FRACTURE TOUGHNESS OF CARBON NANOTUBES MODIFIED CEMENT BASED MATERIALS

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Abstract
In order to increase the fracture toughness of concrete, dispersed fiber reinforcement is increasingly used in practice. The initiation of crack initiation occurs at the nanoscale in the cement matrix. Thus, the use of nano-reinforcement with dispersed nanoparticles can have a positive effect on the fracture toughness of the cement composite. It is proposed to consider carbon nanotubes (CNTs) as such nanofibers.

The article discusses the possibility of using carbon nanotube elements as elements for restraining the development of cracks at the nanoscale in cement composite. The results of testing nanomodified cement stone for strength indicators, fracture toughness indicators, results of nanoindentation, ultrasonic sounding and infrared spectroscopy are presented. A structural model of a cement stone dispersed-reinforced with nanocarbon tubes is considered.

Keywords: fracture toughness, crack resistance, strength, nanoconcrete, carbon nanotubes, stress intensity factor.

Introduction
Concrete is the most commonly used building material around the world. One of its main disadvantages is fracture fragility and low fracture toughness. The use of dispersed reinforcement of concrete composites is a promising direction in solving this type of problem. Dispersed fibers, evenly distributed over the entire volume of the material, create a spatial framework and contribute to the inhibition of developing cracks under the action of destructive forces [1, 2].

The authors put forward a working hypothesis according to which the fracture toughness of cement composites increases with the introduction of carbon nanotubes.

The initiation of crack initiation occurs at the nanoscale in the cement matrix. Thus, the use of nano-reinforcement with dispersed nanofibers can have a positive effect on the fracture toughness of a cement composite. Carbon nanotubes (CNTs) can be considered as such nanofibers. The effect of CNTs on the microstructure and nanostructure of the modified cement stone depends on the type of carbon material, its physical and chemical characteristics, the geometric parameters of the fibers and the uniformity of dispersion in the composite [3-6].

Structural modeling
The presence of carbon nanofibers changes the microstructure and nanostructure of the CNT-modified cement. A decrease in capillary porosity and a decrease in total porosity are observed, followed by an improvement in the pore structure. Reverse micromechanical analysis shows a shift from micropores and mesopores with a size of 100 nm in ordinary Portland cement to small gel pores with a size of 5–12 nm in cement modified with CNTs [7].

In the views of Ange-Therese Akono [7], the model of the modified CNT cement composite consists of 4 scale levels. At the nanoscale, calcium silicate hydrate products are packaged in various structural units, resulting in low C – S – H densities, high C – S – H densities, and ultra-high C – S – H densities. On a microscale, the C – S – H grains are linked by a network of carbon nanofibers forming a C – S – H matrix. On a microscopic scale, capillary pores and unhydrated clinker grains are embedded in the C – S – H matrix.

The physical model of the kinetics of destruction of Guzeev-Piradov-Leonovich concrete [8] is represented by a structure consisting of a system of different-scale grains (clinker, sand, crushed stone) with mutual attraction relations in the form of active forces (Nad) created by physical (Nad), chemical (Nad) and adhesion (Nad) processes as a result of cement hydration, and a subsystem of voids in the hydrated mass (in the form of capillaries (K), pores (P), cracks (T), in which a complex of reactive forces within the limits of their geometric dimensions in the structure (figure). The result of the processes occurring in the capillaries and cracks are deformations in the intergranular matrix, the free flow of which is impeded by rigid clinker grains and nanocarbon tubes, which creates a certain stress intensity at the tops of the dividing cracks (figure 1) The stress intensity, as well as the stress-strain state near the capillary tops and cracks are determined by the criterion of crack resistance (Kc) and the coefficients stress intensity (Kc, Kc) [8–10].
Practical research
Preparation for testing
The additives were pre-mixed with mixing water and introduced into the cement, intensively stirring for 5 minutes. The amount of mixing water was selected in such a way as to obtain a dough of normal density in all cases. The obtained dough was used to make beams with dimensions of 40x40x160 mm and 10x10x20 mm. The experimental research methods were in accordance with the provisions of STB 1114 GOST 23732.

When conducting research on the effect of CNTs on cement stone, the following materials were used as the main components:

1. Portland cement PC 500 D0 was used as a binder according to GOST 10178 of JSC “Belarusian Cement Plant” with the following mineral composition, wt. %: C3S – 58.31, C3S – 13.38, C4AF – 8.01, C2AF – 10.64.
2. Modifying substance - carbon nanomaterial (CNT): average diameter of pipes and fibers 10-300 nm, average length of tubes and fibers 0.01-20 μm, bulk density 0.15-0.22 g / cm³, ash content not more than 5%, specific adsorption surface from 60 m² / g.
3. Superplasticizer (SP) in the form of an aqueous solution - a polycarboxylate copolymer with a density of 1.1-1.14 g / ml, pH = 6-8, a viscosity of 230-330 cps, a content of non-volatile substances of 39-41%, a water-reducing capacity of over 40 %.
4. Water for mixing and subsequent hardening complying with the requirements of STB 1114 GOST 23732.

The formulations of the investigated compositions are presented in table 1.

Fracture toughness
The conditional critical stress intensity factor when testing beams for bending is calculated according to GOST 29167 according to the formula:

$$K_c = \frac{3F_c L_0}{2b^2 t} \sqrt{a_0 b} \left(1.93 - 1.07 \lambda + 14.53 \lambda^2 - 25.11 \lambda^3 + 25.86 \lambda^4 \right)$$

where $a_0$, $b$, $t$, $L_0$ - geometric dimensions of the sample, m;
$F_c$ - load corresponding to the dynamic initiation of the main crack during non-equilibrium tests, MN;

$$\lambda = \frac{a_0}{b}$$

The effect of carbon nanotubes on fracture toughness is shown in Figure 2.

Ultrasound examinations
Ultrasonic measurements were performed with Pulsar-2.2 devices (frequency 50 kHz, wavelength 100 mm) and an ultrasonic rectangular receiver model 50777PR in combination with an oscilloscope and corresponding U-shaped sensors (frequency 5 MHz, transverse wavelength 0.5 mm, longitudinal wavelength 1 mm). The test results are presented in table 2.

Nanindentation
The nanoindentation method is one of the direct methods for studying the mechanical properties of cement materials at the nanoscale. During testing, it is not the size of the sample that decreases, but the size of the deformed region. C-S-H exists in at least three structurally different forms: low, high and ultra-high density, which have different average values of hardness and hardness and different volume concentrations. Nanoparticles of different chemical composition with a high specific surface area and high surface energy are used to target the CSH gel nanostucture. The nanoindentation method makes it possible to assess the effect of nanoparticles directly on the volume fraction of different forms of CSH gel at an early age (6-24 hours) and adulthood (4-6 months) (Figure 3, 4).
Figure 3 — Histograms of the distribution of nanoindentation points by the modulus of elasticity (a, c) and hardness (b, d) for composition No. 2 (a, b) and composition No. 3 (c, d)

Table 3 — Average values of the modulus of elasticity $M$ and stiffness $H$ in three phases. / — after the dividing line, the standard deviation in this phase is indicated

<table>
<thead>
<tr>
<th>Options</th>
<th>№1</th>
<th>№3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus M, GPa / Standard deviation SD</td>
<td>Phase 1 13,0/3,3</td>
<td>21,2/4,9</td>
</tr>
<tr>
<td></td>
<td>Phase 2 23,2/10,6</td>
<td>30,7/9,1</td>
</tr>
<tr>
<td></td>
<td>Phase 3 50,6/8,6</td>
<td>62,8/10,7</td>
</tr>
<tr>
<td>Hardness H, GPa / Standard deviation SD</td>
<td>Phase 1 0,93/0,21</td>
<td>1,04/0,23</td>
</tr>
<tr>
<td></td>
<td>Phase 2 1,84/0,74</td>
<td>1,59/0,87</td>
</tr>
<tr>
<td></td>
<td>Phase 3 2,95/1,45</td>
<td>4,94/1,28</td>
</tr>
<tr>
<td>Phase volume fraction, %</td>
<td>Phase 1 61,9</td>
<td>46,9</td>
</tr>
<tr>
<td></td>
<td>Phase 2 34,0</td>
<td>44,1</td>
</tr>
<tr>
<td></td>
<td>Phase 3 4,1 9,0</td>
<td></td>
</tr>
</tbody>
</table>

According to the results obtained, the distribution in the modulus of elasticity $M$ shifted to the right in the composition nanomodified with carbon nanotubes in comparison with the composition without nanotubes. At the same time, the volume fraction of phase 1 with lower average values of $M$ and $H$ decreased and the volume fraction of phases 2 and 3 with large average values of $M$ and $H$ and with a denser volumetric packing of CSH gel particles increased.
For phases 1, 2, 3 of the distribution Mav for phase 3, which has the maximum average value of Hav of the distribution in H in samples with CNTs, the width of the distribution according to the corresponding Gaussian function has decreased, which is characterized by a decrease in the ratio SD / Mav (SD is the standard deviation - exponent in the Gaussian function), and shows a higher structural ordering of the CSH gel in the sample with CNTs. The change in the relative values of the Gaussian function (Figure 5) indicates a change in the structure of the CSH gel in the samples modified with CNTs.

Figure 5 – The ratio of the standard deviation to the mean value of the modulus of elasticity M and stiffness H in three phases (relative values of the Gaussian function)

1 – composition № 2 (SP); 2 – composition № 3 (SP + CNT)

According to tests by nanoindentation methods in studies [11], it is concluded that when CNTs are added to the cement matrix, there is a tendency to increase the high density CSH gel due to the low density CSH gel.

Infrared spectroscopy (IR)

Using the method of IR spectroscopy, the effect of CNT nanoparticles introduced into the SP-WB super-plasticizer with high water-reducing ability on the structure of Portland cement stone was assessed. Low doses of nanoparticles in relation to cement make it possible to isolate the effect of the effect of nanoparticles on the degree of polymerization of CSH gel separately from the effect on the rate of formation of CSH gel [12].

Table 4 – Dependence of the K coefficient on the modifier introduced into the cement

<table>
<thead>
<tr>
<th>Composition №</th>
<th>Position of the maxima of the absorption band of stretching vibrations of a silicon-oxygen tetrahedron</th>
<th>K_1/K_2/K_3</th>
<th>K_28/K_28</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Main maximum, cm⁻¹</td>
<td>Absolute intensity</td>
<td>Shoulder, cm⁻¹</td>
</tr>
<tr>
<td>Hardening of samples - 1 day</td>
<td>K = I_{a10}^{293}/I_{a10}^{994}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>№1</td>
<td>955</td>
<td>0.0278</td>
<td>973 / 988 / 993</td>
</tr>
<tr>
<td>№2</td>
<td>953</td>
<td>0.0327</td>
<td>976 / 989 / 992</td>
</tr>
<tr>
<td>№3</td>
<td>953</td>
<td>0.0360</td>
<td>976 / 987 / 991</td>
</tr>
<tr>
<td>Hardening of samples - 28 days</td>
<td>K_{28} = I_{a10}^{457}/I_{a10}^{904}</td>
<td>K_{28} = I_{a10}^{972}/I_{a10}^{1017}</td>
<td></td>
</tr>
<tr>
<td>№1</td>
<td>958</td>
<td>0.0114</td>
<td>993 / 1018</td>
</tr>
<tr>
<td>№2</td>
<td>957</td>
<td>0.0157</td>
<td>994 / 1018</td>
</tr>
<tr>
<td>№3</td>
<td>956</td>
<td>0.0164</td>
<td>994 / 1016</td>
</tr>
</tbody>
</table>

*K – the ratio of the relative intensities of the main maximum and the shoulder.

According to the data obtained (Table 4), the absolute intensity of the bands at the maximum of 953-955 cm⁻¹ and at the inflection points for composition № 3 (SP + CNT) is significantly higher than for compositions № 1 and № 2 (without CNTs), and the value of the coefficients K_28 is significantly lower than for compositions without CNTs. Analysis of the IR spectra of the control and modified samples shows that by the 1st day of hardening, the introduced CNTs contribute to some acceleration of the hydration of the main clinker minerals due to the high specific surface area and high surface energy of nanoparticles, which are additional centers of crystallization on the nuclei of neoplasms.

For ages 1 and 28 days, the data of thermogravimetry and IR-spectroscopy, the amount of hydrate water and total chemically bound water did not differ significantly in samples with CNTs compared to samples without nanoparticles. For an age of 28 days in the range (1/λ) = 3000-3600 cm⁻¹, there is no significant advantage in the rate of hydration of alite, the formation of hydrated water, CSH gel, and portlandite in the composition with CNTs. According to IR data in the range (1/λ) = 900-1100 cm⁻¹, the following changes in the structure of the CSH gel are expressed: 1) transition of hydroxides with degrees of polycondensation of silicon-oxygen tetrahedra n_1, n_2 close to 1, observed in IR-spectra at the age of 1 days, due to their combination into structures with a higher degree of polycondensation (28 days); 2) the content of hydroxides of calcium with the degree of polycondensation n_4 in the composition № 3 (SP + CNT) in comparison with the sample of composition № 2 - 10.4%.

Strength indicators

To carry out mechanical tests of specimens for compression and bending, a Testing 2.1005 testing machine was used. The studies were carried out on cement specimens-beams with dimensions of 40x40x160 mm, hardening under normal conditions. The test results are shown in the figure 6.

Figure 6 – Results of tests of cement matrix on a) axial compression, b) bending tension

Analysis of the results obtained indicates the effect of carbon nanotubes on the compressive and bending strength of cement matrix [19]. The increase in compressive strength with the introduction of CNTs was 12% relative to composition № 2 containing a plasticizer without CNTs as an additive. The combined effect of the plasticizer and CNT (composition № 3) had an increase in compressive strength by 21-23% relative to the composition without additive (composition № 1). The increase in
the bending strength of the cement stone was 21% (37 days) with the introduction of CNTs into the plasticizer (composition №3 relative to the composition № 2) and 51% (37 days) with the addition of CNTs and a plasticizer (composition № 3) in relation to the composition without additive (composition № 1).

Heavy Nano Concrete Research

To determine the strength characteristics and fracture toughness indices of nano-concrete, prism samples 100x100x400 mm and cube samples 100x100x100 mm were made [14-15]. The compositions differed among themselves by different contents of the main components of the mixture (Table 5).

<table>
<thead>
<tr>
<th>Component consumption, %</th>
<th>Component consumption, %</th>
<th>CNT modified additive</th>
<th>Workability grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>% from the mass of the binder</td>
<td>Mass fraction of solid nanocarbon to cement, %</td>
<td></td>
</tr>
<tr>
<td>Crushed stone FR 5-10 mm</td>
<td>18</td>
<td>45</td>
<td>0.8</td>
</tr>
<tr>
<td>Crushed stone FR 5-20 mm</td>
<td>19</td>
<td>45</td>
<td>0.5</td>
</tr>
<tr>
<td>Sand</td>
<td>20</td>
<td>38</td>
<td>0.7</td>
</tr>
<tr>
<td><em>D</em></td>
<td>23</td>
<td>39</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* Composition D contains 8% (by weight of cement) sulfoaluminate additive, 9% (by weight of cement) condensed compacted silica fume.

The tests of the samples were carried out on the specialized equipment of the Research Laboratory of PGS BNTU (Figure 7). The test results are shown in Figure 8.

Analysis of research results

1. The results of our studies of fracture toughness are confirmed [7], where it is shown that carbon nanofibers lead to an increase in the fracture toughness of the cement composite. Thus, the addition of 0.1 wt% CNTs led to an increase in fracture toughness by 4.5 % (0.68 ± 0.02 MPa√m), and the addition of 0.5 wt% CNTs - by 7.6 % (0.71 ± 0.04 MPa√m). For the unmodified cement composite, the fracture toughness was 0.66 ± 0.02 MPa√m.

2. Our position on the containment of cracking by carbon fibers at the nano-level coincides with the studies of Ange-Therese Akono [7, 16], which show that carbon nanofibers fill nanopores and connect grains of calcium hydrates (C – S – H), which leads to the effect of bridging and facilitating load transfer, individual CNTs are embedded in hydration products and delay nanocracks. Also in [17], SEM images are demonstrated that confirm the effects of the formation of bridges that transfer the load along nano- and microcracks.
3. Similar to our values of Young's modulus were obtained as a result of studies [7], where it was also established that the presence of carbon nanofibers affects the stochastic distribution of the macroscopic Young's modulus, causing a shift towards higher values (29.86 GPa for simple Portland cement, 31.43 GPa for cement + 0.1 wt% CNT and 36.12 GPa for cement + 0.5 wt% CNT).

4. The results of our studies using nanoinertization coincide with the results [18] in which the author concluded that CNTs modify C-S-H by increasing the amount of C-S at high rigidity, enhancing the cement paste matrix on a nanoscale and reducing porosity. It was also established in [7] that the presence of carbon nanofibers affects the stochastic distribution of the macroscopic Young's modulus, causing a shift towards higher values, which is fully confirmed by our studies.

5. The influence of CNTs on the increase in the strength characteristics of the cement composite in our studies coincides with the results of the studies by Bryan M. Tyson [17] - the increase in the values of flexural strength was 82%. Also in the research of P.V. Ryabchikov [19], it was shown that the increase in the compressive strength of fine-grained concrete with the introduction of CNT was 14.1% (without CNT - 67.4 MPa, with CNT - 76.9 MPa); an increase in tensile strength with a bend of 15.6% (without CNTs - 8.22 MPa, with CNTs - 10.2 MPa); increase in tensile strength during splitting 24.1% (without CNT - 2.20 MPa, with CNT - 2.73 MPa). Our results are also confirmed by the research of S.N. Tolmachev [20]: the strength of cement stone with CNTs increases by 1.5-1.9 times, the strength of solutions increases by 1.3-1.4 times, and the strength of concrete increases by 1.25-1.35 times compared with control formulations.

Conclusion

The studies carried out make it possible to assert that nanocarbon tubes have a significant effect on the properties of cement composites, including their fracture toughness. The use of dispersed reinforcement at the nanoscale is one of the methods for obtaining high-performance concrete, allowing the design of elements of buildings and structures with low strength indicators, but resistant to cracking and durability in general.

References


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