ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 12, No. 2. 2006

Cement Based Foam Concrete Reinforced by Carbon Nanotubes

Grigorij YAKOVLEV[1], Jadvyga KERIENĖ[2], Albinas GAILIUS[2*], Ingrida GIRNIENĖ[3]

[1]*Izhevsk State Technical University, Studencheskaya str. 7, Izhervsk,426069, Russia*
[2]*Vilnius Gediminas Technical University, Saulėtekio 11, LT-10223, Vilnius, Lithuania*
[3]*Vilnius College of Construction and Design, Antakalnio str. 54, LT-10303, Vilnius, Lithuania*

Received 08 June 2005; accepted 05 January 2006

The main task of the presented research was to investigate the carbon nanotubes, synthesized from aromatic hydrocarbons and as well as to investigate the possibilities of production and main technological properties of Portland cement based foam concrete reinforced by dispersed carbon nanotubes. The method of stimulation of dehydropolycondensation and carbonization of aromatic hydrocarbons in chemical active environment (melts of aluminium, copper, nickel, iron salts) was used for carbon nanotubes synthesis. The results of investigation of the synthesized carbon nanotubes by X-ray photoelectron spectroscopy showed that they contain (80 – 90) % of carbon. The examination of the carbon nanotubes microstructure by electron microscope have shown that the nanotubes have a cylindric form, with diameter ranging up to 100 nm and length up to 20 μm. The nanotubes are agglomerated to fiber shaped agglomerates with a diameter up to 30 μm and a length up to 10 mm. The carbon nanotubes were used as a high strength dispersed reinforcement for production of foam non-autoclave concrete produced on the base of Portland cement. The results of the investigation of the reinforced non-autoclave cemente foam concrete showed that the use of carbon nanotubes (0.05 % by mass) in production of these concretes allows to decrease its heat conductivity up to (12 – 20) % and increase its compressive strength up to 70 %.

Keywords: carbon nanotubes, fibrillar structures, dehydropolycondensation, carbonization, X-ray photoelectron spectra.

1. INTRODUCTION

In order to increase the strength of the products without changing their density, the strength of the foam cement concrete matrix should be increased. This may be achieved by increasing the amount of binding materials as well as by decreasing the amount of mineral additives and by reinforcing the concrete matrix [1 – 3].

The fibres, possessing a length of 5 mm to 20 mm can be added to non-autoclave cement foam concretes and be homogenously dispersed throughout the whole foam concrete volume, but they can pierce the pores structure and have no effect on the condition of the pore's walls.

That is why the highly dispersed reinforcing polymer fibres allow for only an insignificant increase in the mechanical properties of articles prepared from non-autoclave concrete. An improvement in physico-mechanical properties of non-autoclave foam concrete after hardening is possible only when the wall pores are reinforced. Taking into account the wall thickness, effective reinforcement can be achieved only by nanotube foam materials, the so called carbon nanotubes, the dimensions of which are of a power less that the wall pore diameter.

Two materials exsist in nature which comply to these requirements and can be used as dispersing reinforcements, i.e.: halloysite $Al_4[Si_4O10](OH)_8 \cdot 4H_2O$ and chrysotile $Mg_6[Si_4O10](OH)_8 \cdot 4H_2O$. Both have a tubular structure and nanoscale diameters (Fig. 1, a).

The structure of these two materials is made up of a two layer packet of the kaolinite type, where between the two layers, a hexagonal layer of water molecules is situated.

Here a difference in transition distances exists between the upper and lower plates which limits it and due to that it can bulge (Fig. 1, b). It was noted in [4], that halloysite contains Cu, Cr, Ni.

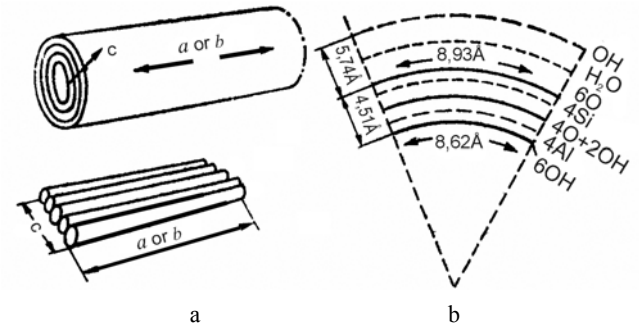


Fig. 1. A scheme illustrating the tubular form of halloysite [4]: a – tubular form; b – tube cutting

The mineral chrysotile – asbestos is used during dispersion reinforcement of cement systems. Here, a latent danger exists to human health during production of asbestos – cement articles, also during maintenance of buildings and constructions connected with the use of asbestos materials. Due to these drawbacks, chrysotile – asbestos needs to be replaced by other dispersive reinforcements with similar properties which are safe to use. On the basis of the mentioned above it may be supposed that synthetic carbon nano formations posses the nearest characteristics to chrysotile – asbestos.

One of the possible forms of metastable carbon nanoforms could be the quasitubular structure, i.e.: a long cylinder form package of atomic "ribbons" cut from a graphitic network (Fig. 2).

One of the main elements of such a structure is the graphite layer – the surface layed out between two proper

*Corresponding author. Tel.: +370-616-00170; fax.: +370-5-2698740.
E-mail address: *albinasgailius@yahoo.com* (A. Gailius)

hexagonals of carbon atoms situated at the top. The graphite layer can form an extension in the form of a full cylinder [5].

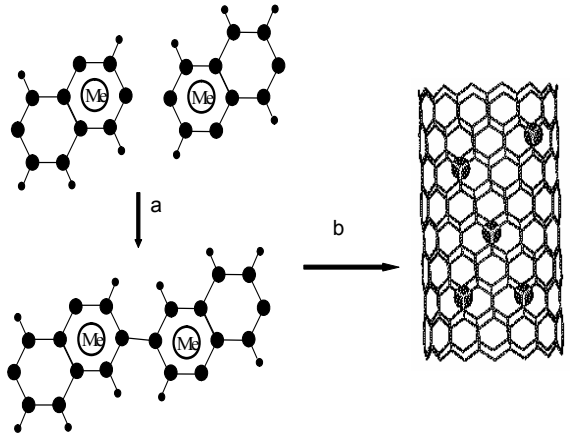


Fig. 2. A possible synthesis scheme for carbon nanotubes from eutectic melts of aromatic hydrocarbons undergoing dehydropolycondensation and carbonization reactions

The length of the nanotubes can reach tens of microns and up to several times surpass its diameter, which generally is only a few nanometers. Inverstigations have shown [6 – 9], that most of the nanotubes are made up of several graphite layers situated one above the other and wounded about one common axis. The distance between the layers practically is about 0.34 nm, which corresponds to the distance between the layers in crystalline graphite.

The ability of functional groups along the axis of the nanotubes [10] to orientate and further on intensivly combine into a crystallohydrate state allowed us to obtain a compositional structure with ultradispersive reinforcements.

The introduction of nano dispersive structures into hardening cement composition of the tubular type allowed us to create a dispersive reinforcement in the compositional material and stimulate growths in it. Here, we waited for the formation of linear fiberous structure new-growths. These formations are possible along the surface of the nanotubes as were found in [11]. That is why, these carbon nanotubes can be used as ultra dispensive reinforcements in non-autoclave foam concretes.

2. CARBON NANOTUBE SYNTHESIS STIMULATED BY DEHYDROPOLYCONDENSATION AND CARBONIZATION REACTIONS

At present, the total volume of nanotube production in the world is calculated to be about several kilograms and is being influenced by the extraordinary high prices (several tens of dollars per gram). The question of practical use in such a situation can be solved by the development of appropriate large-scale methods for production of nanotubes at relatively low prices.

It was proposed to synthesize nanotubes from condensed hydrocarbon raw materials (aromatic hydrocarbons or polymers) by using the low-energy carbonization in gel-matrix method to lower the energy needs and create a larger possibility of obtaining various tubulenes. We used anthracene and phenylanthracene as the starting material. Melts of aluminium, copper, cobalt, manganese, chromium chlorides as well as its mixtures of chlorides and ultradispersive powders of the corresponding metals were used also.

Anthracene, phenylanthracene or its mixture was added to the melt in the form of a finely dispersed powder with a molar ratio of 1 : 5 to 1 : 10. The mixture was then heated in a flask over a sand bath with intensive mixing.

Depending on the reaction composition the temperature was varied from 400 K to 570 K, the reaction time was from 2.5 to 10 hours. The process was held finished when the reaction mixture color changed to black. Then the reaction mixture was washed with acids (hydrochloric and nitric acid) to isolate the product and separate the salts. The precipitate was washed with water for several times up to a pH = 7 and dried in oven at $T = 373$ K. Then it was treated with organic solvents, like benzene, chlorobenzene, acetone to remove the unreacted hydrocarbons and other low-molecular compounds of the reaction. To eliminate the possibility of sticking, the obtained product was dispersed in alcohol or acetone and with the help of ultrasonic field (80 kHz, 20 V) created by a piezoelement type CTS-19 (dimensions $0.67 \times 8 \times 20$ mm^2). The obtained black color material after treatment was resistant to acids and alkali and withstood temperatures up to (900 – 1000) °C in the air.

A technology was developed for low-temperature carbon nanotube synthesis [12] and patented in 2001 (Russian patent № 2169699).

3. INVESTIGATION OF SYNTHESIZED NANOTUBES

We used X-ray photoelectron spectroscopy (XPS) to investigate the synthesized nanotubes. Specimens for investigations by XPS were deposited on indium substrates. Spectra were recorded on a X-ray photoelectron magnetic spectrometer (AlK_α emissions) and X-ray electron spectrometer ES-2401 (MgK_α emissions) in a vacuum of 10^{-5} Pa.

The XPS spectra of specimens obtained from a mixture of anthracene and phenylanthracene in a media of ultra dispersed powered of copper monochloride and copper are given in Fig. 3, while in Fig. 4 – in the same media but only polyphosphoric acid was added.

According to the presented spectra, relatively intensive peaks were observed for carbon and oxygen in Fig. 3 and for carbon, oxygen and phosphorus in Fig. 4. It was determined according to the obtained spectra that there were approximately 15 % oxidized groups present in the product, where carbonyl (286.5 eV) and carbonate (288 eV) dominate.

Apparently the treatment of the reaction mixture with nitric acid causes partial oxidation of the carbon – metal containing system.

The XPS spectra were used to determine the dehydropolycondensation – carbonization product composition and its relationship to the purification conditions: carbon (80 – 84) %, oxygen (11 – 16) %, chlorine (1.5 – 5.5) %, copper (0 – 2.3) %, phosphorus (0 – 1) %, nitrogen (0 – 1) % (in atomic percentage).

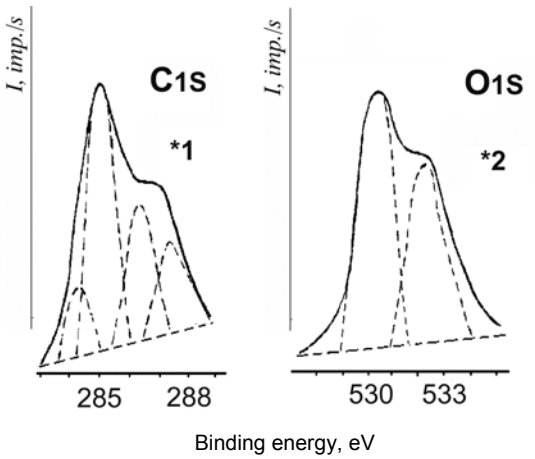


Fig. 3. XPS spectra (C1s, O1s) of carbon – metal containing specimens obtained from mixture of anthracene, phenylanthracene and copper monochloride with microdispersed copper

According to the data obtained from XPS investigation we can say that the product of stimulated dehydropoly-condensation – carbonization of aromatic hydrocarbons contained (80 – 90) % of carbon, depending on the method used for purification.

The scanning electron microscope investigation showed that the obtained material is composed of fibre shaped agglomerations (length up to 10 mm) with a complex inner structure containing nanostructures of a cylindrical shape.

In Fig. 5, a, scanning electron microphotograph is given of a specimen obtained as a result of dehydropoly-condensation in a mixture of anthracene and phenyl-anthracene in a media of ultra-dispersed powder of copper and its chloride. This sample contains cylindrical fibre shaped particles with a diameter of 1 micron to 30 microns (Fig. 5, a) which are composed of nanostructures of the same form (Fig. 5, b) with diameters up to 100 nm and length up to 20 μm (Fig. 5c).

Investigations into the main reaction mechanisms of stimulated carbonization of aromatic hydrocarbons in the system << Lewis acids-salts of transitional metals >> allow us to say that the formation of crystalline carbon samples in these systems occurs at low temperatures. During the carbonization process, the carbon transforms into nanoparticles encapsulating the initial reagents and/or its conversion products and covering them with a few orderly layers of graphite.

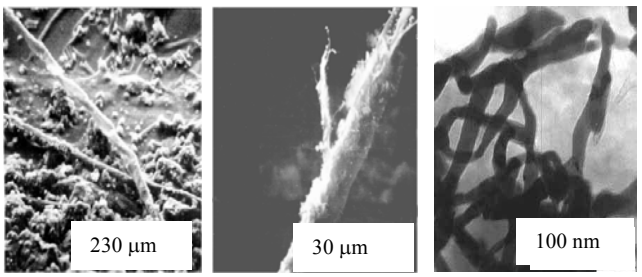


Fig. 5. Microstructure of carbon – metal containing new – growths obtained from aromatic hydrocarbons by the stimulated dehydropolycondensation and carbonization method: a – general view; b – a fragment of cleaved fibre shaped formation ; c – carbon nanotubes

4. NANODISPERSIVE REINFORCEMENT OF FOAM CONCRETES

The developed carbon nanotubes were used as a high-strength nanodispersive reinforcement in compositional crystallohydrated materials to improve the physico-mechanical properties of non-autoclave cement foam concretes. The admixture used was a product with a density of 0.086 g/cm^3, containing carbon nanotubes with a diameter of (40 – 60) nm and filled with copper. Traditional technology methods with technical foam were used to prepare the cement foam concrete. The admixture wetted poorly, so the surface was treated with a surfactant based on a solution of lignosulfonate salt.

The choice of the composition to be used for foam concrete mixture preparation was made based on the desired grade of foam concrete up to a density of 350 kg/m^3. The amount of reinforcement phase in the mixture was 0.05 % based on the initial mass. The

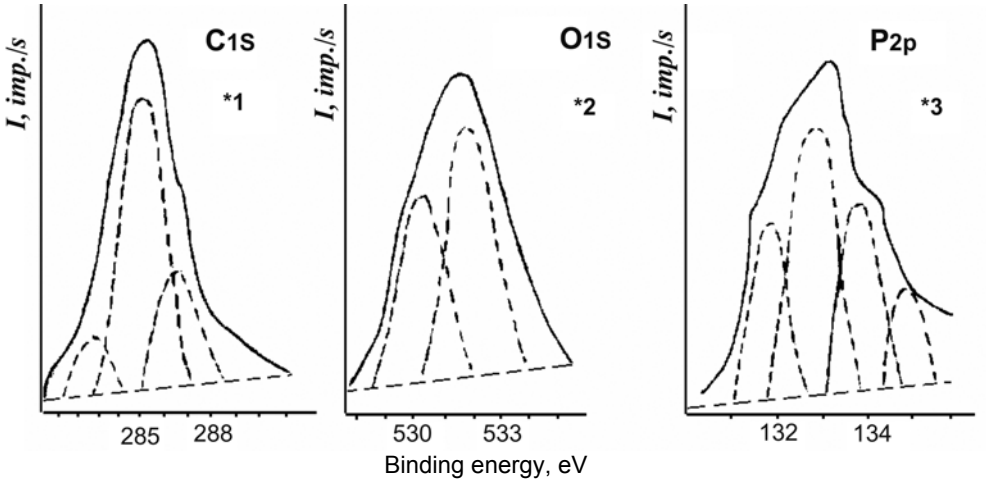
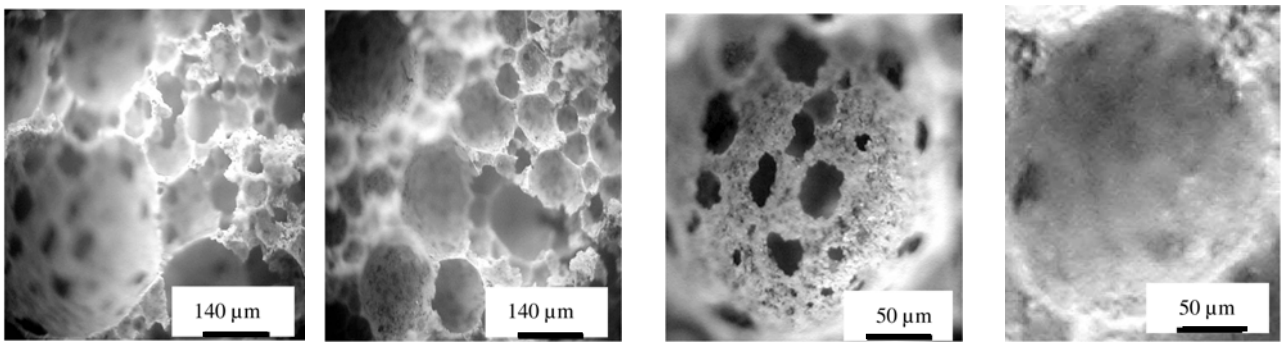


Fig. 4. XPS spectrum (C1s, O1s, P2p) of carbon – metal containing specimens obtained from a mixture of anthracene and phenylanthracene, polyphosphoric acid and ultradispersed copper

Table 1. Physico-mechanical characteristics of cement foam concrete

№	Amount of nanotubes, % based on the composition mass	Average density, kg/m^3	Compressive strength, MPa	Heat conductivity coefficient, λ, W/mK	Pore diameter, μm	Condition of wall pores
1	0	330	0.18	0.07	40 – 600	perforated
2	0.05	309	0.306	0.056	60 – 150	homogeneous



a b c d

Fig. 6. Cement foam concrete structure: a – without nanotubes, b – with 0.05 % nanotubes; pore walls; c – without nanotubes (perforated), d – stabilised with addition of 0.05 % of nanotubes

physico-mechanical properties of the prepared specimens (100×100×100) mm were determined by the standard methods and the results are given in Table 1.

As we can see from Table 1, the modification of cement foam concretes by the addition of carbon nanotubes allowed us to decrease in average density from 330 kg/m^3 to 309 kg/m^3 and at the same time to increase the compressive strength by 70 % (from 0.18 MPa to 0.306 MPa). The modification allowed to lower the heat conductivity by 20 % (from 0.07 W/m K to 0.056 W/m K).

The comperative analysis of the compressive strength values of cement foam concretes with densities up to 350 kg/m^3 and the compressive strength values of 500 kg/m^3 density cement foam concrete, not reinforced and reinforced by carbon nanotubes, showed that the modification by carbon nanotubes allows to increase the compressive strength of cement foam concrete approximately by the same percent, inspite of its density value. The compressive strength value of 500 kg/m^3 density not reinforced cement foam concrete by carbon nanotubes is 0.87 MPa, compressive strength value of the same density cement foam concrete reinforced by carbon nanotubes is 1.45 MPa (increased by 65 %).

The distribution of nanotubes throughout the cement foam concrete plays the role of centers for directive crystallization, which on one part brings about the development of a fibrillar structure on the pore walls, which in turn ensures its continuity and uniformity (Fig. 6, d), while on the other hand ensures an orderly structure orientated supermolecular sheath about the nanotube. This causes an increase in cement foam concrete strength and lowering of heat conductivity in the cement foam concrete article.

The microstructure investigation results have shown, that the presence of carbon nanotubes in the foam cement concrete stabilizes its structure (Fig. 6, d) and ensures the absence of pore wall percolation indications, which occur generally in common foam concretes (Fig. 6, c).

Generally the presence of not reinforced foam concrete pores with perforated walls causes a decrease in its strength and in all, a decrease in mechanical properties of the investigated material as well as in its heat conductivity.

A better pore size uniformity (Fig. 6, b) was observed in foam concretes containing an admixture of carbon nanotubes, while in concretes without carbon nanotubes, due to intensive percolation of wall pores (Fig. 6, a) causes them to combine into lager ones, which in turn increases the heat conductivity of the foam concrete and deteriorates its maintenance characteristics. The stabilization in foam concrete structures is mainly due to the reinforcement effect of the addition of fibrillar structures and ordering effect due to the formation of a supermolecular structure in the cement pore walls.

In that way we ensured the development of effective foam concretes with modified pore walls which was a result of reinforcement with carbon nanotubes.

CONCLUSIONS

1. The results of the investigation of the carbon nanotubes synthesized using the method of stimulation of dehydropolycondensation and carbonization of aromatic hydrocarbons in chemical active environment (melts of aluminium, copper, nickel, iron salts), carried out by using X-ray photoelectron spectroscopy and electron microscopy, showed that the carbon nanotubes obtained by this way contain (80 – 90) % of carbon, they have the cylindric form, their diameter is ranging up to 100 nm and length up to 20 μm. The nanotubes are agglomerated to fiber shaped agglomerates with a diameter up to 30 μm and length up to 10 mm.

2. The use of carbon nanotubes (0.05 % by mass) as the reinforcement for production of foam non-autoclave

concrete, produced on the basis of Portland cement, allows to decrease its heat conductivity up to (12 – 20) % and to increase its compressive strength up to 70 %.

REFERENCES

1. **Kahmer, H.** Fibrous Concrete Successfully Used in Structural Precast Component Production *Concrete Plant + Precast Technology* 67 (8) 2001: pp. 26 – 31.
2. **Tagnit-Hamou, A., Vanhove, Y., Petrov, N.** Microstructural Analysis of the Bond Mechanism Between Polyolefin Fibers and Cement Pastes *Cement and Concrete Research ISSN 0008-8846* 35 (2) 2005: pp. 364 – 370.
3. **Girnienė, I., Laukaitis, A.** The Effect of the Hardening Conditions on Foam Cement Concrete Strength and Phase Composition of New Formations *Materials Science* (*Medžiagotyra*) *ISSN 1392-1320* 8 (1) 2002: pp. 77 – 82.
4. **Penkalia, T. V.** Articles of Crystallochemistry. Ed. Frank – Kamenskij. Leningrad: Chemistry, 1974: 496 p. (in Russian).
5. **Dresselhaus, M. S., Dresselhaus, G., Eklund, P. C.** Science of Fullerenes and Carbon Nanotubes. Academic Press, 1997: 1216 p.
6. **Kodolov, V. I., Shabanova, I. N., Makarova, L. G., Khokhriakov, N. V., Kuznecov, A. P., Nikolaeva, O. A., Keriene, J., Yakovlev, G. I.** Research of Structure of Products of the Stimulated Carbonization of Aromatic Hydrocarbons *Journal of Structural Chemistry* 42 (2) 2001: pp. 260 – 264 (in Russian).
7. **Ebbesen, T. W**. Wetting, Filling and Decorating Carbon Nanotubes *J. Phys. Chem. Solids* 57 (6 – 8) 1996: pp. 951 – 955.
8. **Zhang, X., Cao, A., Li, Y., Xu, C., Liang, Ji, Wu, D., Wei, B.** Self-organized Arrays of Carbon Nanotube Ropes *Chem. Phys. Lett*. 351 2002: pp. 183 – 188.
9. **Kurt, R., Bonard, J. M., Karimi, A.** Structure and Field Emission Properties of Decorated C/N Nanotubes Tuned by Diameter Variations *Thin Solid Films* 398 – 399 2001: pp. 193 – 198.
10. **Yakovlev, G. I.** Structural Organization of Interphase Layers at Creation of Crystallohydrated Composite Materials *Thesis on Completion of a Scientific Degree of the Doctor of Engineering Science* Perm, 2004: 35 p. (in Russian).
11. **Seeger, T., Redlich, Ph., Grobert, N., Terrones, M., Walton, D. R. M., Kroto, H. W., Ruble, M.** SiO-coating of Carbon Nanotubes at Room Temperature *Chem. Phys. Lett.* 339 2001: pp. 41 – 46.
12. **Babuchkina, S. N., Kodolov, V. I., Kuznecov, A. P., Nikolaeva, O. A., Yakovlev, G. I.** Way of Obtaining Carbon-Metals Containing Nanostructures. Patent of Russia Federation 2169699, B.J. 2001, № 18 (in Rusian).