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ВЛИЯНИЕ МНОГОСЛОЙНЫХ НАНОТРУБОК НА РАЗРЫВНУЮ ПРОЧНОСТЬ

Акад. НАН Беларуси, докт. техн. наук, проф. ХРУСТАЛЕВ Б. М.[1)], докт. техн. наук, проф. ЛЕОНОВИЧ С. Н.[1)], докт. наук, проф. ЭБЕРХАРДШТАЙНЕР Й.[2)], доктора техн. наук, профессора ЯКОВЛЕВ Г. И.[3)], ПЕРВУШИН Г. Н.[3)]

[1)]Белорусский национальный технический университет, Минск, Беларусь,
[2)]Институт механики материалов и конструкций, Венский технический университет, Вена, Австрия,
[3)]Ижевский технический университет, Ижевск, Россия

INFLUENCE OF MULTILAYER NANOTUBES ON FRACTURE TOUGHNESS

NASB Acad., Dr. Sc. (Engineering), Prof. KHROUSTALEV B.[1)], Dr. Sc. (Engineering), Prof. LEONOVICH S.[1)], Dr. Sc., Prof. EBERHARDSTEINER J.[2)], Dr. Sc. (Engineering), Prof. YAKOVLEV G.[3)], Dr. Sc. (Engineering), Prof. PERVUSHIN G.[3)]

[1)]Belarusian National Technical University, Minsk, Belarus,
[2)]Institute for Mechanics of Materials and Structures, Vienna University of Technology, Vienna, Austria,
[3)]Izhevsk State Technical University, Izhevsk, Russia

1. Introduction

Problems of carbon nanotubes dispersion during modification of cement pastes

When developing cement pastes with improved mechanical characteristics, application of carbon nanodispersed systems [1, 2] are very efficient. The introduction of carbon nanosystems into mineral binding matrix composition is established [3–5] in order to result in micro-structures with forming new crystalline hydrate formations of higher density and strength.

The main purpose of this work is to establish an opportunity of dense cement concrete structure modification by means of multilayer carbon nanotubes Graphistrength by «Arkema» as a nanodispersed additive and to evaluate their influence on the modified cement matrix structure.

According to the technical literature [6, 7], the modification with carbon nanotubes results in an improvement of 15–20 % of the mechanical characteristics of cement concretes. At the same time the mineral matrices are able to increase their strength up to 2–3 times [8] after introduction of carbon nanosystems into the composition of the binder in the amount of 0,0024 % of the binder mass, as it is shown by several investigations. According to [9, 10] carbon nanotubes are able to change the matrix microstructure «due to increased content of calcium hydrosilicates of high density and decreased nanoporosity».

The main reason for contradictions of results obtained by different investigators is an insufficient extent of carbon nanotubes dispergation because they originally become granules due to superactivity during their synthesis. In this context the proper use of suitable equipment in ethanol medium for carbon nanotubes dispergation, as mentioned in [11] is of great importance. Li et al. [12] implemented ultrasonic treatment of multimural carbon nanotubes in the solution of sulfuric and nitric to provide better bond between cement matrix. In [13] polyacrilic acids and ultrasound was used to achieve homogeneous dispersion of multimural carbon nanotubes in water solution. In general, the open literature reports on an (insignificant) increase of the mechanical strength of cement matrix modified with carbon nanotubes.

The main reason of insufficient influence of nanosystems on the structure and properties of modified cement matrix is incomplete dispergation of nanotubes. During synthesis they generate bells or granules up to a size of 400–900 μm with high surface energy. At the same time nanoparticles hardly disperse into single nanostructures in water dispersive media and they require special technologies for their dispergation. The main goal when working with carbon nanotubes is to disintegrate bundles and large agglomerates arising during synthesis and to provide their stabilization in water suspension and steadiness of these nanotubes suspensions in storage.

To stabilize suspensions with nanostructures different surface-active agents (surfactants) [14] are used. Their molecules are adsorbed on the solid-liquid phase boundary surrounding separate nanotubes and their bundles [15, 16].

There are two ways of the process of synthesized nanoparticles dispergation i. e. obtaining particles with synthesized or ligand particles for material. In the first case there is an opportunity of surface modification of nanoparticles, e. g. substitution of ligands. And in the second case operations are performed with nanomaterial where collective properties of nanoparticles are of special importance. Hydrodynamic cavitation is the most optimal way of carbon nanotubes dispergation. Hydrodynamic cavitation has been used for about 50 years in industry. Although ultrasonic cavitation is widely used for intensification of technological processes, it requires higher energy expenditure in ultrasonic transmitters than in hydrodynamic cavitation devices. Due to this fact hydrodynamic devices are more prospective to be used for liquid medium cavitational treatment where interacting liquid flows produce cavitation. In general, the energy expenditure of hydrodynamic cavitation is 10–15 times less compared to ultrasonic cavitation.

Multilayer carbon nanotubes Graphistrength by «Arkema» consisting of layers of nanotubes with an outer diameter of 10 to 15 μm and an average density of 50–150 kg/m^3 were dispersed.

After the dispergation of the carbon nanosystems in the hydrodynamic device, carbon nanosystems with an effective diameter of 168,3 nm and with the a minimum diameter of 73,3 nm were obtained.

Sedimentation processes in suspensions are unavoidable due to the different densities of dispersion medium and discontinuous phase. In course of time, solid phase particles aggregate and precipitate. After 30 days storage the effective diameter of the nanosystems was 403,7 nm due to coagulation. However, sedimentation is a reversible process and the suspension can be dispergated again. The investigation of carbon nanotubes microstructure dispersions conformed polydispersity of carbon nanostructures in surfactant Polyplast SP-1 medium.

Coagulation of nanostructures with formation of large agglomerates takes place after one month storage of the dispersions. At the same time separate nanotubes were observed.

2. Materials and research methods

Samples for mechanical tests were produced in compliance with standard technique. Properties of the fine cement concrete on the Portland cement «П400-Д0» (CEM II/A-S 32.5R) and on the glass sand with fineness modulus M = 3,08 were investigated.

Carboxymethyl cellulose in combination with superplasticizing admixture Polyplast SP-1 was used as surfactants for carbon nanotubes dispergation. Sodium carboxymathyl cellulose is an anionic polymer i. e. the product of cellulose and monochloracetic acid interaction. Super plasticizing admixture Polyplast SP-1 is a mixture of sodium salts of polymethilennaphthalenesulfuric acids.

The microstructure and microanalysis of the concrete cement matrix were studied on bitmapped electronic microscopes FEI Quanta 200, XL 30 ESEM-FEG by «PHILIPS» and JSM JC 25S by «JEOL».

The analysis of nanosystem sizes in suspensions was performed on BI-MAS/plus 90 device. Total heat generation and rate of heat generation change were studied in thermos calorimeter.

Carbon nanotubes dispersion results in cement matrix structures with formation of a compact defect-free cover on the solid phase surfaces including cement and aggregate particles. This cover provides better bond with surfaces of these particles. Spatial skeleton cells in the structure of the modified cement matrix are formed due to contact interactions of the structured boundary layers. Spot contacts provide ultimately filled system where collective transition to the bond in short range order causes harsh strengthening due to spatial packing formation.

3. Testing specimens

The testing specimens were made of concrete mix from local raw materials (cement, crushed stone, sand). The size of specimens was 100×100×100 mm.

Two types of specimens where applied to investigate the stress intensity factor on normal separation and cross-section shift (fig. 1). Initiators of the crack were made after cooling to ambient temperatures by means of a saw after full preheating.

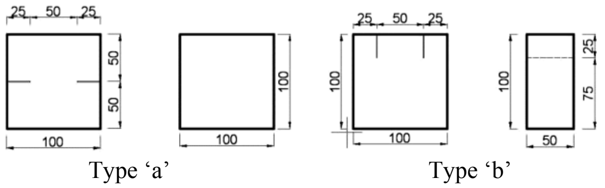

Fig. 1. Testing specimens

4. The definition method of stress intensity factor on normal separation and cross-section shift

Regularity of crack resistance is investigated by fracture mechanical methods. In this work the so-called nonequilibrium test is accepted as the basic method to experimentally determine crack resistance and toughness of destruction [17–22].

The nonequilibrium test is characterized by loosing the deformation stability of the specimen at the localization moment of deformation up to maximum loading with dynamic activating of crack.

The crack resistance characteristics are applied to:

- compare different concrete mixes, and the technological process of manufacturing and concrete quality control;
- assessments of concretes enabling a reasonable selection for construction;
- structural calculations with taking into account defects and application conditions;
- cause studies of structure destructions.

Type 'a' specimen cubes with two initial cracks were used for determining K_{IC}. The tests were performed under the scheme of central compression on a press by means of two supports made of metal bars (fig. 2a, b). The cube destruction occurs unstably within a plane of a moving crack between the two oppositely cuts.

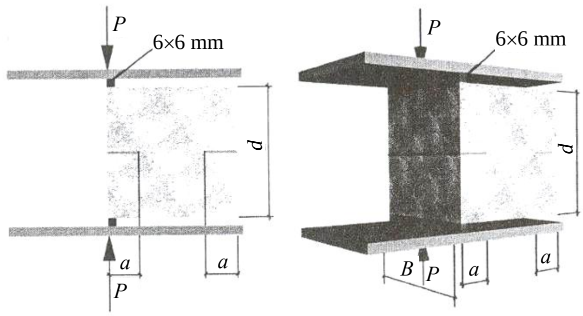

Fig. 2a. Scheme of test specimens of type 'a'

Fig. 2b. Specimens before and after K_{IC} tests

The value of K_{IC} was determined according to the following equation

$$K_{IC} = \frac{P}{Bd^{1/2}}\left[18{,}3\left(\frac{a}{d}\right)^{1/2} - 430\left(\frac{a}{d}\right)^{3/2} + 3445\left(\frac{a}{d}\right)^{5/2} - \right.$$
$$\left. -11076\left(\frac{a}{d}\right)^{7/2} + 12967\left(\frac{a}{d}\right)^{9/2}\right], \qquad (1)$$

where P – the load, destroying the specimen, in MN; B – the thickness of the specimen; d – height or width of the specimen; a – depth of a cut (all dimensions in meter).

The crack resistance on cross-section shift was determined in tests with type ‘b’ specimens by means of a loaded plate between the two parallel cuttings (fig. 3a, b). The big advantage of this test is that the type ‘b’ specimen can be gained from the already tested type ‘a’ specimen (the same cube). Thus, the factor of normal separation K_{IC} and cross-section shift K_{IIC} were defined on one and the same concrete fragment.

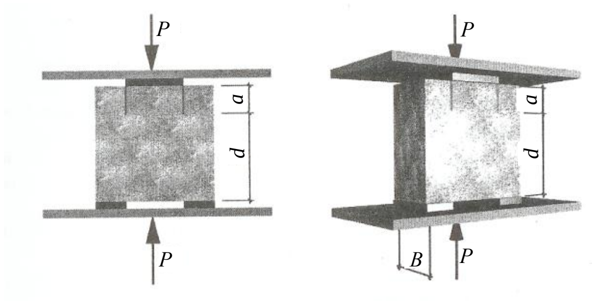

Fig. 3a. Scheme of test specimens of type ‘b’

Fig. 3b. Specimens before and after K_{IIC} tests

5. Experimental data K_{IC}, K_{IIC}, E, G_{IC}

Table 1

Experimental data of concrete cube tests on fracture toughness.
Determination of stress intensity factor at normal separation K_{IC}

Samples	Date of fabrication	Date of test	Mass of sample, g	Size of ample, cm	Ultimate load P, kN	Average value of load P, kN	$K_{IC_{cp}}$, MN·m$^{-3/2}$	Specific energy of quasi-static destruction $G_{IC} = K_{IC}^2/E^*$, N/m
К-2	08.08.2011	06.09.2011	2390	10×10××10	9,87	10,64	0,623	11,25
К-3			2410	10×10×10	9,70			
К-4			2406	10×10,1×10	12,34			
В-2			2402	10×10×10	8,49	10,08	0,59	10,09
В-3			2386	10×10×10	9,18			
В-4			2384	10×10×10	12,56			
2F-2			2388	10×10×10,1	6,47	8,99	0,526	8,02
2F-3			2396	10×10,1×10	11,74			
2F-4			2402	10×10,1×10	8,76			
К-1	09.08.2011	06.09.2011	2422	10×10,1×10,1	11,16	**10,52**	0,616	10,99
К-3			2410	10×10×10	6,73			
К-4			2418	10×10,1×10	13,67			
О-1			2414	10×10×10	10,17	9,54	0,558	9,03
О-3			2416	10×10×10,1	8,85			
О-4			2406	10×10×10	9,61			
Ю-1			2398	10×10×10	11,67	**11,20**	0,656	12,47
Ю-2			2396	10×10,1×10	10,38			
Ю-3			2423	10×10×10	11,54			

The stress intensity factor on cross-section shift was determined according to the following equation

$$K_{IIC} = \frac{P}{2aB}\sqrt{lY(l,b)}, \qquad (2)$$

where P – the load, destroying the specimen, in MH; $Y(l, b)$ – correction index = 0,97; B – width of the specimen; a – depth of a cut (all dimensions in meter).

The stiffness properties of the investigated concrete were determined using ultrasonic measurements. Knowing the path length, the measured travel time (t) can be used to calculate the complex modulus of elasticity (E) as follows

$$c_l = \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}}, \qquad (3)$$

where c_l – ultrasonic pulse velocity; ν – Poisson's ratio; E – complex modulus of elasticity; ρ – density of concrete specimens.

Fig. 4. Ultrasonic pulse velocity method

Consideration of the elastic deformation of concrete enables to define the specific energy of quasi-static destruction (G_i) through the quasi-static stress intensity factor

$$K_i = \sqrt{G_i E_b}. \qquad (4)$$

Table 2

Experimental data of concrete cube tests on fracture toughness. Determination of stress intensity factor at cross-section shift K_{IIC}

Samples	Date of fabrication	Date of tests	Ultimate load P, kN	Average value of load P, kN	$K_{IIC_{cp}}$, MN·m$^{-3/2}$
1	2	3	4	5	6
К-2(1)	08.08.2011	07.09.2011	73,92	75,48	4,7
К-2(2)			72,11		
К-3(1)			55,23		
К-4(1)			77,81		
К-4(2)			78,06		

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1	2	3	4	5	6
В-2(1)	08.08.2011	07.09.2011	85,32	92,45	5,75
В-2(2)			96,32		
В-3(1)			100,90		
В-3(2)			83,55		
В-4(1)			87,25		
2F-2(1)			76,12	83,93	5,22
2F-2(2)			86,51		
2F-3(1)			83,99		
2F-3(2)			83,44		
2F-4(1)			89,61		
2F-4(2)			64,65		
К-1(1)	08.08.2011	07.09.2011	87,40	88,83	5,532
К-1(2)			87,44		
К-3(1)			95,36		
К-3(2)			75,94		
К-4(1)			93,60		
К-4(2)			80,37		
О-1(1)			85,21	93,94	5,851
О-1(2)			97,60		
О-3(1)			93,36		
О-3(2)			82,83		
О-4(1)			98,58		
О-4(2)			94,95		
Ю-1(1)	08.08.2011	07.09.2011	102,2	98,55	6,1377
Ю-2(1)			100,7		
Ю-2(2)			92,58		
Ю-3(1)			98,72		
Ю-3(2)			88,73		

Table 3

Experimental data of concrete cube tests on fracture toughness. Determination of K_{IC} and K_{IIC}

Samples	Ultimate load (scheme 1), kN	$K_{IC_{cp}}$, MN·m$^{-3/2}$	Ultimate load (scheme 2), kN	$K_{IIC_{cp}}$, MN·m$^{-3/2}$
К-1	9,13	0,534	29,0 45,38	2,826
К-2	6,89	0,403	–	–
К-3	5,93	0,347	44,51 41,70	2,772 2,597
К-4	7,53	0,441	43,40 49,36	2,702 3,075
О-2	7,55	0,442	57,39 53,89	3,574 3,356
О-3	5,70	0,334	48,45 48,08	3,017 2,994
О-4	7,44	0,435	57,59 59,36	3,586 3,697
О-2*	0	–	43,20 40,35	2,69 2,513

6. Conclusions

The presented results allow to conclude, that the method of nonequilibrium tests of cubes with initiated cuts delivers a quite adequate picture of the crack resistance and toughness of destruction of usual and high-strength concrete.

From non-destructive stiffness tests using ultrasonic pulse velocity measurements, the value of the complex modulus of elasticity was determined.

The experimental results of the stress intensity factors K_{IC} and K_{IIC} allow to analyze cracking and concrete destruction, and to develop new high strength materials and to perfect designing.

Based on own experimental results the energy of quasi-static destruction G_i were measured in addition.

Cement concretes modified with multilayer carbon nanotubes change its morphology of crystalline hydrates with formation of the contact zones of increased density of the aggregate surface according to microstructural analysis of new formations. Such structures increase the strength resistance of the concrete, which is proved by results of physical and mechanical tests of the concrete modified with carbon nanotubes.

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