PERSPECTIVES OF APPLICATION OF NANOTUBES IN MODERN COMPOSITE BUILDING MATERIALS

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ABSTRACT

There are described the perspectives of application a carbon and hydro silicate nanotubes in modern building compositional materials …

Key words: carbon and chrysotile nanotubes, compositional building materials, reinforcement.

ACTUALITY OF THE TOPIC

Modern technology is in need of materials, including construction, for usage in extreme conditions. This requires the creation of new materials with properties that are absent for those natural and traditionally used. The combination of materials with different properties led to the creation of composite materials with new technological and performance properties. The most important advantage of composite materials is the possibility of creating products with given properties that best correspond the conditions of use in a best way. Composite materials can have properties practically unattainable using traditional construction materials. Composite materials consist of a binder that provides the integrity of the material and various fillers (reinforcing, weighting, or conversely, lightening (gases), etc.), providing various required functional characteristics of products. Depending on the type of reinforcing filler (fibrous, flake, ribbon or powder-like), composite materials are divided into fibrous, flake, dispersion-hardened or mixed-reinforced. The efficiency of obtaining the material with the desired properties depends on the proper selection of fillers and matrix (and their compatibility). Basis for efficient production of new composite materials is knowledge of the physicochemical nature of phenomena and the ability of purposeful formation of required and unique performance characteristics at nanoscale level. The level of binding energy between the neighboring crystals predetermines the future strength of polycrystalline materials. The influence of mineral fillers on the processes of hydrate formation is expressed in different ways, often in a more rapid

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formation of gel-like products of different composition or in the formation of specific structures (calcium hydrocarboaluminate and others). Practical research of the influence of mineral additives on structure formation of cement concrete [1] shows us that the use of microfillers improves concrete strength by 1.5-2 times at a constant water-cement ratio. This is because the smallest particles of microfiller which are similar in size to the colloid ones and are located between the grains of cement or near them, form new centers of crystallization. This speeds up this process and increases the strength of cement stone and concrete. At a certain ratio of the particle size of cement and filler there is an effect of hardening of binding [2]. It is determined that, in dense concrete, depending on the given tasks and properties of original materials, it is wise to substitute from 20 to 50% of cement for microfillers. Associating of a properly chosen microfiller into the concrete compound provides reducing water demand of cement produced as well as saving the proper rheology and adhesion properties of cement paste. A given strength of cement and concrete is provided and at the same time setting qualities and creeping of concrete are reduced[3]. Comprehensive study of hydration of the separate clinker minerals and Portland cements showed us that in all cases, milled mineral fillers accelerate the processes of hydration (an increase of volume of the hydrates formed and an increase of intensity of the process) significantly (for about 1.5-2 times). During the process the period of formation of individual hydrates is shifted to an earlier stage. A similar effect of fillers can be explained by high surface energy that is spent on formation of thermodynamically stable state by means of the phenomena of chemisorption and the subsequent formation of crystalline hydrate nuclei[4]. Thus, by applying mineral agents, we can control the structure formation of cement stone and get the best structure and properties of concrete under specific operating conditions.

It has long been known that the use of fibers as a reinforcing component can solve many problems, dramatically increasing the strength properties of products and constructions at the nanoscale level and as a result in the whole volume while reducing the consumption of materials and thermal heat capacity at the same time. The higher the dispersion of the particle is, the greater activity should be expected from it. An interest to nanoparticles can be explained by their unique properties. Nanoparticles, in particular carbon and silica nanotubes, which have very high tensile strength, are characterized by a huge surface potential concentrated in nanovolume. Their use as one of the components of the polycrystalline composite materials can serve as a promoter intensifying of the process of forming in a matrix of smaller crystals. The number of these crystals is much bigger than without them. The strength of microcrystalline materials is higher than that of coarse-crystallines. In the production of special high-strength composites the fine-grained fibrous (reinforcing) fillers such metal, carbon, silicate are used. Despite the extremely high publication activity on the application of carbon fibers, which indicates their importance, the data on their use in technology of building materials are very poor due to low volumes of their production. Building materials require thousands of tonnes of them. At the same time, Russia has the world's largest reserves of fibrous mineral – chrysotile which has nanotubes with the diameter of ≈ 30 nm aggregated into threads, which are a natural composite material. It easily splits into filaments. (*Fig. 1*) By techno-economic indicators this mineral at present day is out of competition. Chrysotile is a layered magnesium hydrosilicate, it has a tubular morphology crystals, which consist of a twisted in tube and condensed between each other tetrahedral (silica oxygen) and octahedral (burcite) layers (*Fig. 2*). Twisting the layers into a tube is explained by the fact that the unit cell parameters of brucite layer are a bit bigger than those of silica oxygen. Compensation of tenses in the condensed layer leads to the formation of the tube, the outer layer of which is brucite - $Mg(OH)_2$. Magnesium (an alkaline-earth element) causes an alkaline reaction of aqueous suspension of chrysotile asbestos, while the surface hydroxyl groups cause an increased reactionary reactivity of chrysotile as a filler.

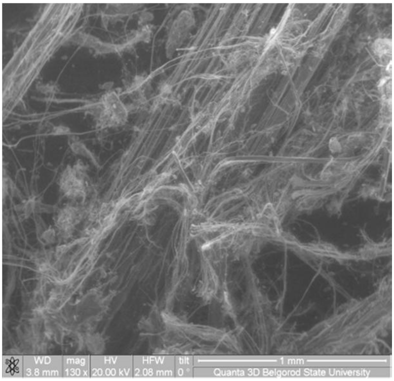

Fig. 1 – View of Bazhenov fiber commercial chrysotile P-3-60

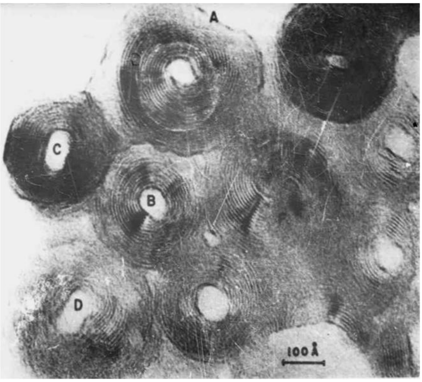

Fig. 2 – Electron-microscopic picture of a cross section of chrysotile fibers [5]

Currently researchers are paying great attention to disperse reinforcement [6-8] and to nanomaterials [9-12]. Nanotubes in a fiber concrete are nanoreinforcing elements of a cement matrix. The consequence is an increase of its compressive strength, tensile and impact strength. The uniqueness of the application of carbon nanotubes astralenes with the diameter of <1 nm is in effect on the growth of the strength of cement stone at dosages of hundredths or even thousandths of a weight percent of cement [13].

Unfortunately, very little attention is wrongly paid to nanosilicates. In this work it is only possible to briefly describe the most effective ways of application nanotubes, especially of those with the modified surface. The representative of the silicate nanofibrous reinforcing fillers is a modified by thixotropic appretams fine-grained chrysotile "Silodeks Sx24" by VR Grace Co., Ltd. Firm. It was designed to give thixotropic properties to high-strength polymer composites. It should be noted that the range of possible uses of nanofibers in the development of nanomaterials technology is expanding rapidly.

The most promising is the reinforcement of cement matrix of concrete on micro and nanoscale levels. While doing this the fiber concrete is received. Fiber concrete, as well as traditional concrete is a composite material including additional distributed in a volume fiber reinforcement [14] That means that during preparing the concrete mix the correct proportion of natural, artificial, synthetic or metallic fibers of a special section are added into it. The properties of fiber concrete as a composite material are determined by the properties of its components. Steel or non-metallic (carbon, silicate or polymer) fiber is one of the most important components of fiber-reinforced concrete. Dispersed reinforcement by a fiber allows to offset the major shortcomings of concrete to a higher extent. They are low tensile strength and brittle fracture. Fiber-reinforced concrete have several times higher characteristics such as: compressive strength, axial tension, bending tension, the initial modulus of deformation, shear strength, frost resistance, water resistance, crack resistance, heat resistance, fire resistance, abrasion, fatigue strength, resistance to cavitation, impact strength (toughness)

The most important characteristic of fiber reinforced concrete is a tensile strength. It is not only a direct characteristic of the material, but also indirect and it shows its resistance to other influences, as well as its durability.

A very important characteristic of fiber-reinforced concrete is an impact strength (toughness), which depending on the material and the degree of reinforcement is from 3 to 20 times greater than conventional concrete in terms of destruction, which ensures its high technical and economic efficiency when used in building structures and their repair.

The aim of our development is the creation of high-strength compositions for use in extreme conditions.

To achieve this goal we should have got a fibrous silicate nanofillers that improve the technological and operational properties of composite materials, i.e, allowing to get more qualitative products from original materials.

The original materials and the composites obtained were studied by modern methods of analysis - X-ray phase and structural, transmission and scanning electron microscopy, photoelectron spectroscopy, electron microdiffraction, chemical, pH-testing, derivatography, infrared spectroscopy.

For serial large-scale production of nanoreinforced building materials with new and unique technological and operational properties some items are required:

✓ large-scale production of nanofibers with low cost with given technological characteristics;

✓ development of technologies of introduction of the nanofibers in the technological mixes;

✓ studying the properties of nanocomposite construction materials and development of production technologies

Hardening of composite materials is achieved by selecting the efficient composition of components and strengthening of ties between them. In studying the influence of the degree of filling of the composite material by the fibrous component it was found that by increasing the mass content of fiber of the same length the tensile strength and elastic modulus increase compared to the unfilled matrix. For example, for a composite with a fiber length of 3 mm the increase in strength is the highest concentrations of filler up to 10%, at a concentration of 10 to 40% of filler the strength of samples is increased lesser. The increase of fiber content of more than 40% does not lead to a further increase in the strength of the samples.

For samples with equal mass content of fibers of various lengths (from about 25 microns to 10 mm), we saw an increase in tensile strength with increasing fiber length, which can be explained by an increase in force that holds the fiber matrix, which, in turn, reaches a maximum and a further increase of length of the fibers doesn't lead to its increase. Characteristic ratio (the ratio of fiber length to its diameter) depends on the type of the matrix and is chosen empirically.

We worked out the dispersion technologies of chrysotile production to nanofibers and their introduction into the concrete mixtures. We made structural and morphological studies of changes in the hydration products of cement clinker minerals and formation features of their structure with the introduction of nanofibers. We obtained materials with higher technical and economic indicators. The application of nanochrysitile allows to receive high-strength concrete with a compressive strength of 100 MPa or more. Basing on these data we can reasonably say about the influence of nanotubes on a grade (at the age of 28 days.) strength of the composite cement and a very substantial increase in its hardening on the early stages This reduces energy costs in manufacturing from the concrete of handling strength. Application of nanoconcretes reduces the turnover forms (in production) and the formwork (in-situ concreting of building structures), increasing economical effectiveness efficiency. In addition, nanoreinforcing of porous [15], constructional heat-insulating and heat-insulating concretes provides a significant increase in their strength, which is one of the major problems of building materials science.

Perspectives for further practical use. Traditionally they have paid and continue to pay particular attention to the influence of fillers on the mechanical strength of the product, but the fillers can improve also technological properties. They can regulate flow (giving thixotropy to mixtures and, consequently, improving their stability of shape and moldability), reduce the chemical and thermal contractions in volume (the elimination of cracking). Fillers can change the electrical, magnetic and thermal properties, reduce flammability (flame resistance), to change the friction coefficient, optical properties (color and coloration), density, porosity, hardness (wear resistance), corrosion resistance, permeability, tensile strength, bending and impact and of course, the cost [16]. We created nanoreinforcing filler for using it in composite materials operating in extreme conditions, but it can be successfully applied in all economic sectors, particularly in high voltage electric-power industry, because in addition to the properties listed, it has high-arc resistance.

The following areas of rational use of nanofiber concretes can be possible (construction and repair):

- Monolithic design, construction and spatial coverage: fortifications, explosive and burglar structures, baffle dams, lining of tunnels and irrigation canals, water tanks and other liquids, highways, industrial floors and bridge decks, fire-retardant plaster, etc.;
- Prefabricated elements and structures: piles, railroad ties, pipes, beams, stairs, wall panels, roof panels and roof tiles, floating dock modules, offshore structures, plates of airfield, road, walkway covers and mounting channels, curtain elements of bridges, piling, heating elements, the elements of spatial surfaces and structures, ornamental accessory.

CONCLUSIONS

Production of building materials of new generation with nanodispersed reinforcement is one of the most promising branches. The effectiveness of the introduction of nanotubes of chrysotile as a krentyi agent with high surface energy in the cement composition is based on lowering the energy threshold of the beginning of crystal formation from an aqueous solution, which is saturated with ions of cement clinker minerals, as a result of its interaction with water.

The studies confirm the probability of the impact on hydration and physical and mechanical properties of hardening cement compositions using aggregates and fillers of specific nature.

For composite materials used in various fields of modern and advanced equipment, the technology of production of fine-grained chrysotile with desired properties (nanofiller) was investigated. It reduces shrinkage deformation and prevents the formation of cracks in thin-walled and large-sized products.

Tests showed us that the designed filler can be successfully used in building compositions, including porous materials, adhesives, mastics, putties, high-strength mortar concrete, concrete shielding of nuclear reactors and other.

The observed effect of the length of reinforcing fillers is of great importance in the technology of composite materials: no need to seek for maximal filling of the matrix by only one fiber and the fiber should not be used much longer than required for optimal composition.

The commercial production of nanofiller, production of composite materials and products from them for a modern and projected technology is organized.

In the future, for targeted development of new construction of nanocomposites with desired properties in-depth studies aimed at developing new technologies of surface modification of nanofibril are needed because the fibrous morphology of the nanocrystals substantially increase the strength of the matrix of composite materials. By modification of the filler we can obtain the required technological properties of the mixtures and properties of indurated compositions.

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