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SHORT COMMUNICATIONS

Influence of Iron on the Kinetics of Formation of Chrysotile Nanotubes of Composition $(Mg, Fe)_3Si_2O_5(OH)_4$ under Hydrothermal Conditions

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INTRODUCTION

It is known that natural serpentine-group minerals often contain FeO, Fe_2O_3, Al_2O_3, and minor amounts of NiO, Cr_2O_3, MnO, and CoO. Fe^{3+} and Al^{3+} may substitute for Mg^{2+} in the octahedral sites and in part for Si^{4+} in the tetrahedral sites, and other cations occur in octahedral coordination [1]. These substitutions affect the unit-cell parameters and properties of the minerals. The presence of iron oxides in serpentines is very common: up to 16 wt % were reported in lizardite [2] and up to 21 wt %, in antigorite [3]. The iron analog of antigorite, greenalite, occurs in nature [4]. The maximum content of iron oxides in chrysotile is lower; in particular, the FeO content varies from a few tenths percent to 9 wt % depending on the formation conditions [1]. Of special interest is the determination of the upper limit of iron oxide incorporation in the structure of chrysotile and the influence of iron oxides on the formation of cylindrically wrapped layers in its structure, which leads to the development of tubes. This issue has recently received much attention in connection with the synthesis and elucidation of the conditions and mechanism of formation of inorganic nanotubes, which show a number of physicochemical properties that may be valuable for practical applications [5, 6]. The solution of the above problems is also important for the investigation of the genesis of natural asbestos, which was previously demonstrated by the example of an investigation of the influence of iron content in initial Mg- and Mg–Fe components on the formation mechanism and structure of fibrous amphiboles under hydrothermal conditions [7, 8]. The experimentally determined physicochemical conditions of the synthesis of chrysotile asbestos, their influence on the formation of chrysotile, and the mechanism and kinetics of nanotube formation must be maintained to a certain degree in natural systems. The obtained data can be used for the interpretation of the transformations of pyroxenes, olivines, and serpentines during hydrothermal metamorphism.

This study focused on the estimation of the effect of iron incorporation in the structure of synthetic nanotubular chrysotile on the mechanism and kinetics of its formation under hydrothermal conditions. Only one unsuccessful attempt to synthesize pure iron chrysotile in the Fe_2O_3–SiO_2–H_2O system was reported by Roy and Roy [9]. Therefore, during the first stage of our study, we estimated the conditions of the synthesis of Mg–Fe chrysotile with the maximum substitution of iron for magnesium compatible with the formation of tubular structures [10]. The synthesis of chrysotile was carried out by the hydrothermal treatment of Mg–Fe enstatite with a varying FeO content in water and aqueous NaOH solutions at temperatures of 250–450°C and pressures of 30–100 MPa. These experiments produced a range of chrysotile compositions, $(Mg,Fe)_3Si_2O_5(OH)_4$, which allowed us to determine the maximum iron incorporation compatible with the formation of tubes [10]. It was also found that Fe^{2+} was partly oxidized during the hydrothermal synthesis of chrysotile to Fe^{3+}, which can occupy both octahedral and tetrahedral sites [11, 12]. When higher amounts of FeO were introduced into the precursors, platy serpentine with the lizardite structure was formed. Korytkova et al. [10] showed that the amount of incorporated FeO affects the formation of tubular Mg–Fe chrysotile and controls some of its characteristics (unit-cell volume, optical properties, and thermal stability), morphology, and size of tubes. Of particular interest is also the estimation of the influence of iron introduction into the system on the mechanism and kinetics of nanotubular chrysotile formation.

EXPERIMENTS

The hydrothermal synthesis of nanotubular chrysotile was carried out in autoclaves by the method described elsewhere [13]. Enstatite synthesized by the solid-phase method with FeO contents of 10, 15, 25, 35, and 50 wt % and a grain size of less than 63 μm (sieved through 0.063 mm mesh) was used as a precursor. Starting mixtures for chrysotile synthesis were composed of enstatite and magnesium and iron oxides, which were added to provide the desired chrysotile stoichiometry. The mixtures were hydrothermally treated in water and aqueous NaOH solutions with concentrations from 0.3 to 2 wt % at temperatures of 200–500°C with a step of 50°C, pressures of 30–100 MPa, and experiment durations from 0.5 h to 3 days. The ratio of the solid and liquid phases (S : L) in the initial mixtures varied from 1 : 50 to 1 : 70. The mixtures were loaded into platinum crucibles with caps, which were inserted into stainless steel (1Kh18N9T) autoclaves with a volume of 65 cm^3. The autoclaves were placed into a vertical electric furnace and heated to the desired temperature. After annealing at a certain temperature, the furnace was switched off, and the autoclaves cooled in the furnace. Several experiments were conducted with quenching, but this resulted in no detectable influence on the state and amount of hydrothermal products. The products of hydrothermal treatment were removed from the crucibles and repeatedly rinsed with distilled water until neutral pH values were reached. The precipitate was separated by decanting, dried, and studied by physicochemical methods. The samples were investigated by chemical and X-ray diffraction analysis (DRON-3,CuK_α radiation), optical microscopy (Nicon Eclipse E200 microscope), and transmitted electron microscopy (EM-125 electron microscope with an accelerating voltage of 75 kV).

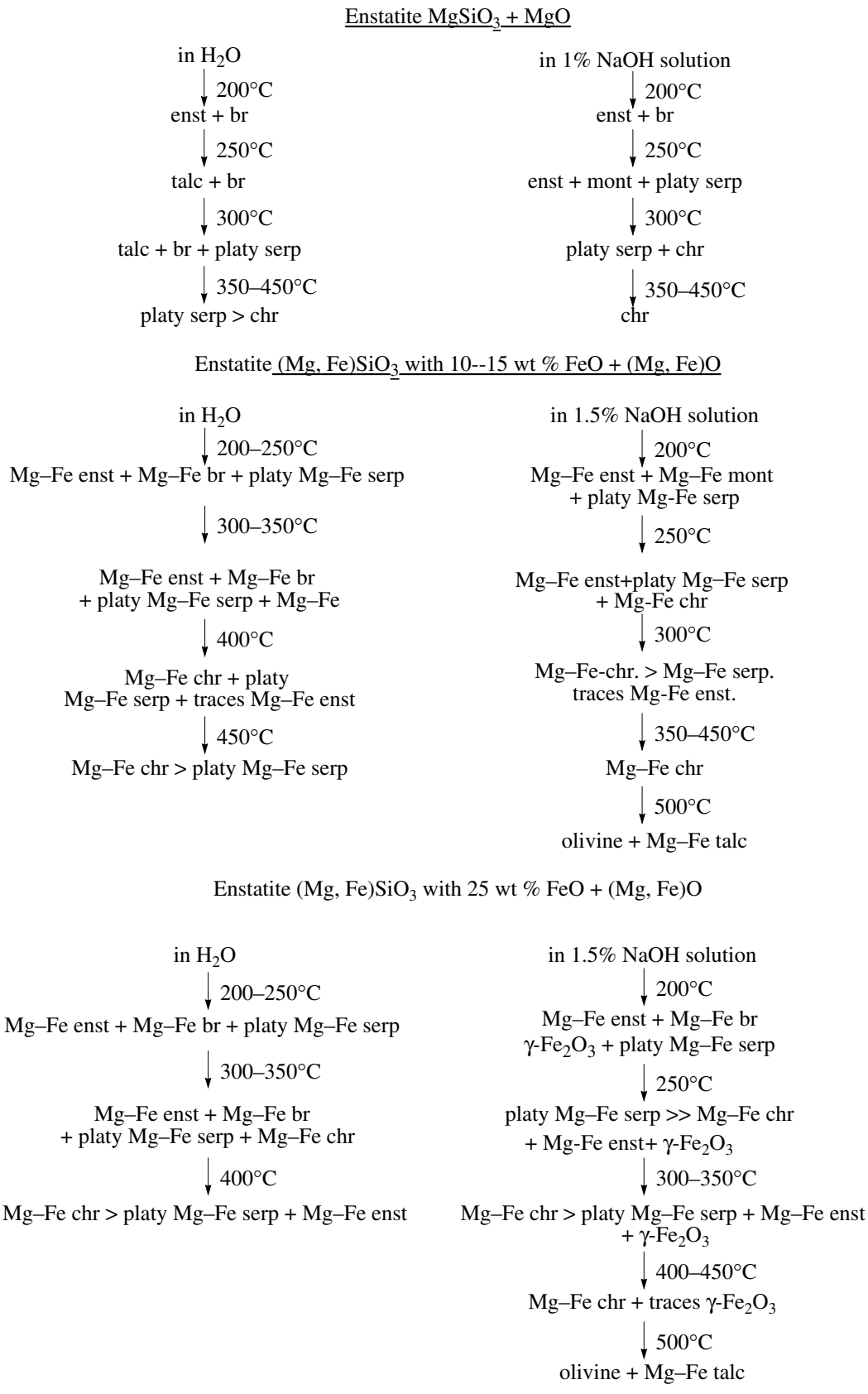
Kinetic curves were constructed on the basis of the results of X-ray phase analysis. The conditions of recording X-ray diffraction patterns for the kinetic analysis of phase formation were carefully standardized. The relative abundances of chrysotiles were determined from the intensity of their diffraction peaks without interferences from other phases. Since the uncertainty of semiquantitative X-ray phase analysis is related mainly to the factor of sample structure and the degree of imperfection of the crystal lattice, in order to reduce the error, the samples were specially prepared, and parameters were calculated from the intensities of the (002), (020), (004), and (060) reflections with the averaging of the results using the method described in [14]. The obtained data were compared and supplemented by quantitative measurements under the optical microscope. The products of hydrothermal treatment were examined in immersion oils, and the measurements of refraction indexes were performed for the identification of phases and estimation of their amounts. Several mounts were prepared from each sample, and the obtained results were averaged. The difference between the results obtained by semiquantitative X-ray phase analysis and optical microscopy was always below 20–25%.

RESULTS AND DISCUSSION

The investigation of chrysotile nanotube formation with the composition $(Mg,Fe)_3Si_2O_5(OH)_4$ under hydrothermal conditions revealed several factors controlling the character and rate of phase crystallization in the systems considered: composition of hydrothermal solution, parameters of hydrothermal treatment, and iron content in the starting mixtures. A general feature of all the systems is the multistage transformation of initial compounds during a gradual increase in the temperature of their hydrothermal treatment. The evolution of precursors is schematically shown in Fig. 1, where the hydrothermal transformations of Mg–Fe components with various FeO contents are compared with those of the pure magnesian initial mixture ($MgSiO_3$ + MgO).

At a temperature of 200°C (P = 30–100 MPa), the treatment in both distilled water and aqueous NaOH solutions caused only MgO hydration to brucite, whereas enstatite did not change under such conditions. An increase in temperature up to 250°C resulted in enstatite hydration accompanied by the partial release of magnesium ions into the solution. The single-chain structure of enstatite is rearranged to form hydrous magnesium phyllosilicates, talc in hydrothermal experiments with water and montmorillonite in experiments with NaOH solutions. Under 250°C, montmorillonite is partly transformed into a magnesian hydrous trioctahedral 1 : 1 phyllosilicate, $Mg_3Si_2O_5(OH)_4$, with the serpentine (lizardite) structure. In distilled water, the trioctahedral structure of talc was transformed into the trioctahedral structure of serpentine at a higher temperature (300°C). The recrystallization of lizardite into chrysotile in water was observed only at a temperature of 350°C, whereas in NaOH solutions, this process occurred extensively at 300°C and resulted in the complete transformation of starting mixtures into nanotubular chrysotile at 350°C.

The addition of FeO to the precursors affected both the formation conditions and the character and rate of phase formation in the systems considered, and the amount of iron in the precursors is the main controlling factor. For instance, the addition of less than 5 wt % FeO to the starting mixtures depressed the lower temperature boundary of lizardite formation and temperature of its recrystallization into chrysotile; part of the Mg ions were replaced by Fe, but the general sequence



Phase abbreviations: enst, enstatite; br, brucite; serp, serpentine; chr, chrysotile; and mont, montmorillonite.

Fig. 1. Flow chart showing the transformation paths of initial mixtures during hydrothermal treatment.

of phase formation was not affected in this system. The addition of higher amounts of FeO (10–15 wt %) to the mixtures of enstatite and (Mg, Fe)O solid solution significantly affected the character and rate of their transformation under hydrothermal conditions. In addition to the aforementioned decrease in the temperature of lizardite and chrysotile formation, the number of transitional phases decreased. For instance, in experiments with water at temperatures of 200–250°C (P = 30–100 MPa), the magnesium and iron oxides that were added to Mg–Fe enstatite to provide the chrysotile stoichiometry of the starting mixtures were hydrated to Fe–Mg brucite, the sheet structure of which is formed by layers of magnesium and iron ions octahedrally coordinated by oxygen atoms. The newly formed brucite reacted with enstatite under the same pressures and temperatures. An increase in temperature and pressure is favorable for enstatite hydration and transformation of its structure upon incorporation of magnesium and iron ions into the structure of serpentine without an intermediate phase (talc). An increase in the temperature of hydrothermal treatment up to 300°C activated serpentinization and induced recrystallization of the newly formed platy serpentine into fibrous chrysotile. The recrystallization of lizardite intensified at higher temperatures of treatment, and chrysotile was much more abundant than lizardite in the experimental product obtained at a temperature of 450°C.

In alkaline NaOH solutions, the mixtures with enstatite containing 10–15 wt % FeO were less stable than the magnesian starting materials. The decomposition and hydration of components were observed already at 200°C (P = 30–100 MPa), when Mg–Fe montmorillonite and platy Mg–Fe serpentine (lizardite) were formed. The latter is produced by a slight transformation of the montmorillonite structure. The similarity of the trioctahedral structures of these hydrous phyllosilicates suggests that they can be easily transformed at elevated temperatures and pressures. The recrystallization of lizardite into tubular chrysotile was observed already at a slight temperature increase (up to 250°C), and nanotubular chrysotile was the main phase in the products of hydrothermal treatment at 300°C. Monophase chrysotile was observed after hydrothermal treatment at 350°C.

In experiments with the precursors based on enstatite with a FeO content of 25 wt % or more, the character of phase formation in the systems showed some changes, especially significant in alkaline solutions. The sequence of phase transitions observed during a gradual increase in the temperature of hydrothermal treatment of such FeO-rich precursors in water is identical to that observed during the treatment of precursors with enstatite containing 10–15 wt % FeO. In contrast, the attack of alkaline solution on the starting mixtures based on enstatite with 25 wt % FeO resulted in different transformations. Their hydration at 200°C (P = 30–100 MPa) produced Mg–Fe brucite, maghemite γ-Fe_2O_3, and platy Mg–Fe serpentine. Mg–Fe montmorillonite was not detected in the products of these experiments. An increase in temperature up to 250°C caused an extensive formation of platy serpentine, a small portion of which recrystallized into tubular chrysotile, and maghemite. The prevalence of tubular chrysotile over platy serpentine in the products of hydrothermal treatment was documented at 300–350°C, whereas the product of 400–450°C experiments was composed of tubular chrysotile with a minor admixture of maghemite.

The precursors based on enstatite with 35 wt % FeO were transformed into the assemblage of Mg–Fe montmorillonite, maghemite, and platy Mg–Fe serpentine during the hydrothermal treatment in NaOH solutions at temperatures of 300–350°C (P = 30–100 MPa), and only at 400°C, a small fraction of serpentine (about 7%) recrystallized into tubular chrysotile. The hydrothermal treatment in alkaline NaOH solutions of precursors based on enstatite with 50 wt % FeO at 400°C produced platy Mg–Fe serpentine and maghemite only under the experimental durations used in our study. Chrysotile was not formed from such precursors.

The kinetics of the formation of nanotubular Mg–Fe chrysotile with varying contents of iron oxides were investigated at a temperature of 350°C and a pressure of 70 MPa in solutions containing 1.5 wt % NaOH (Fig. 2).

In order to compare the rates of formation of Mg–Fe chrysotiles and Mg chrysotile, Fig. 2 presents the kinetic curve of Mg chrysotile crystallization from the $MgSiO_3$ + MgO mixture under the same temperature and pressure. The analysis of the obtained data revealed significant variations in the rate of chrysotile formation in the $Mg_3Si_2O_5(OH)_4$–$(Mg,Fe)_3Si_2O_5(OH)_4$ series.

The most distinctive is the kinetics of nanotubular chrysotile formation from the mixture of $MgSiO_3$ enstatite and magnesium oxide. The kinetic curve displays a considerable induction period, which is followed by rapid chrysotile formation. The existence of such an induction period is related to the stability of the enstatite lattice, which must be substantially rearranged for the transition from the single-chain structure of the initial phase to the sheet structure of the synthesized compound. The high rate of chrysotile formation after the induction period is probably related to the small sizes of particles of the formed transitional layer phases with a platy morphology, which promoted their rapid transformation into nanotubular chrysotile, and to the elevated concentrations of magnesium and silicon in the hydrothermal solution owing to the relatively slow transformation of enstatite into sheet-structured phases.

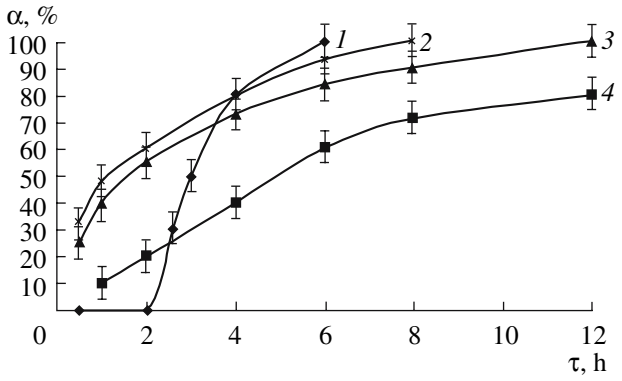


Fig. 2. Content of nanotubular chrysotile in the mixtures of the composition (Mg, Fe)SiO_3 as a function of the time of their treatment in NaOH solution (1.5 wt %) at 350°C and 70 MPa. Curves *1, 2, 3*, and *4* correspond to FeO contents in the mixtures of 0, 10, 15, and 25 wt %, respectively.

The addition of FeO to the precursors changed the character of kinetic curves of chrysotile formation. They display rapid extensive formation of Mg–Fe chrysotiles from mixtures based on enstatite with 10–15 wt % FeO during the first few hours of hydrothermal treatment. This is probably related to an increase in the rates of dissolution, crystallization, crystal lattice rearrangement, and nucleation of new phases in Mg–Fe mixtures at elevated temperatures and pressures. This suggestion is supported by the aforementioned depression of the low-temperature boundary of lizardite and chrysotile formation and the decrease in the number of transitional phases during the transformation of precursors. During the development of the process in the following hours of hydrothermal treatment, the formation of chrysotile was somewhat decelerated and became more regular. However, precursors with higher FeO contents (including enstatite with 25 wt % FeO) were much more slowly transformed under the influence of alkaline hydrothermal solutions, although the rate of their chemical transformation was much higher than that of magnesian precursors during the first hours of treatment. On the other hand, in contrast to the latter, the rate of transformation of iron-bearing mixtures is uniform but significantly lower: the complete transformation into chrysotile was not observed at this temperature even during the 48-h treatment of the mixtures in NaOH solutions. The slower serpentinization of such FeO-rich precursors compared with precursors with lower FeO contents is probably related to their lower solubility and formation of maghemite, which is stable under hydrothermal conditions, at the expense of Fe^{2+} oxidation to Fe^{3+} during hydrothermal treatment.

The electron microscopic examination of the products of hydrothermal treatment at a temperature of 350°C and a pressure of 70 MPa allowed us to trace structural and morphological transformations of precursors with time in the systems considered (Fig. 3). It was found that the first two hours of hydrothermal treatment produced only platy crystals from pure magnesian precursors and mainly platy serpentine with a small amount of short and relatively thick nanotubes of Mg–Fe chrysotile (150–250, occasionally, up to 400 nm long and 45–65 nm outer diameter) from the mixtures based on enstatite with 25 wt % FeO. Most of these tubes are characterized by cylinder-in-cylinder and sleeve forms. Tubular chrysotile was much more abundant than platy serpentine in the products of the two-hour hydrothermal treatment of precursors based on enstatite with 10–15 wt % FeO. The tubes often show a cylinder-in-cylinder morphology; they are 550–800 nm long and 20–45 nm in outer diameter. The 6-h hydrothermal treatment of all the mixtures produced abundant cylindrical tubes with rare morphological defects (Fig. 3). An increase in the duration of the hydrothermal treatment of precursors up to 12 h, and precursors based on enstatite with 25 wt % FeO up to 15–20 h leads to the formation of structurally homogeneous cylindrical chrysotile tubes. It should be noted that the addition of FeO to the precursors caused changes in the size of tubes, which became shorter and thicker, especially during the formation of chrysotile from the mixtures based on enstatite with 25 wt % FeO. As the FeO content of initial enstatite increased up to 35 wt %, platy serpentine was predominant in the products of hydrothermal treatment, whereas nanotubes accounted for about 7% of the products and showed an increasing width (outer diameter reached 55–65 nm) and a small length of about 200–300 nm.

Thus, the kinetic investigations showed that, within the compositional range considered here, the rate of nanotube formation is controlled by the content of FeO in the precursor, the rate of formation and stability of transitional phases, and conditions of hydrothermal treatment (temperature and chemical composition of

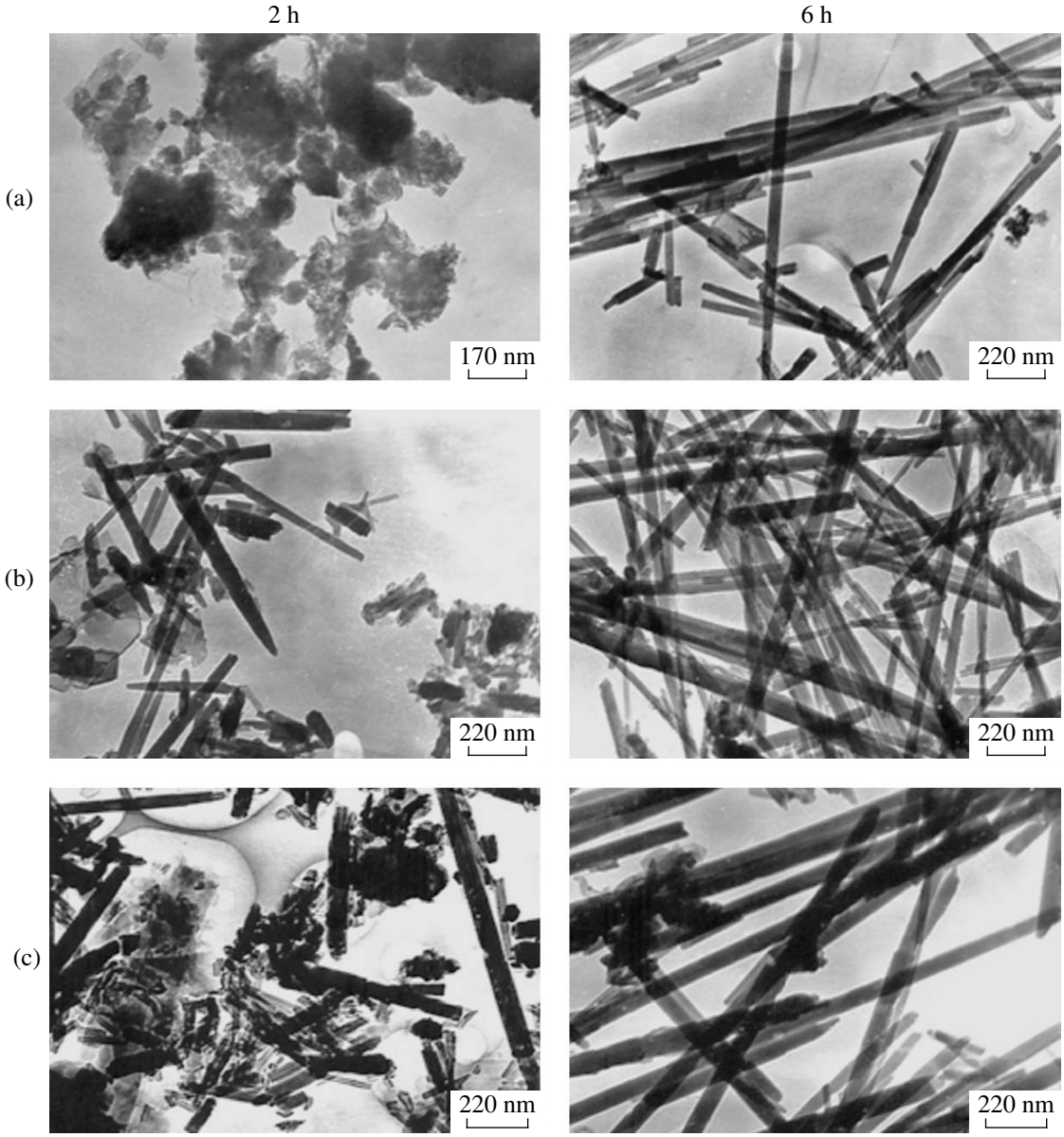


Fig. 3. Transmitted electron microscope images of the products of hydrothermal treatment in NaOH solutions (1.5 wt %) at a temperature of 350°C and a pressure of 70 MPa for various durations of treatment of various mixtures: (a) $MgSiO_3$ + MgO, (b) (Mg, Fe)SiO_3 (10 wt % FeO) + (Mg, Fe)O, and (c) (Mg, Fe)SiO_3 (25 wt % FeO) + (Mg, Fe)O.

hydrothermal solution). Variations in the rate of chrysotile formation depending on its iron content are probably related to different solubilities of precursors containing different amounts of FeO under elevated temperatures and pressures and some crystal chemical distinctions in the structure of the octahedral layer of Mg–Fe chrysotiles [15].

CONCLUSIONS

It was found that the sequence and rate of formation of $(Mg,Fe)_3Si_2O_5(OH)_4$ chrysotile under hydrothermal conditions are controlled by the amount of FeO introduced into the precursors, the composition of hydrothermal solutions, and the temperature of the hydrothermal treatment of the starting materials. The rate of formation and stability of transitional compounds exert a significant influence on the rate of nanotube formation.

The parameters of the structural and morphological transformations of precursors during the formation of the nanotubular chrysotile were estimated. By varying iron content in the precursors, it is possible to obtain chrysotile with the desired morphology and size. It was demonstrated that the formation of chrysotile nanotubes is always preceded by compounds with a sheet

structure, irrespective of the composition of initial components.

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