

NANOTUBULAR CRYSTALS OF GARNIERITE $\text{Ni}_6(\text{OH})_8[\text{Si}_4\text{O}_{10}]$

A. Smolikov¹, A. Vezentsev², V. Beresnev³, V. Pavlenko¹, L. Zagorodniuk¹, P. Turbin^{3,4}

¹V.G. Shukhov Belgorod State Technological University, Belgorod, Russia

E-mail: smolikov@bsu.edu.ru, E-mail: pavlenko@yandex.ru;

²Belgorod National Research University, Belgorod, Russia;

³V.N. Karazin Kharkiv National University, Kharkiv, Ukraine

E-mail: beresnev-scpt@yandex.ru;

⁴Scientific Center of Physical Technologies of Ministry of Education and Science of Ukraine and National Academy of Science of Ukraine, Kharkiv, Ukraine

E-mail: turbin-scpt@yandex.ru

The influence of nature of initial components on synthesis conditions and morphology of nanotubular crystals of garnierite (Ni-chrysotile) has been studied. The synthesis of garnierite based on SiO_2 , $\text{Ni}(\text{OH})_2$, and NiSiO_3 has been implemented at temperature 673 K and pressure 98.1 MPa in the time interval of 12...15 hours. Nanotubes were formed with an outer diameter of about 20 nm, contained alkali (1...10% NaOH) or salt (0.5...3%). It was shown that the types of tubes "cone in cone" and "tube in tube" are forms appropriate for distilled water. The synthesis conditions and the size of garnierite nanotubes strictly correspond to the parameters, inherent to Mg-chrysotile.

INTRODUCTION

Chrysotile is magnesium hydrosilicate ($\text{Mg}_6[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$) of the serpentine group – a unique mineral, which combines technical and economic indicators, which does not have substitutes so far. Serpentine group minerals are widely used in radiation protection. In the literature, there are few studies on the synthesis of chrysotile and its structural analogs; this initiated experiments at high temperatures and pressures. Conditions for the synthesis of chrysotile are studied in detail by A.I. Vezentsev [1]. Isomorphism of ions is observed in natural minerals [2]. Thus, isomorphous analogs acquire a number of new valuable features. Nickel minerals are used in catalysis, in particular. During full replacement of Mg with Ni, the structural analogue of chrysotile – garnierite is formed. The literature does not describe experiments on the effect of the nature of the starting components for garnierite synthesis conditions.

A number of researchers [3–8, etc.] have synthesized nickel analogue of chrysotile – garnierite ($\text{Ni}_6[(\text{OH})_8|\text{Si}_4\text{O}_{10}]$) of stoichiometric composition $3\text{NiO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$, based on the fact that nickel ideally replaces magnesium in the structure of natural minerals by equality ionic radii of Mg^{2+} and Ni^{2+} . W. Noll & H. Kircher [3] found that garnierite is easily formed under the same conditions as that for chrysotile, and its crystals as well as chrysotile, are characterized with fibrous habit. D.M. Roy & R. Roy [4] synthesized various analogues of chrysotile, in particular – garnierite, to the experimental confirmation of the causes twisting layers of crystals of chrysotile, theoretically based by Pauling. These researchers, in the absence of sodium chloride (or potassium) produced not tubular, but flake isometric crystals. J.J. Scholten & A.M. Kiel [5] in the study of synthetic fibers garnierite's found along with the casual fibers not completely rolled in a tube fibers.

The aim of this paper is detailed study of interrelation of technological parameters for syntheses of garnierite. Thus, it is required to: 1) define the most

active raw material components from the next of line: Ni_2O_3 , NiO, $\text{Ni}(\text{OH})_2$ or $\text{NiSiO}_3\cdot x\text{H}_2\text{O}$ with quartz or silicic acid, that have different crystal and chemical structure; 2) study the influence of pH of surroundings of syntheses and some additives at morphology of nanotubular crystals of garnierite; 3) determine optimal temperature and pressure.

The processes of formation and growth of garnierite's fibrils were studied using x-ray and electron-microscopy analysis methods.

1. EFFECT OF THE NATURE OF THE INITIAL COMPONENTS ON THE PROCESS OF HYDROTHERMAL SYNTHESIS OF GARNIERITE IN DISTILLED WATER

It was determined [8] that the nature of raw materials for the synthesis of chrysotile has a big effect on their reactivity. We have carried out similar studies for the synthesis of garnierite. Hydrothermal treatment of the charge in this series of experiments was carried out at 673 K and a pressure of 98.1 MPa.

The charge for the synthesis of components:

1) From of Ni_2O_3 and quartz (SiO_2). In this case, the mixture had a significant amount of unreacted raw components, even after 10 days of hydrothermal treatment at 673 K. The products of hydrothermal treatments include according to the X-ray analysis: garnierite, Ni_2O_3 and quartz. The same results were obtained when replacing the quartz with the milled quartz sand.

2) From of NiO and quartz (SiO_2). On the basis of X-ray diffraction data it was found, that NiO is relatively easy hydrated to $\text{Ni}(\text{OH})_2$ under hydrothermal conditions. For complete conversion of charge in garnierite at 673 K, hydrothermal treatment for 8 days is required. This is due to lower solubility and larger size of grains of quartz, compared with amorphous forms of silica. In this case, the obtained fibrils have a length of up to 3...5 mm – the largest in these series of experiments. There was no fibers of «cone in cone» type between the fibrils.

3) From of $\text{Ni}(\text{OH})_2$ and quartz glass (SiO_2). The process of the growth of fibrils is the same as in the previous case. The rate of interaction of components is conditioned by low solubility of quartz. The length of fibrils is lesser, than in the previous case (1...2 μm).

4) From of Ni_2O_3 and silica acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Ni_2O_3 interacts poorly with $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (as in the first case): the X-ray reflections show the presence of Ni_2O_3 along with the reflections of garnierite even after 48 h of isothermal autoclaving.

5) From of NiO and silica acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Garnierite from these components is formed at 673 K within 15 h. The average fiber length is the same as in the case of $\text{Ni}(\text{OH})_2$ and quartz. Many fibrils have a crystal habit of «cylinder in cylinder» with a diameter of 30...150 nm and a length of about 3 μm (Fig. 1).

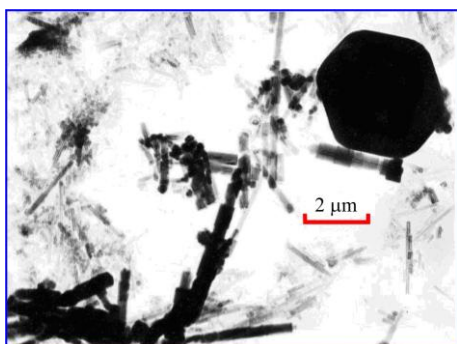


Fig. 1. Fibrils of garnierite, type «cylinder in cylinder» obtained from NiO and silica acid at 673 K, 98.1 MPa and isothermal holding time of 15 hours

6) From of $\text{Ni}(\text{OH})_2$ and silica acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Charge components, as in the previous case, quickly react with each other, forming garnierite.

7) From of $\text{Ni}(\text{OH})_2$ and nickel hydro silicate ($\text{NiSiO}_3 \cdot x\text{H}_2\text{O}$). All components of the charge interact entirely within 12 hours between $\text{Ni}(\text{OH})_2$ and $\text{NiSiO}_3 \cdot x\text{H}_2\text{O}$ (in this case $x = 3.11$). The product of synthesis consists only of the cylindrical filaments with an outer diameter of 20...30 nm (Fig. 2).

pH index of the suspension of all compositions in distilled water without chemical additives is ~ 7.

X-ray diffraction analysis of the products of synthesis, mentioned above, are shown in Fig. 3. X-ray metric studies show, that the most reactive of those mixtures are those, which consist of the substances, that have the lattice, which is closest to the synthesized garnierite, thus, the process of formation and growth of fibrils is faster and requires lesser energy.

Thus, the most active components are $\text{Ni}(\text{OH})_2$, $\text{NiSiO}_3 \cdot x\text{H}_2\text{O}$ and silicic acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). The further experiments have been conducted with these components.

2. SYNTHESIS OF GARNIERITE WHILE ADDING ALKALI AND SALTS

Garnierite's cylindrical fibrils with a smooth outer surface, and the same outer diameter as that of natural chrysotile are formed while adding 1...10% alkali or 0.5...3% salts to the charge (see Fig. 2).

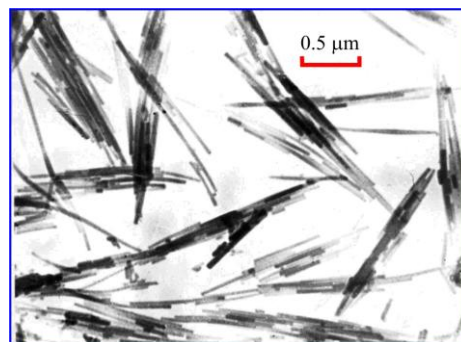


Fig. 2. Garnierite fibrils, obtained from $\text{Ni}(\text{OH})_2$ and silica acid at 673 K and isothermal holding time of 15 hours

3. EFFECT OF THE TEMPERATURE OF REACTION ON THE PHASE FORMATION

During the investigation process, the charge was autoclaved at 473...673 K and at pressures of water vapors of 9.81...245 MPa and isothermal dwell time of 0.5 to 240 h. Fibrils of garnierite are consistently formed at temperatures 473...673 K. The rate of interaction between the components of the charge at 473 K is very small – for their interaction ~ 2 days are needed; increasing the temperature up to a certain limit accelerates formation and growth of fibrils. For a complete interaction of all the components ~ 15 hours at 673 K is enough. Pressure has no appreciable effect on reaction speed of the components.

Specific surface area of the synthesized garnierite is 55 m^2/g , and the density is 3850 kg/m^3 .

SUMMARY

1. The most active nickel-containing ingredients during the synthesis of garnierite are $\text{NiSiO}_3 \cdot x\text{H}_2\text{O}$; $\text{Ni}(\text{OH})_2$, followed by NiO and Ni_2O_3 , which are only slightly less active. Silicic acid and quartz glass is more active than quartz.

2. Fibrils of garnierite, as well as fibrils of chrysotile are produced in relatively wide ranges of temperatures (473...673 K) and pressures (9.81...245 MPa).

3. Using electron microscopy method, it was shown in this paper, that the main parameter that determines the morphological features and the degree of perfection of the structure of the formed fibrils is the pH of the medium, the type and the amount of modifying impurities involved in the reaction.

4. The obtained data have shown that in alkaline and saline solutions charge components interact with each other faster than in distilled water.

5. It was determined that in distilled water not only cylindrical fibrils are mainly formed, but also the fibrils with a structure of «tube in tube» with a helical twist of layers and «cone in cone» type, that have a large spread of values not only in length, but also in diameter.

6. Cylindrical fibrils with a diameter of ~ 20...30 nm were obtained in solutions with concentration of 1...10% alkali or 0.5...3% salt.

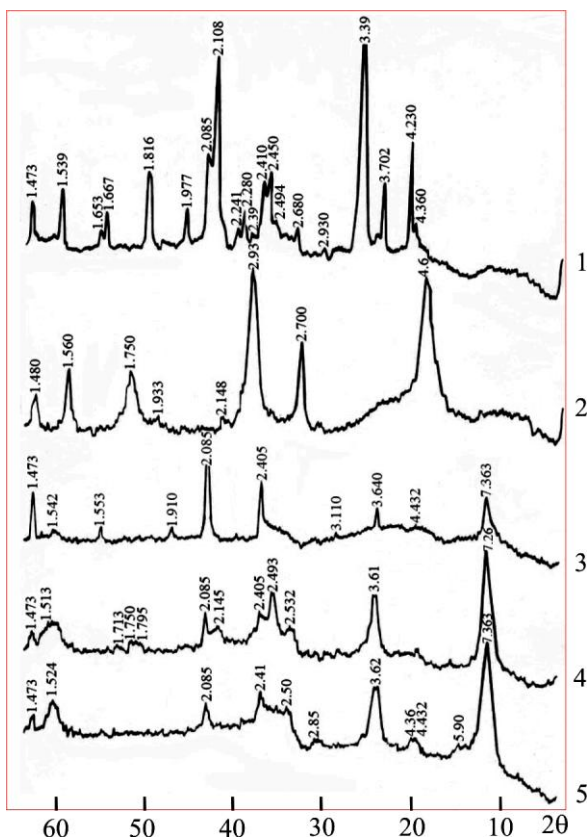


Fig. 3. Fragments of X-ray pictures of the products of synthesis, obtained at 673 K, 98.1 MPa, from the charge consisting of 1 – NiO and natural quartz (72 hours); 2 – Ni(OH)₂ and silica glass (30 hours); 3 – of Ni₂O₃ and silicic acid; 4 – of NiO and NiSiO₃·xH₂O (20 hours); 5 – Ni(OH)₂ and NiSiO₃·xH₂O (15 hours)

7. The garnierite with a certain dispersion composition with a very high reproducibility was obtained in this paper. It was found out, that in all the experiments after reaching a certain length, which is up to 1...2 μm in most of cases, the growth of fibrils stops,

and the further increase of hydrothermal processing does not lead to increasing of their length.

8. The synthesis conditions for garnierite and chrysotile are identical. Garnierite and chrysotile have fibrils of the same size and the same morphology.

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НАНОТРУБЧАТЫЕ КРИСТАЛЛЫ ГАРНИЕРИТА Ni₆(OH)₈[Si₄O₁₀]

А. Смоликов, А. Везенцев, В. Береснев, В. Павленко, Л. Загороднюк, П. Турбин

Изучено влияние природы исходных компонентов на условия синтеза и морфологию нанотрубчатых кристаллов гарниерита (Ni-хризотила). Осуществлен синтез гарниерита на основе компонентов SiO₂, Ni(OH)₂ и NiSiO₃ при температуре 673 К и давлении 98,1 МПа во временном интервале 12...15 ч. Нанотрубки, сформированные с наружным диаметром ~ 20 нм, содержали щелочь (1...10% NaOH) или соли (0,5...3%). Показано, что типы трубок «конус в конусе» и «трубка в трубке» являются формой соответствующей дистиллированной воде. Условия синтеза и размеры нанотрубок гарниерита строго соответствуют параметрам, характерным для Mg-хризотила.

НАНОТРУБЧАСТІ КРИСТАЛИ ГАРНІЄРИТУ Ni₆(OH)₈[Si₄O₁₀]

А. Смоликов, О. Везенцев, В. Береснев, В. Павленко, Л. Загороднюк, П. Турбін

Вивчено вплив природи вихідних компонентів на умови синтезу і морфологію нанотрубчастих кристалів гарнієриту (Ni-хризотилу). Здійснено синтез гарнієриту на основі компонентів SiO₂, Ni(OH)₂ і NiSiO₃ при температурі 673 К і тиску 98,1 МПа в часовому інтервалі 12...15 год. Нанотрубки, сформовані із зовнішнім діаметром ~ 20 нм, містили луг (1...10% NaOH) або солі (0,5...3%). Показано, що типи трубок «конус у конусі» і «трубка в трубці» є формою відповідною дистильованій воді. Умови синтезу і розміри нанотрубок гарнієриту точно відповідають параметрам, характерним для Mg-хризотилу.