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STRUCTURE AND PROPERTIES OF CALCIUM SULFATE HEMIHYDRATE MODIFIED WITH CARBON NANOTUBES

СТРУКТУРА ТА ВЛАСТИВОСТІ НАПІВГІДРАТУ СУЛЬФАТУ КАЛЬЦІЮ, МОДИФІКОВАНОГО ВУГЛЕЦЕВИМИ НАНОТРУБКАМИ

СТРУКТУРА И СВОЙСТВА ПОЛУГИДРАТА СУЛЬФАТА КАЛЬЦИЯ, МОДИФИЦИРОВАННОГО УГЛЕРОДНЫМИ НАНОТРУБКАМИ

Abstract. This paper presents research of the influence of concentration of nanomodifiers in the form of carbon nanotubes on the structure and physical and chemical properties of calcium sulfate hemihydrate. With the same nanomodifier content in the gypsum matrix, the maximum increase in strength is achieved by using CNTs functionalized with hydroxyl groups and makes 27–29 %. The increase in strength of the CNT-containing gypsum composite occurs due to the accelerated process of calcium sulfate dihydrate crystallization at the grapheme surface.
Keywords: gypsum binders, nanomodifiers, carbon nanotubes, nanocomposites, strength.
Анотація. У даній статті приведені дослідження впливу концентрації наномодифікаторів у вигляді вуглецевих нанотрубок на структуру та фізико-хімічних властивості напівгідрату сульфату кальцію. При одинаковому вмісті наномодифікатора в гіпсовій матриці максимальне збільшення міцності досягається за рахунок використання вуглецевих нанотрубок, функціоналізованих гідроксильними групами, і становить 27–29 %. Збільшення міцності гіпсової композиції, що містить вуглецеві нанотрубки, відбувається з початком прискорення процесу кристалізації дигідрату сульфату кальцію на поверхні графену.
Ключові слова: гіпсові в'яжучі, наномодифікатори, вуглицеві нанотрубки, нанокомпозити, міцність.
Аннотация. В данной статье приведены исследования влияния концентрации наномодификаторов в виде углеродных нанотрубок на структуру и физико-химические свойства полугидрата сульфата кальция. При одинаковом содержании наномодификатора в гипсовой матрице максимальное увеличение прочности достигается за счет использования углеродных нанотрубок, функционализированных гидроксильными группами, и составляет 27–29 %. Увеличение прочности гипсового композита, содержащего углеродные нанотрубки, происходит за счет ускоренного процесса кристаллизации дигидрата сульфата кальция на поверхности графена.
Ключевые слова: гипсовые вяжущие, наномодификаторы, углеродные нанотрубки, нанокомпозиты, прочность.

Introduction

Last time the development of nanostructured materials has become one of the relevant scientific directions of science about nanomaterials [1-4].

Creation of nanocrystalline materials, coatings and strengthening layers with improved performance properties is essential to the optimization of structures, improvement of their reliability, energy-saving, and resource-saving as well as the improvement of strength and antiwear properties of materials

Review of papers

The articles [5-8] represent the analysis of up-to-date approaches to implementing nanotechnology principles in the science of construction materials. The assessment of the impact of nanomaterials on the initial stage of the structure formation process – heterogeneous nucleation (nucleation) has been conducted. The authors of papers investigated the influence of main factors on heterogeneous nucleation, and thus it was determined that the mentioned factors form three mechanisms of influence of primary nanomaterials on the material structure formation process.

A.A. Yeliseyev and A.A. Gusev [9, 10] represent the most important features of functional nanomaterials including their structure, physical properties, and synthesis and research methods; moreover, they describe cases of use of nanomaterials for creating nanoelectromechanical systems, various devices for nanoelectronics and molecular electronics as well as for creating magnetic recording media. These books represent the main methods for obtaining isolated nanoparticles, ultradispersed powders, and dense nanocrystalline materials. Size effects in isolated nanoparticles and dense nanocrystalline materials were discussed in detail. The works also demonstrate an essential role of interfaces in the formation of structure and properties of nanomaterials. The analysis of visualized patterns describing peculiarities of structure and properties of substances in the nanocrystalline state was performed [10].

Various methods for obtaining ultradispersed (nano-) materials were considered namely, mechanical, physical, chemical and biological methods. Up-to-date ideas on electrical, magnetic, thermal, optical, diffusion, chemical, and mechanical properties of nanomaterials were summarized [11-14]. The materials properties dependence on the material structure and geometrical dimensions of nanoparticles, storage and transportation of nanomaterials were also examined.

Based on the performed analysis of reference sources it seems reasonable to study the impact of carbon nanotubes on the structure and main physical and chemical properties of calcium sulfate hemihydrate.

Research objective

Research of the influence of concentration of nanomodifiers in the form of carbon nanotubes on the structure and physical and chemical properties of calcium sulfate hemihydrate.

Research methods

Methods of X-ray phase analysis and calorimetric tests have been used to investigate the mineralogical composition and kinetics of processes occurring in a modified matrix. The structure, size, and morphology of newgrowths have been investigated by means of scanning electron microscopes.

In order to improve the performance of carbon nanotubes (CNT), CNT's surface has been chemically modified with the functional groups [14]. Carboxylation of carbon nanotubes has been carried out by the interaction of nanotubes with various oxidizing agents [16-18]. For the oxidization of CNTs by hydroxyl groups, a mechano-chemical method [14, 18] has been used, which involves the milling of CNTs and alkali within 60 minutes.

Research findings: The influence of the content of nanomodifiers – carbon nanotubes on the structure and main physical and chemical properties of gypsum binders has been determined.

The analysis of gypsum binder and building gypsum-based samples (both non-modified and modified with the CNTs) has been performed during the research.

During this research, we have used carbon nanotubes obtained from a catalytic hydrocarbon pyrolysis unit at the Center for Carbon Nanomaterials of the Vladimir State University named after A.G. And N.G. Stoletovs, Russia [14, 16-18].

The multi-walled carbon nanotubes (CNT) have over 30 layers, length 2-5 μm; diameter 10-60 mm, specific surface area 120 m^2/g, purity 95 % [19].

Gypsum binder with the addition of surfactant in the amount of 0,4 % of the dry weight of binder has been used as a reference standard (Table 1).

Carbon nanotubes have been added in the form of a suspension that has been prepared as follows: multi-walled carbon nanotube powder has been first added to a plasticizer water solution with further processing in an ultrasonic dispersion machine, which has enabled us to obtain the stable dispersion of waterborne nanoparticles. Polycarboxylate P-11 from the Macromer Research and Development Enterprise (Vladimir, Russia) [14, 16-18] and Sika Retarder plasticizer (Switzerland) have been used as plasticizers. The suspension preparation process has been controlled based on the parameters as follows: suspension density, colloidal system stability (zeta-potential determination), CNT concentration, and viscosity.

The conducted research studies on the determination of ultimate bending strength and compression strength of bending test beams at 2 hours have shown that the increased nano-additive content results in the improvement of structural characteristics of a composite material. The maximum increase in strength (27–29 %) can be achieved by using carbon nanotubes with hydroxyl groups. When using the initial nanotubes the increase in strength is 13–15 %.

During the research studies, the analysis of the initial gypsum binder, building gypsum-based samples (unmodified and modified with carbon nanotubes) has been conducted (Table 3) with the use of X-ray diffractometer X`Pert PRO MPD 3040/60 Fa. PANalytical (Institute of Ceramics, Glass and Construction Materials (IKGB TU Bergakademie Freiberg)). The following materials have been used as structural models of mineral components for the full-profile quantitative X-ray phase analysis: gypsum $CaSO_4 \cdot 2H_2O$ (№01-074-1433); bassanite $CaSO_4 \cdot 0{,}5H_2O$ (№01-081-1849); anhydrite $CaSO_4$ (No.01-086-2270), carbon C (№01-075-2078) [19].

Changes in the mineralogical composition can be identified in a cyclic mode. Each cycle lasts 5 minutes and 16 seconds.

Results of the quantitative X-ray diffraction analysis using the Rietveld method are given in Table 2.

The X-ray photograph (Fig. 1, Curve 1) of the gypsum sample at the 1st cycle shows a large amount of both calcium sulfate hemihydrate (24 %) and calcium sulfate dihydrate (up to 67 %) after 1 hardening cycle. The hydration process is completed after 95 minutes at the 18th cycle (Fig. 1, Curve 2). Main impulses of intensity of the reflected lines of calcium sulfate dihydrate correspond to 6200, 4250, and 3300.

Table 1.

Content and properties of the reference standard (over 100%)

Gypsum, %	Surfactant, %	W/G %	pH	Setting time, min		Strength, MPa:	
				Start	End	Compression strength	Bending strength
100	0,4	59	7,2	6	8	4,6	2,2

Date in the X-ray photograph of CNT-modified gypsum binder hardening are indicative of the intensification of the hydration processes. The hydration process is also completed at the 18th hardening cycle (upon the expiration of 95 minutes); however, calcium sulfate dihydrate formation rate is considerably higher. The lines of main impulses of calcium sulfate dihydrate correspond to 11300, 9900, 6000 (Fig. 2).

During the hydration of unmodified building gypsum within 18 cycles (95 minutes), the process is running with the formation of $CaSO_4 \cdot 2H_2O$ in the amount of up to 88%. Under the same conditions, the hydration of modified gypsum reaches 93%, and the amount of unreacted $CaSO_4$ even slightly drops (Table 2).

Based on the data of quantitative X-ray patterns and X-ray patterns over time, the addition of CNTs results in the hydration process enhancement as well as more complete conversion of calcium sulfate hemihydrate to dihydrate.

The analysis of the microstructure of gypsum composition samples has shown that by adding the modifying additive a denser structure of gypsum samples has been formed, which improves the physical and mechanical properties of the calcium sulfate matrix.

It may be assumed that nanodispersed CNT additives act as "crystallization nuclei" on the surface of which calcium sulfate matrix structuring occurs with the achievement of improved structural characteristics of the gypsum composition [15, 20].

Based on the research studies and calculations performed by V.E. Vaganova, V.V. Reshetniak, V.N. Derevianko [15, 20], the interaction of a calcium sulfate dihydrate molecule with the graphene-like surface has been proved using quantum chemical analysis methods. Besides, it has been found that a calcium sulfate dihydrate molecule tends to chemically interact with the surface of the CNTs through a calcium ion due to the overlap of 3p valence Ca^{2+} orbitals and 2p carbon orbitals [15, 20].

The change in the charge of a Ca^{2+} ion (around 17% compared to the initial charge) and in charges of other atoms by no more than 2 % due to the interaction of $aCaSO_4 \cdot 2H_2O$ molecule with the graphene-like surface is indicative of a slight change in the chemical activity of peripheral atoms of the molecule which are involved in intermolecular interactions in a calcium sulfate dihydrate crystal [15, 20]. Thus, strength properties of the CNT-modified gypsum binder has been improved through the accelerated processes of calcium sulfate dihydrate crystallization at the graphene-like surface.

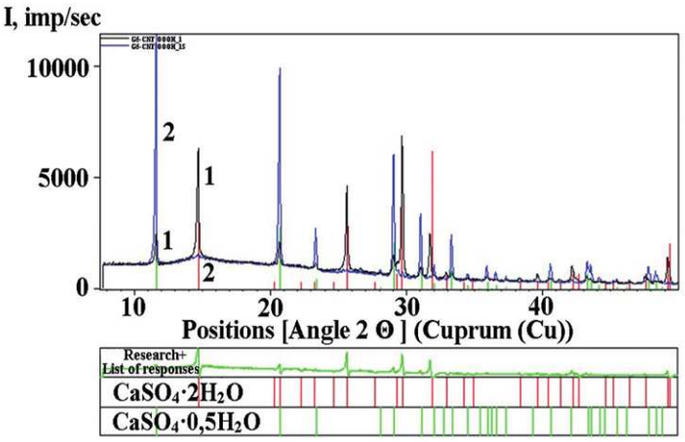

Fig. 1. Rietveld diagram of building gypsum hardening through time G-5:
1 – after the 1st cycle;
2 – after the 18th cycle.

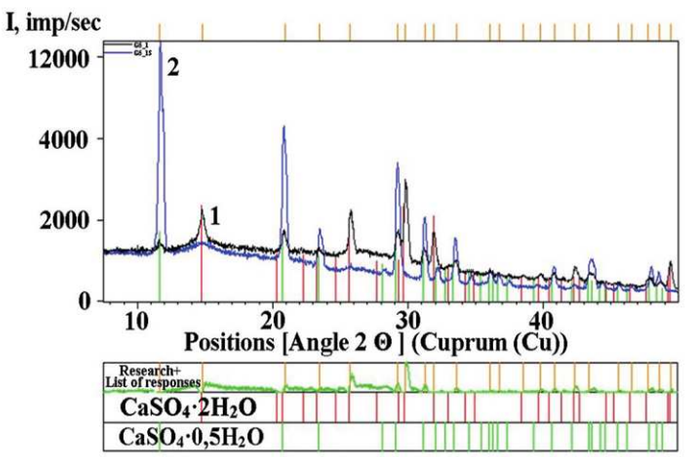

Fig.2. Rietveld diagram of building gypsum hardening through time G-5:
modified with CNTs:
1 – after the 1st cycle;
2 – after the 18th cycle.

Table 2.

Changes in mineralogical composition, % Wt

Hardening cycles	$CaSO_4 \cdot 0,5H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4$	Impurities
Mineralogical composition of unmodified calcium sulfate hemihydrate after 1 hardening cycle, Curve 1, Fig. 6	24	67	4	5
Mineralogical composition of unmodified calcium sulfate hemihydrate after 18 hardening cycles, Curve 2, Fig. 6	3	88	4	5
Mineralogical composition of modified calcium sulfate hemihydrate after 1 hardening cycle, Curve 1, Fig. 7	14	77	4	5
Mineralogical composition of modified calcium sulfate hemihydrate after 18 hardening cycles, Curve 2, Fig. 7	1	93	1	5

Conclusions

The introduction of carbon nanostructures into gypsum compositions leads to the increased mechanical strength through the formation of a fine crystalline needle-shaped structure of higher density. With the same nanomodifier content in the gypsum matrix, the maximum increase in strength is achieved by using CNTs functionalized with hydroxyl groups and makes 27–29 %. The chemical fictionalization of the surface of carbon nanotubes contributes to the reduced sedimentation effect that is typical for nanoparticles; moreover, it makes it possible to achieve more uniform nanostructure dispersion throughout the modified material volume and provides chemical interaction between the substance matrix and nanotubes.

The interaction of calcium sulfate dihydrate molecule with the graphene-like surface is a chemical process, which has been confirmed by quantum-chemical analysis methods. The increase in strength of the CNT-containing gypsum composite occurs due to the accelerated process of calcium sulfate dihydrate crystallization at the graphene-like surface.

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