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Nanotubular Crystals of Co-chrysotile (Co-hydro Silicate)

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The purpose of this work is to determine the optimal parameters of synthesis of nano-tubular crystals Co-chrysotile. The optimal temperature ranges and pressure for the synthesis of nano-tubular crystals Co-chrysotile 573 – 673 °K, 19.6 – 98.1 MPa at the time of isothermal exposure from 15 to 24 h.

Keywords: Co-chrysotile nano-tubes, Synthesis, Optimal parameters.

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1. INTRODUCTION

The first attempt to synthesize the cobalt chrysotile (Co_6 [$(OH)_8$ | Si_4O_{10}]) stoichiometric $3CoO\ 2SiO_2\ 2H_2O$, was made in the early 40-ies of the 20-th century [1]. Theoretical premise of was that the divalent cobalt's cation has ionic radius ($r_{Co+2} = 8.2 \cdot 10^{-11}$ m) close to the radius of the magnesium cation ($r_{Mg+2} = 7.8 \cdot 10^{-11}$ m), therefore, must there cobalt structural analogue of chrysotile. The structure of these fibrous hydro silicates is the same: the first (inner) tetrahedral layers of nanotubes consist from silicon-oxygen network and the second (external) octahedral layer – net of hydroxide brucite type. According to Pauling's theory twisting of these (serpentine) layers in the form of tubes due to the fact that the parameters of the silicon-oxygen cell grid is slightly smaller than the cell parameters brucite layer.

The next attempt to synthesize nanotubes Co-chrysotile, undertaken in 12 years [2], was not successful, but later in the synthesis in a reducing environment [3–7] obtained cobalt chrysotile fibers. Co-chrysotile forms easily, under the same conditions as that for chrysotile and its crystals as for chrysotile fiber characteristic habit. Tubing wall cobalt chrysotile consist of 4 layers thinner than that of Mg-and Ni-chrysotile (garnierite): 11 layers in chrysotile and 9 in garnierite. The outer diameter of the cobalt chrysotile fibers is less than its analogs – magnesium chrysotile and garnierite, due much greater disparity between the tetrahedral and octahedral layers of the crystal lattice.

2. EXPERIMENTAL

The purpose of this work is to determine the optimum temperature and pressure for the synthesis of nano-tubular crystals Co-chrysotile. We syntheses of Co-chrysotile from the precipitation of stoichiometric composition (ratio of CoO: SiO_2 = 3:2 as the chrysotile) obtained from solutions $CoSO_4$, H_2SiO_3 nH_2O (or Na_2SiO_3) and NaOH as we used charges from $Co(OH)_2$ and H_2SiO_3 nH_2O. Study of precipitation [6], 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 morphology.

The precipitate was washed from Na_2SO_4, and 5 g was placed in an autoclave, filled calculated amount of distilled water with hydrazine (to creation reducing conditions). The resulting slurry was autoclaved at 473 – 673 °K, 9.81 – 245 MPa and isothermal exposure time from 2 to 240 h.

We controlled the formation and growth of fibrils Co-chrysotile by x-ray phase and electron microscopic analyzes.

3. RESULTS AND DISCUSSION

Investigation of the products of hydrothermal crystallization at 473 °K, 9.81 – 245 MPa precipitation ratio CoO: SiO_2 = 3:2 obtained from solutions $CoSO_4$, Na_2SiO_3 and NaOH, showed that after 2 h of autoclaving products are formed predominantly squamous morphology (as films) with few layers, begins to twist as rolls in the tube (Fig. 1). As the temperature increases to 673 °K this pattern is observed in 2 h, i. e., the temperature affects the kinetics of the process. Pressure has almost no effect on the rate of crystallization. On the basis of these conclusions, the following experiments were carried out by recrystallization of precipitation at 673 °K and 98.1 MPa. Kind of product recrystallized precipitate for 10 hours and micro-electron diffraction from curled the layers shown in Fig. 2a. Draws attention to the fact of incomplete stage of structure (edges of nano-plate particles are too thin, and in many cases do not have sharp edges). Embryos of cobalt chrysotile fibrils observed in a small number in the gel-like mass.

Fig. 2b presents form of products recrystallization sediment and micro-electron diffraction pattern of the nanotubes after the 24 h exposure. Products of recrystallization after 240 h autoclaving have almost the same form.

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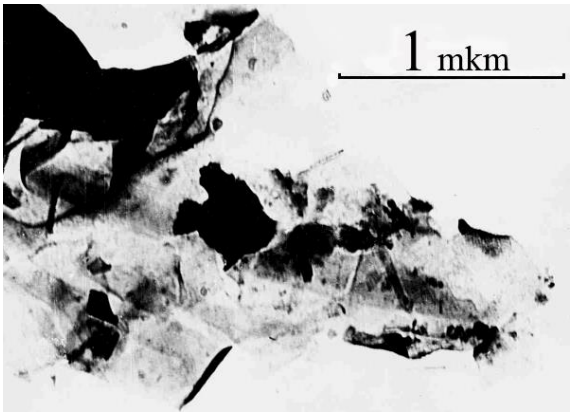
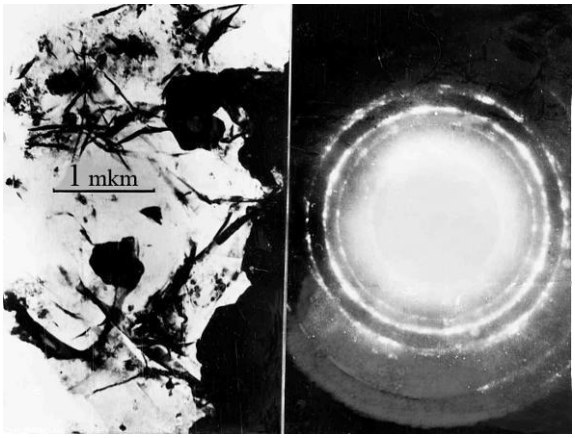
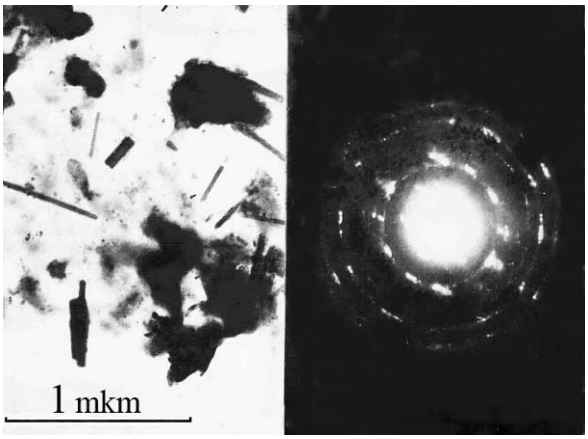


Fig. 1 – Embryonic layers of cobalt chrysotile observed in the products of hydrothermal treatment sludge (slurry) at 473 – 673 °K, 9.81 – 245 MPa



a



b

Fig. 2 – The transformation of embryonic layers, shown in Fig. 1, into tubular fibers and micro-electron-diffraction-patterns of recrystallization products. Autoclaving time: Fig. 2a – 10 h, Fig. 2b – 24 h.

It can be argued that these photographs illustrate the initial stage of the formation of tubular fibrils and the resulting fibrils to grow in length, apparently, due to dissolution of small embryos fibrils during recrystallization, based on the theory of Pauling's a mismatch between brucite and silicon oxide layers, as the cause of the twisting of the layers in the tube. Original film, apparently bent differently, therefore, can twist in the form of tubes with cylindrical coaxial layers, and with the layers arranged conically. Micro-electron-diffraction patterns obtained by micro-diffraction from thin edges of lamellar particles indicate the presence of diffuse background or circular picture of Debye-Scherer, indicating incomplete primary level of structure of embryonic layers.

Not getting enough of the fiber fraction and after washing of sodium nitrate, it was decided to try to synthesize cobalt chrysotile from the charge, consisting of cobalt hydroxide, crystals which have, as in brucite, hexagonal shape with negligible thickness, and silicic acid in the molecular ratio corresponding to the magnesium chrysotile.

The rate of full interaction between the components of the charge from (of) $Co(OH)_2$ and silica acid ($SiO_2\ nH_2O$) at 473 °K is small – for their interaction will need ~ 40-hours, increasing the temperature up to a certain limit accelerates the formation and growth of fibrils. For full interaction components is about 15 h at 673 °K. X-ray amorphous product was after a hydrothermal treatment.

The interaction between cobalt hydroxide and silicic acid leads to the formation of fibers, which are electron micrographs were observed in the form of separate tubular empty fibrils or they aggregates (Fig. 3). The study of these fibrils by electron micro-diffraction showed that they electron-amorphous. Synthesis product contains 100 % of the tubular fibers.

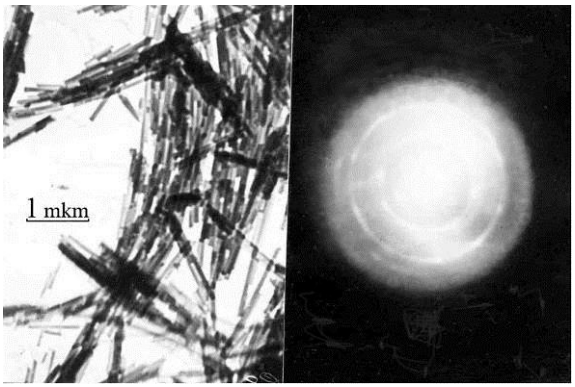


Fig. 3 – Micro-electron-diffraction pattern of cobalt chrysotile fibrils, synthesized for 40 hours from cobalt hydroxide and silicic acid

E.N. Korytkova et al. [8] have recently been synthesized in the system $MgO–CoO–SiO_2–H_2O$ isomorphic substituted in the octahedral sites of the Mg-Co-chrysotile composition $(Mg, Co)_6 [(OH)_8 | Si_4O_{10}]$ in accordance with the theory of isomorph's miscibility [9].

4. CONCLUSIONS

From the above results it is clear that the temperature of the hydrothermal process is the main factor that affects the speed of the phase formation in the system.

Temperature hydrothermal treatment is the dominant factor in the process of hydrothermal crystallization.

The processing time to a lesser extent, affects the

synthesis Co_6 [$(OH)_8$ | Si_4O_{10}].

The pressure in the range studied (9.81 – 245 MPa) has no appreciable effect on the rate of reaction components.

The optimal temperature ranges and pressure for the synthesis of nano-tubular crystals Co-chrysotile 573 – 673 °K, 19.6 – 98.1 MPa at the time of isothermal holding from 15 to 24 h.

Found that in all the experiments beyond a certain length, ~ up to 1 mkm, the growth of fibrils stops, longer hydrothermal treatment does not increase the length.

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