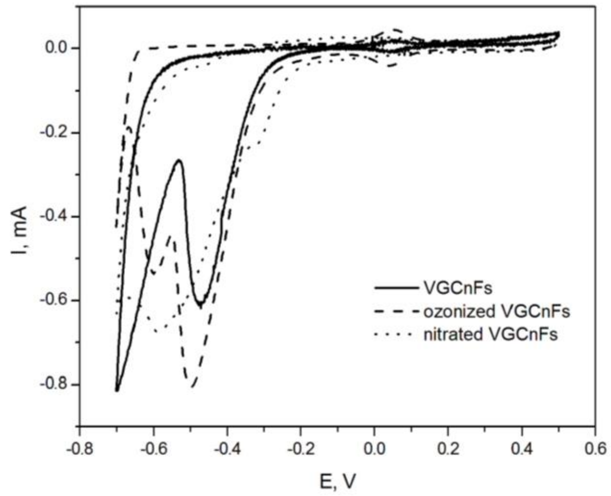


Fig. 3. Cyclic voltammetry curves registered in 0.25M water solution of H_2SO_4 of unmodified, nitric acid treated and ozone treated VGCnFs, $Er \rightarrow -0.7$ V ↔ 0.5 V (where Er means rest potential of the electrode)

Differences in localization of peaks on the reduction side for unmodified fibers and those oxidized in nitric acid, as well as the presence of the additional reduction peaks for ozonized VGCnFs at potential – 0.58 V and for nitrated VGCnF at potential – 0.32 V indicate the character change of the surface functional groups. Shift of the reduction peak in the direction of higher potentials in case of VGCnFs subjected to nitric acid modification indicates more reactive character of the functional groups containing a weaker C-O bond. For fibers modified in ozone a much higher over-potential is needed in order to reduce the surface oxygen groups, which is indicated by reduction peak movement in the direction of lower potentials. It means, that during the oxidation of carbon nanofibers in ozone less reactive oxygen groups including bonds C = O (for example carbonyl or carboxyl type) are created of their surface. The effect of the chemical modification and the increse of the amount of oxygen groups on fibers surface was the change of hydrophilic character of carbon nanofibers to hydrophilic. In case of unmodified carbon fibres the fibers floated on the water surface, while those after chemical modification gaved the suspention in water.

The Seebeck coefficient values obtained for as-received carbon nanofibers and the cement – carbon nanofibers composites are presented in Table 2. It was shown that the modification of fiber surface does not deteriorate the thermal properties of cement composites with respect to the cement samples with unmodified fibers. On the contrary, it keeps it on the same level. The values of Seebeck coefficient for cement composites with all kinds of carbon nanofibers are comparable and equal about 8.50 μV/K. The variation of the Seebeck voltage (with copper as the reference) versus the temperature difference for cement composites with the addition of modified and unmodified carbon fibers is presented in Fig. 4. The plotted curves confirm that the Seebeck voltage of cement pastes with modified and unmodified carbon nanofibers is proportional to the temperature difference and is independent on the oxidation degree of carbon nanofibers.

Table 2. Thermal, electrical and mechanical properties of carbon fibers and its composites with cement paste

Type of carbon nanofibers	As-received	Ozonized	Nitrated
Seebeck coefficient for CF, μV/K	26.74 ± 0.70	26.70 ± 0.22	26.02 ± 0.73
Seebeck coefficient for cement paste with CF, μV/K	8.50 ± 0.30	8.32 ± 0.35	8.34 ± 0.41
Resistivity for cement paste with CF, Ω·cm	$1.24 \cdot 10^2$ ± ± 0.12	$2.32 \cdot 10^2$ ± ± 0.09	$1.84 \cdot 10^2$ ± ± 0.36
Cement composite bending strength, MPa	3.0 ± 1.1	3.2 ± 1.6	3.9 ± 0.9

On the other hand, the results of resistivity of cement pastes with carbon nanofibers indicate that the additive of carbon fibers, regardless of oxidation treatment, influences positively the electrical properties of cement composites. Typical cement matrix without additives shows very low conductivity, with resistivity, depends on different literary sources, ranging from 10^4 to 10^{11} Ω·cm in relation to moisture content [2, 7]. Owing the electrical resistance of composite, the electrical conductivity can be calculated from the following equation [7, 8]:

$$\sigma = \frac{1}{\rho}, \quad (1)$$

where σ and ρ are the electrical conductivity and resistivity, respectively. The values of resistance presented in this paper for the cement composites with modified and unmodified VGCnFs show that the presence of carbon nanofibers increases the conductivity of the cement matrix (Table 2). The values of the cement paste resistivity with unmodified and modified carbon nanofibers equaled from $1.24 \cdot 10^2$ Ω·cm to $2.32 \cdot 10^2$ Ω·cm, respectively, and were comparable with the results obtained for 4 mm long carbon fibers [7]. However, in contrast to the other results, in case of carbon nanofibers with length about 20 nm, the percolation threshold was achieved for much higher content was equal to 3 wt.%. Moreover, the chemical modification of carbon nanofibers decreases insignificantly the electrical conductivity of cement composite. For carbon nanofibers subjected to nitric acid as well as ozone treatment the increase of electrical resistivity of cement paste was observed. The lowest conductivity of cement composite was achieved for VGCnFs oxidized in ozone. The similar results were obtained by Chung and coworkers [6, 18]. The authors of papers modified the cement paste by the isotropic-pitch based carbon fibers with 1 cm length which were initially oxidized in ozone. It was shown that during ozone treatment the surface oxygen concentration and change the surface oxygen groups from C – O to C = O configuration occurred. As consequence, the decrease of contact angle between fiber and water and the increase of the contact electrical resistivity between fiber and cement paste were observed. In our case, the oxidation of carbon nanofibers led also to the increase of amount of oxygen functional groups. As stated in cyclic voltammetry measurements, in case of ozone treatment oxygen functional groups with more durable bonding C = O were created leading to the more hydrophilic surface of carbon nanofibers, better wettability and higher resistivity of cement paste.

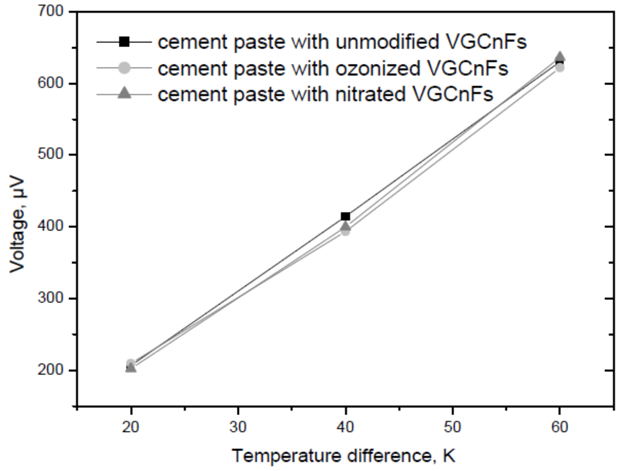
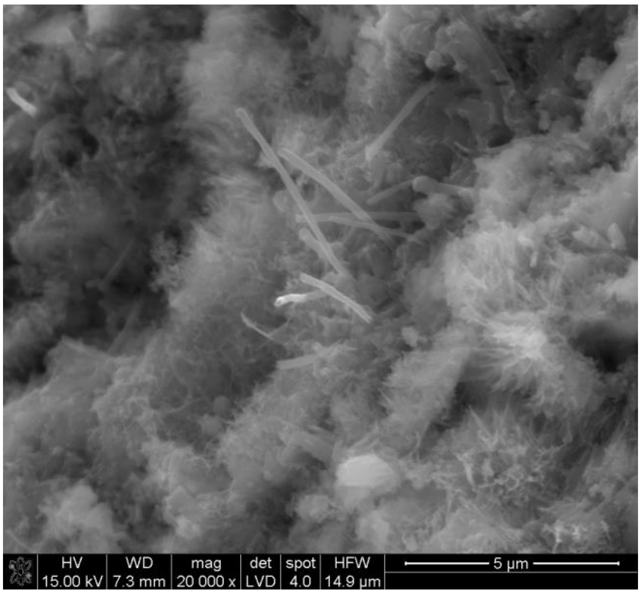


Fig. 4. Seebeck voltage versus temperature difference for the cement composites with unmodified and modified VGCnFs

According to Sun [5] the conductivity of carbon fibers reinforced cement composites is composed of ionic conductivity, hole conductivity, and electronic conductivity. When the carbon fibers reach the percolation threshold the conductive network is formed and the most important component of the cement composite conductivity is electronic conductivity. But in this case the electronic conductivity can be also enhanced by the positive hole transportation.

The positive holes are created on the carbon fibers surface under the electric field and can drift from the cold end to the warm end through the conductive network. In our case, the increase of electrical resistivity for cement paste with oxidized carbon fibers is caused by the higher amount of functional groups, which disturb the hole transportation, and lead to the lower conductivity of composite. On the other hand, the higher amount of functional groups on the carbon nanofiber surface results in better wettability and dispersion in cement paste. As can be seen in Fig. 5 a, in case of cement paste with unmodified VGCnFs, the fibers have the tendency to accumulate in one place, whereas the oxidized fibers are spread uniformly in cement paste (Fig. 5 b).

The chemical oxidation of carbon fibers surface causes also the higher adhesion to the cement matrix what is manifested by the higher electrical resistivity and higher bending strength of cement composites with VGCnFs. In case of cement pastes modified with carbon nanofibers subjected to nitric acid and ozone treatment the increase of bending strength was observed. The values of bending strength for cement composites with unmodified and modified in ozone and nitric acid carbon nanofibers equaled respectively: 3.0, 3.2 and 3.9 MPa.



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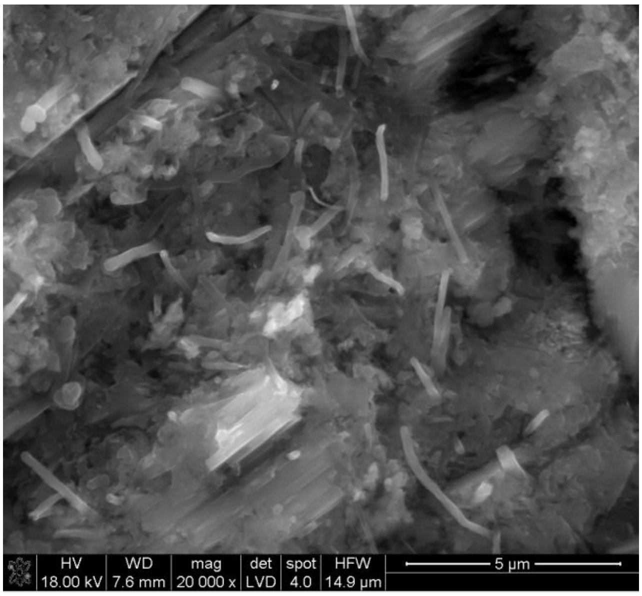

b

Fig. 5. Microstructures of cement composites modified with unmodified (a) and modified (b) carbon nanofibers

4. CONCLUSIONS

Differences in cathodic peak location for VGCnFs fibers, unmodified and oxidized in nitric acid and in ozone, indicate the change of surface functional group type. It is especially visible in the case of VGCnFs fibers subjected to nitric acid and ozone treatment. Instead of one peak registered on the curve for unmodified VGCnFs fibers, there are two well-developed peaks that indicate the change of the chemical character of carbon nanofiber surface. The creation of more reactive groups like carboxylic or hydroxyl on carbon nanofibers surface subjected to nitric acid treatment leads to the better adhesion of nanofibers to cement paste and as consequence give the higher value of bending strength. Moreover, the chemical modification of nanofibers, both with ozone and in nitric acid, alters the fiber surface character from hydrophobic to hydrophilic, and enables proper distribution of fibers in the cement paste. In such case it is unnecessary to apply other dispersants or additives to disperse the nanofibers in cement matrix.

The thermal and electrical tests of cement composite with nanofibers proved that the chemical modification of carbon nanofibers surface does not influence on the thermal properties of composite, but increases their electrical resistivity. The higher amount of functional groups on the oxidized carbon nanofibers leads to the lower amount of holes, and as consequence, the hole conductivity of cement composite decreases slightly. However, the specific microstructure of vapor grown carbon nanofibers, regardless of chemical surface composition, results in the excellent electrical properties of nanofibers and causes the significant increase of cement composite conductivity in comparison to pure cement paste. The obtained results were comparable with cement composite modified with much longer carbon fibers.

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