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Properties of Isomorphs Analogs of Chrysotile

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Fiber is an important component of high-strength reinforcing composite materials. Everyone knows that nano-tubular crystals of chrysotile have unique physical and mechanical properties, but not everyone knows that chrysotile has little studied structural (isomorphic) analogues. The purpose of this work is to determine the optimal parameters of synthesis and base properties of nano-tubular crystals Mg-Ni chrysotiles. The optimal temperature ranges and pressure for the synthesis of nano-tubular crystals all synthesed chrysotile 473-673 K, 19.6-98.1 MPa at the time of isothermal exposure from 10 to 15 h.

Keywords: Chrysotile nanotubes, Reinforcing component of nano-composites, Nano-tubes of Mg-Ni-chrysotiles, Synthesis, Optimal parameters, Properties.

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1. INTRODUCTION

Fiber-composites – the most promising type of advanced high strength composite materials. Reinforcement of nano-fibers increases the elastic modulus of the composite, hinders the formation, development and facilitates the fusion of microcracks in the matrix. The mechanism of inhibition is expressed by the development of microcracks in the formation of bonds of high strength fibers in zones of stress concentration at the edges of the cracks, and to reduce stress concentration by reducing the fracture dimensions and curvature of the edges. Thus, blocking the microcracks, liquefying the probability of germination in their destructive defect shifting realization of this probability to higher strain the fiber component increases the ultimate elongation of the matrix and thus increases the limits of both components working together.

Quality composite materials determined by the type and properties of the components used, including special role belongs to chrysotile, which is effective and inexpensive nano-reinforcing filler composite materials for different purposes [1-5]. Nano-chrysotile fibers increase the flexural strength and elongation (tensile strength of chrysotile fibers reaches 3000 MPa), heat resistance, thermal stability of shape and size, reduce the coefficient of thermal expansion and the cost of products.

Workability composite mixtures depends not only on the type of filler, its size and shape of particles, but the surface reaction activity. Chrysotile in the composite is active filler due to the presence on the surface of the nano-fibers a large amount of reactive hydroxyl groups, by which the introduction of chrysotile in a technological mixture process technological properties may be controlled primarily fluidity and thixotropy. To give the desired composition thixotropic enough to enter nano-chrysotile into it from 0.5 to 2 %.

Due to the high reinforcing ability asbestos has long used in composite materials, but their properties vary not only depending on the deposits, but even within one ore deposit. The chemical composition of asbestos depends on geochemical conditions of its formation. Composition of commercial chrysotile asbestos unstable. It contains various impurities – the host rocks, magnesium hydroxide, magnetite, which due to their high dispersion, as chrysotile very, very difficult to remove, so to clean chrysotile from impurities is not feasible economically.

Inconstancy of the chemical composition of natural chrysotile and determines the volatility of its properties. Chrysotile various fields differ significantly in thermal, mechanical (tensile strength, elasticity and firmness) and physicochemical properties (size of electro-kinetic potential, pH of aqueous suspensions, the adsorption capacity, etc.). Furthermore, it is known that the physical and mechanical properties of the composite material defined by uniform distribution of the reinforcing component which is dependent on the fiber length, degree of rigidity and fuzz (dispersion), and therefore the properties of finished products reinforced with fibers of natural chrysotile may not be constant, whereby use it for critical purposes is undesirable.

Chrysotile synthesized from products that do not contain harmful impurities use better. Furthermore, it is possible to vary the composition of the charge and hence the properties of the synthetic asbestos. Depending on the synthesis conditions can produce fibers of various lengths and morphology. Hollow nanotubes synthetic chrysotile and its analogues have a constant chemical composition and properties. Application of synthetic chrysotile and its structural analogs will provide material with stable properties.

The purpose of this work is to determine the optimal parameters of synthesis and properties of nano-tubular crystals Mg-Ni-chrysotiles.

2. STRUCTURAL AND MORPHOLOGICAL FEATURES OF CHRYSOTILE

Anyone interested in asbestos, know that there is a fibrous mineral of serpentine group. Chrysotile fibers are nano-tube with an outer diameter of ~ 30 nm and the internal – from 5 to 11 nm, [6, 7]. Elementary packet serpentine 0.73 nm thick composed of two layers: the upper brucite-like (octahedral) and bottom of the silicon (tetrahedral). Brucite-like layer of chrysotile such elementary package consists of a layer of magnesium cations and/or nickel, cobalt, iron, located between two layers of hydroxyl groups [8].

Idealized crystal chemical formula of chrysotile has $Mg_6[(OH)_8 \mid Si_4O_{10}]$. In natural samples of chrysotile is a deviation from this formula by isomorphic substitution of magnesium iron, nickel and aluminum, and silicon – by aluminum.

Theoretical premise it was that the divalent nickel's cation has ionic radius ($r_{Ni+2} = 6.9 \cdot 10^{-11}$ m) is equal the same that radius of the magnesium cation ($r_{Mg+2} = 7.2 \cdot 10^{-11}$ m), therefore, must there nickel magnesium-nickel structural analogues of Mg-chrysotile. The structure of all these fibrous hydro silicates is the same: the first (inner) tetrahedral layers of nano-tubes consist from silicon-oxygen network and the second (external) octahedral layer – net of hydroxide brucite type. Tubing wall of Mg-chrysotile consist of 11 layers and 9 in Ni-chrysotile (garnierite), because the outer diameter of the nickel chrysotile fibers is smaller less than its magnesium analogs.

3. EXPERIMENTAL

We synthesized the following minerals isomorphic series chrysotile – garnierite: pure magnesium chrysotile, and with partial (1/3, 1/2, 2/3) and complete replacement of magnesium by nickel.

We syntheses of Mg-Ni-chrysotiles from the precipitation of stoichiometric composition (ratio of $(MgO + NiO) : SiO_2 = 3 : 2$ as in the chrysotile) obtained from solutions $MgSO_4$, $NiSO_4$, $H_2SiO_3 \cdot nH_2O$ (or Na_2SiO_3) and NaOH as we used charges from $Mg(OH)_2$ $Ni(OH)_2$ and $H_2SiO_3 \cdot nH_2O$. Study of precipitatio, obtained from solutions of salts, showed that these sediments are composed of nano-sized X-ray amorphous particles strongly hydrated phase with a layered structure, which at hydrothermal recrystallization transformed into hydro-silicates certain chemical composition and fibrillar morphology.

The precipitate was washed from Na_2SO_4, and 5 g was placed in an autoclave with volume 18 ml, filled calculated amount of distilled water. The resulting slurry was autoclaved at 473-673 °K, 17.62-98.1 MPa and isothermal exposure time from 2 to 48 h.

We controlled the formation and growth of fibrils Mg-Ni-chrysotiles by x-ray structural and electron microscopic analyzes.

4. RESULTS AND DISCUSSION

On the basis of our experiments we identified: optimal parameters of recrystallization the precipitates – there are 673 K, 98.1 MPa and time of isothermal exposure is 15 h. Synthesis product contains 100 % of the tubular fibers. Found that in all the experiments beyond a certain length, ~ up to 2 mkm, the growth of fibrils stops, longer hydrothermal treatment does not increase the length.

Energy dispersive analysis of the spectra of samples with ratios of Mg: Ni, ≈ 1: 1 and 2 : 3 shows that these relations Mg: Ni practically maintained for all data samples fibrils.

Electron microscopic method showed that on the morphology of the formed tubular Mg-Ni-fibrils as well as on the morphology of the Mg-fibrils affects the pH of the solution: at pH <11, fibrils variable outer diameter (with sleeves) type of the "tube in tube" and of the "cone into cone" with a diameter from 25 to 150 nm with an average length of 1 – 2 mm and cylindrical fibrils in diameter 25 – 35 nm; at higher pH fibrils uniform diameter throughout the length – 26 – 30 nm and a length of 1 – 2 microns. All the fibrils are hollow [9 – 11].

Electron diffraction patterns established spatial disorder tapered individuals chrysotile. Cone fibrils give unusual diffraction pattern, representing mostly the superposition of two diffraction patterns from the sides of the cone. The electron diffraction patterns from individual tubular fibrils showed that they have a two-layered monoclinic unit cell.

Synthesized mono-mineral serpentine phase with characteristic chrysotile 7 Å reflection according to the roentgenometric analysis. It has been established that in the isomorphous series of chrysotile – garnierite with increasing nickel content in the crystal lattice parameter c is reduced from 1.470 to 1.450 nm, and the parameters a and b are increased: a from 0.528 to 0.530 nm; b of from 0.914 to 0.918 nm.

Thermal analysis showed that the content of the constitutional water in the studied minerals correspond to the theoretical, mass. %: For chrysotile $Mg_6[(OH)_8 \mid Si_4O_{10}]$ – 13,05; isomorphic serpentines: $Mg_4Ni_2[(OH)_8 \mid Si_4O_{10}]$ – 11,57; $Mg_3Ni_3[(OH)_8 \mid Si_4O_{10}]$ – 10,95; $Mg_2Ni_4[(OH)_8 \mid Si_4O_{10}]$ – 10,39 and garnierite $Ni_6[(OH)_8 \mid Si_4O_{10}]$ – 9,45.

Mineral density defined pycnometrically equal: at synthetic chrysotile 2.43 g/cm^3, at mineral $Mg_4Ni_2[(OH)_8 \mid Si_4O_{10}]$ – 2,86 g/cm^3, at $Mg_3Ni_3[(OH)_8 \mid Si_4O_{10}]$ – 2 99 g/cm^3, at $Mg_2Ni_4[(OH)_8 \mid Si_4O_{10}]$ – 3,22 g/cm^3, at pure Ni garnierite – 3.85 g/cm^3.

Specific surface area by adsorption of water vapor respectively amounted: 72.98; 66.01; 62.32; 58.63; 55.35 m^2/g.

Defined carcinogenic effects of synthetic chrysotile asbestos with different length and thickness of the crystals, as well as its isomorphic analogues versus with natural chrysotile asbestos [12, 13]. It was established that chrysotile synthesized in an alkaline medium, are less pronounced in comparison with natural, carcinogenic activity and synthesized in distilled water do not possess quite.

All synthesized chrysotile and their structural analogues studied comprehensively, laboratory tested in various compositions. Most suitable compositions tested in a production environment.

5. CONCLUSIONS

Properties of fiber composites depend on the type and condition of the fibers that are used. Synthetic chrysotiles should be preferred for giving the desired stability properties of composites.

From the results of our experiments it is clear that the temperature of the hydrothermal process is the dominant factor in the process of hydrothermal synthesis. The pressure in the range studied (9.81-245 MPa) has no appreciable effect on the rate of reaction components. Equilibration time in the system depends on the synthesis temperature. The optimal temperature ranges and pressure for the synthesis of nano-tubular crystals Mg-Ni-chrysotile 573-673 K, 19.6-98.1 MPa at the time of isothermal holding from 15 to 24 h.

In hydrothermally conditions synthesized minerals isomorphic series of chrysotile – garnierite and identified unlimited isomorphism in this series.

It is shown that the magnesium and nickel included in the structure of synthetic minerals in accordance with their original value.

Crystallographic characteristics and physiochemical properties of the synthetic minerals vary according to the composition of the octahedral layer of crystals.

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