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Serpentine Mineral Amorphization in the Technology of Obtaining Magnesia-Silicate Reagent for Immobilizing Heavy Metals

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Abstract

The processes were studied concerning the amorphization of three structural types of serpentine minerals (antigorite, lizardite, and chrysotile) and the formation of an active metastable phase resulting from thermal impact. It has been established that the level of antigorite activation is lower than the activation level for lizardite and chrysotile.

Key words: serpentine minerals, thermal activation, metaserpentine, amorphous phase, micromorphology, activity

INTRODUCTION

Serpentine minerals are widely distributed in the nature and are part of such mining waste products, as overburden rock chrysotile asbestos, magnesite, vermiculite, olivinite deposits, waste products resulted from the enrichment of copper-nickel ores. Besides traditional scopes [1] serpentinite is proposed to use as a precursor for obtaining thermoactivated products whose properties differ from the properties initial serpentinite due to the formation of a metastable phase such as metaserpentine within certain temperature range [2]. Earlier, attempts were undertaken in order to employ thermally activated serpentine minerals in various fields. For example, serpentinite was used for obtaining a magnesia binder *via* roasting within the temperature range of 668–720 °C [3], as well as for purifying waste water (the temperature of activation amounting to 650–700 °C) [4]. However, thermally activated serpentinites have not found any practical application due to various reasons of technical and economic character, including instability of their properties.

The instability of metaserpentinities could be explained, in our opinion, by the variability of serpentinites, which might be judged from an impressive list of special names given earlier to serpentine-like formations [5]. The further studies of serpentinites have revealed their complexity, multicomponent composition as well as the presence of three properly serpentine minerals such as antigorite, lizardite and chrysotile [5]. For years of time, studies are being carried out at the ICTREM, KSC RAS, aimed at developing the technology of obtaining and using a magnesia silicate reagent resulted from serpentine minerals in order to immobilize heavy metals (HM) [6]. The reagent obtained via the thermal activation of serpentine of minerals does not contain any toxic components; it is intended, first of all, to rehabilitate contaminated naturally occurring water sources and purify man-caused reservoirs having hydraulic connection with underground and surface waters.

It has been established that the reagent causes to precipitate low-soluble HM compounds not only as the result of increasing solution pH value and of hydrolytic reactions, but also due to

the formation of low-soluble silicates. Owing to this fact, the reagent could be used for profound water treatment [7]. So, the concentration of HM in water purified with the use of this reagent amounts to about 0.01–0.02 mg/L at $\text{pH} \leq 8.5$, which is comparable, for example, with the requirements for fish-industry reservoirs.

The efficiency of technological processes with the application of thermally activated serpentine depends on the content active phase therein. Active it is accepted to name the state of solids characterized by the presence of non-equilibrium defects is accepted to name active state [8]. In serpentine minerals, defects can arise under such heating conditions when the crystal lattice of serpentine, as the result of dehydration, loses hydroxyl water without forming any new compounds [9]. The authors of [10] have made an assumption that the endothermic effect with the maximum at 630–750 °C inherent in all the serpentine minerals corresponds to the decomposition and amorphization of serpentine minerals with removing the constitutional water. This assumption has been confirmed in the works devoted to the studies on the process of phase formation in the course of roasting serpentines [5, *etc.*]. Dehydrated roentgen-amorphous serpentine $3\text{MgO} \cdot 2\text{SiO}_2$ has been named metaserpentine. The absence of free oxides MgO and SiO_2 within the temperature range of 400–700 °C and the authors of [9] consider the presence of metaserpentine pseudomorphosis with respect to the initial serpentine to be an evidence for the existence of metaserpentine. The investigation of serpentine employing the method of Raman microspectroscopy has revealed that there is parallel formation of forsterite and enstatite structures occurring within a juvenile metaserpentine matrix. In this case the temperature of serpentine processing is lower than the temperature corresponding to the maximum exothermic effect of forsterite formation [11]. Such a course of mineral formation indicates, according to the opinion of authors [12], in the presence of microscopic non-uniformities within the material those are characterized by amorphous liquation structure and the hyperactivity of components.

In the present work, an attempt has been made to perform systematic studies concerning the change of antigorite, lizardite and chryso-

tile properties in the process of thermolysis. The features of the structure of various serpentine types, which could affect the process of amorphization, are considered. The structure of serpentine minerals consists of two-storied layers (1 : 1) formed through connecting one tetrahedral grid with one octahedral grid via common oxygen atoms[5]. In the structure of magnesian serpentines there is a certain disproportion between octahedral and tetrahedral grids. According to three different methods of the compensation of this disproportion, the structural layers of serpentines could be flat (lizardite), cylindrically bent (chrysotile) and wavy (antigorite).

In the structure of lizardite, the disproportion of grids is overcome due to shifting the atoms from ideal positions. Structural stresses, inherent in lizardite, hinder relatively large crystals from growth. In the structure of chrysotile, whose unit cell covers two layers, there is a shift of atoms occurring too, though to a lesser extent, since the curvature of layers in a real cylindrical structure only partly compensates the disproportion. In the wave-like structure of antigorite, as opposed to the cylindrical structure of chrysotile, every layer could theoretically reach an ideal value of grid radius (to compensate the disproportion) [5]. Thus, owing to the wavy bends of the layer the structure of antigorite is more stable as compared to lizardite and chrysotile. In particular, this is confirmed by the fact that the size of crystal edge of the unit cell for antigorite is much higher in comparison with those for other serpentines. The comparison of the structural features for serpentine minerals and the amorphization level therein in the course of heat treatment has been performed with the application of XRD phase analysis and electron microscopic investigation. The first method allows one to obtain an integral characteristic of a sample under investigation, whereas with the help of the second method one could estimate changing the state of separate particles for the minerals.

MATERIALS AND METHODS

In this work, we used the samples of serpentines with different structural types. An al-

most monomineral sample of antigorite (the Pilguyarvi massif, the Pechenga ore field, Murmansk Region), according to [13] has the following chemical composition, mass %: SiO₂ 40.7, MgO 36.0, FeO 5.7, Fe₂O₃ 2.2, Al₂O₃ 2.2, CaO 0.3, MnO 0.16, Na₂O 0.06, K₂O 0.05, NiO 0.04, TiO₂ 0.04, H₂O 11.8, CO₂ 0.07.

Lizardite was presented by two samples of sungulite taken from the Habozoro olivinite deposit and the Kovdor vermiculite deposit (the Salma-Kovdor belt, Murmansk Region). The determination of the activity was performed for the first sample having the following chemical composition, mass %: SiO₂ 42.8, MgO 37.3, Fe₂O₃ 0.9, Al₂O₃ 1.3, CaO 1.4, TiO₂ 0.4, H₂O 14.9, CO₂ 1.8.

As a sample of chrysotile we employed serpentinite-magnesite from the Khalilovo magnesite deposit (Orenburg Region) with the following composition, mass %: SiO₂ 31.1, MgO 31.1, FeO 1.0, Fe₂O₃ 4.3, Al₂O₃ 1.9, CaO 4.3, H₂O 10.8, CO₂ 11.6. Besides, orthochrysotile the sample contains dolomite and magnesite with the mass fractions of 14.8 and 8.6 %, respectively.

Thermally treated serpentine samples were obtained *via* calcination the material in a muffle furnace. For this purpose we placed serpentinite dispersed by a thin layer over a metal pallet to the furnace heated up to a preset temperature; after reaching a required mode of operation the sample was held within 20 min. The present mode of roasting was chosen basing on the results of preliminary studies; those have demonstrated that the activation level is the greater the greater is the heating rate for the material. Under the conditions of roasting realized in the laboratory muffle furnace the optimum duration of the processing amounted to 20 min.

The XRD analysis was carried out with a DRON-2.0 diffractometer employing CuK_α radiation, the electron microscopic investigation was carried out with the use of SEM LEO 420 scanning electron microscope.

The activity of initial and thermally treated serpentinite samples was determined as the total content of acid-neutralizing components according to the technique described in [7].

RESULTS AND DISCUSSION

Antigorite and lizardite were taken from geological samples, whereas the sample of

chrysotile represented a serpentine-containing rock grinded in an industrial mill. The micropfractographic analysis was performed for antigorite and lizardite grains. The sample of antigorite (Fig. 1, a, b) belongs to a microscopically dense variety of serpoites with a plain-blistering break [10]. As opposed to antigorite, the surface of lizardite split is characterized by a jagged break, looseness, roughness, and lamination manifestations. The grains of lizardite represent the conglomerates of chaotically arranged layered microblocks (see Fig. 1, c-e).

The features of the internal structure of particles are displayed in the XRD profiles of minerals in the form of changing the ratio between basal ($d = 7.3-7.4$ Å) and non-basal reflexes (Fig. 2, a, b). For antigorite, the mentioned ratio is much greater as compared to that of lizardite [5].

The XRD profile of chrysotile is characterized by an increased background and an increased diffusivity of reflexes (see Fig. 2, c). The amorphization attributes arising for the initial mineral [14] could be explained by an intense mechanical impact in the course of its grinding [5]. The analysis of XRD profiles of the samples obtained under various roasting temperatures demonstrates that with increasing in the temperature (up to the temperature of beginning the crystallization of forsterite) the level of minerals' amorphization grows, too. The general tendency for all the serpentine minerals consists in decreasing the intensity of reflections and increasing in their diffusivity, as well as the formation of halo and increasing the background.

A considerable increase in the background within the range of small diffraction angles, which indicates appearing mixed-layer formations [14], is observed for lizardite and chrysotile samples activated by thermal treatment within the temperature range of 550–750 °C. The background for antigorite increases a little, too, though to a lesser extent.

Alongside with the mentioned above process one can observe a diffuse broadening of main reflexes and wide dim halo to occur. The position of antigorite halo maximum ($d = 3.6$ Å) is close to the value corresponding to amorphous silica ($d = 3.94$ Å) [15], whereas shifting the maximum could be explained by the presence of a magne-sial component within the amorphous phase.

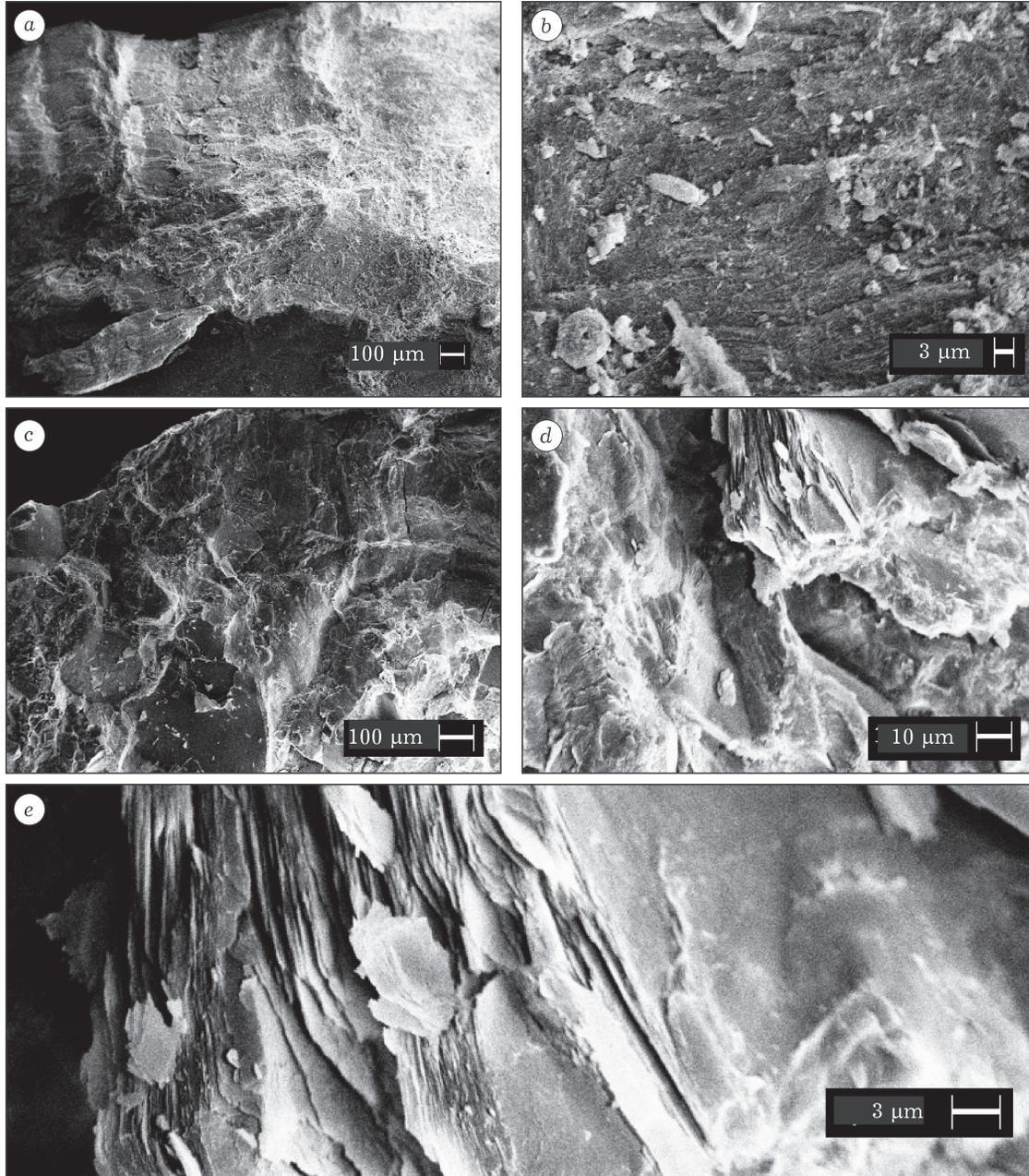


Fig. 1. Surface morphology of antigorite (a, b) and lizardite (c–e) grains.

Decreasing the lizardite and chrysotile basal reflexes with increasing the temperature, as opposed to antigorite, occurs in a more intense manner. As compared to the initial mineral, the intensity of basal reflexes 001 in the case of thermally treated lizardite and chrysotile exhibits a 1.5- to 2-fold decrease for the samples calcinated at 550 °C, a 3- to 7-fold decrease for the samples calcinated at 600 °C, whereas the signal completely disappears at the calcinations temperature of 650 °C. The intensity

of basal antigorite reflexes almost does not change up to the temperature of activation amounting to 600 °C being reduced a little as the result of roasting at 650 °C.

For the amorphized antigorite sample obtained at 700 °C, one can observe main basal reflexes of the initial mineral, which indicates the conservation of order in newly formed high-temperature phases inherent in layered antigorite being confirmed by the results of micro-morphological analysis. From the data present-

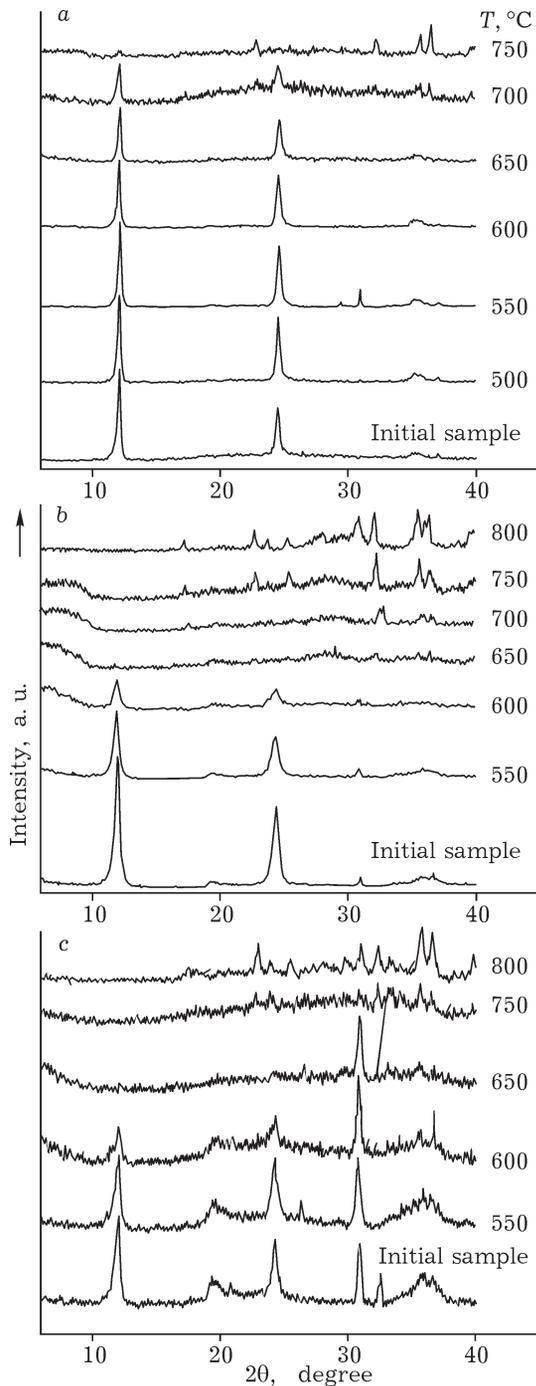


Fig. 2. XRD profiles for antigorite (a), lizardite (b) and chrysotile (c) samples obtained at different roasting temperature.

ed in Fig. 3 one can see that the initial antigorite (see Fig. 3, a) contains large particles with the size higher than $10\ \mu\text{m}$, as well as aggregates consisting of fine lamellar particles with different contours, but with a distinct faceting. Fine particles mainly are of elongated shape, their size does not exceed $1 \times 4\ \mu\text{m}$. The specific surface area of the sample amounts to $9.39\ \text{m}^2/\text{g}$.

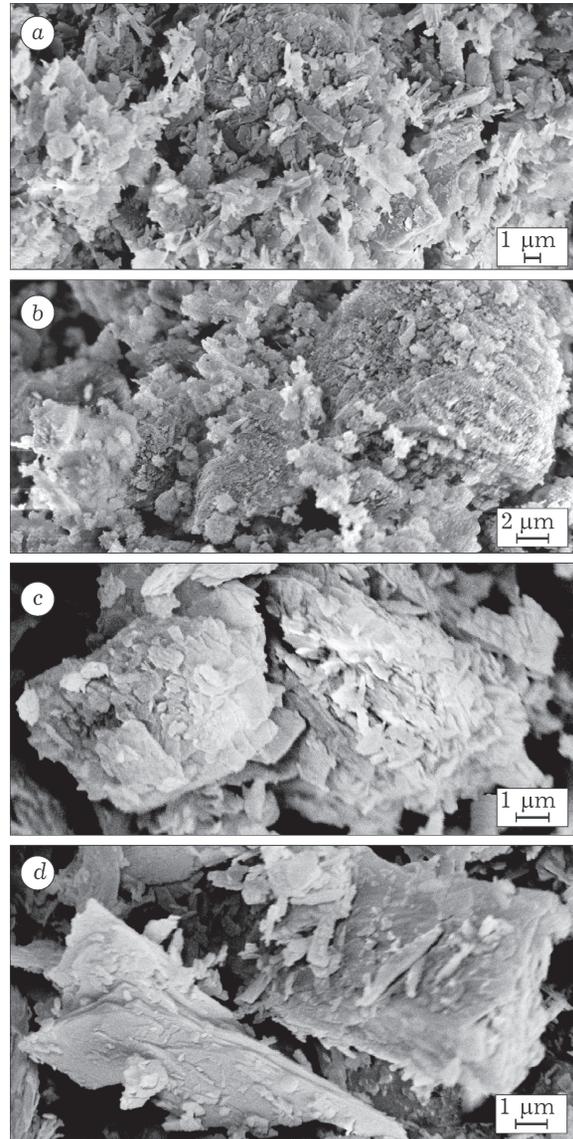


Fig. 3. Morphology of antigorite particles: a – initial sample; b–d – samples after thermal treatment at 650, 700 and 750 °C, respectively.

After roasting at 650 °C (see Fig. 3, b) the morphology of large particles changes insignificantly. It could be only noted that their surface becomes more loosened due to segregating neoformations. Fine particles become isometrically round-shaped, with dim edges. The maximal size of fine particles does not exceed $1\ \mu\text{m}$. Besides fine flaky particles, there are their clusters present in the sample, with the size amounting to about several micrometers. The porosity of the mineral influences the luminescence of particle surfaces metallised with gold, which is registered by forming flashes when passing an electron beam. The glow of sepa-

rate fine particles could be explained by slow draining charge from them due to the absence of tight contact between large particles and the substrate. The specific surface area of antigorite sample calcinated at 650 °C, is somewhat lower as compared to the specific surface area the initial sample and is equal to 7.14 m²/g. This decrease, to all appearance, could be connected with changing the morphology of fine particles.

The increase in the temperature of roasting up to 700 °C results in disappearing friable neoformations as well as in compacting the material (see Fig. 3, c). Large particles break up to give conglomerates with uncertain shape. For the sample of antigorite calcinated at the temperature of 750 °C one can observe large particles with prismatic shape and thin plates with even edges, less than 1 μm thick (see Fig. 3, d).

As opposed to antigorite, the morphology and texture of the surface of chrysotile particles, as a most amorphized mineral (according to the data of XRD phase analysis), almost

does not change after roasting, except for the occurrence of microcracks within a thermally treated sample (Fig. 4). It should be noted that after intense mechanical impact in a ball mill the relief of chrysotile grain surface could be considered as a mechanical balling microrelief [16]. To all appearance, the surface of initial chrysotile particles is already partly amorphized, thus no occurring neoformations after roasting can be registered.

The results of the morphological and fractographic analysis of initial and activated lizardite are presented in Fig. 5. A comparative analysis of grain morphology for the samples of the mineral demonstrates that as the result of temperature impact micro fissuring uses to develop (see Fig. 5, a, b). On the surface of lizardite grain split and at the edges of separate plates one can distinctly see as well as in the case antigorite, friable flaky neoformations (see Fig. 5, c, d).

Starting from the aforementioned features of changing under roasting the serpentine minerals of different type one could assume that the content of metaserpentine in thermally activated lizardite and chrysotile samples should be higher in comparison with that for antigorite.

The results of determining the activity of serpentinites are presented in Fig. 6. It is seen that the activity lizardite and chrysotile exposed to roasting within the temperature range of 600–750 °C is more than twice higher than the activity of the most amorphized antigorite samples.

From the theoretical standpoint, the maximal activity of ideal serpentine mineral Mg₃Si₂O₅(OH)₄ consisting of 43.0 % MgO, 44.1 % SiO₂ and 12.9 % H₂O is equal 24.7 mg-eq/g as calculated for calcinated residue. For the samples of antigorite, lizardite and chrysotile this value amounts to 20.5, 23.0 and 21.0 mg-eq/g, respectively. The experimental data demonstrate that the maximal amorphization level for antigorite is equal to 34 %, whereas for lizardite and chrysotile this value amounts up to 82 and 94 %, respectively.

From our point of view, one could explain the experimental fact obtained by the features of antigorite crystal structure. Let us consider the conclusions made in [17] in the course detailed studies on temperature effect on the structure of different lizardite polytypes. According to the authors of [17], the character of the structural response of lizardite to the

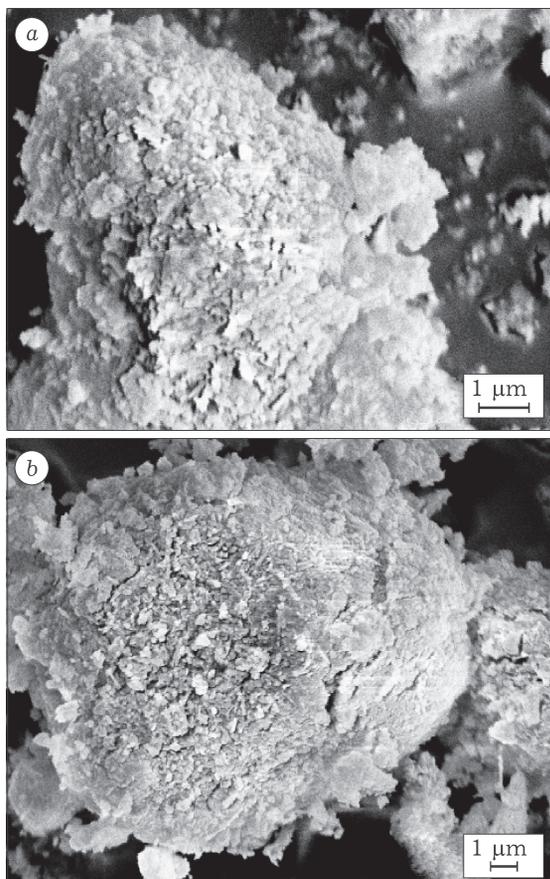


Fig. 4. Morphology of chrysotile particles: a – the initial sample, b – a sample after thermal treatment at 700 °C.

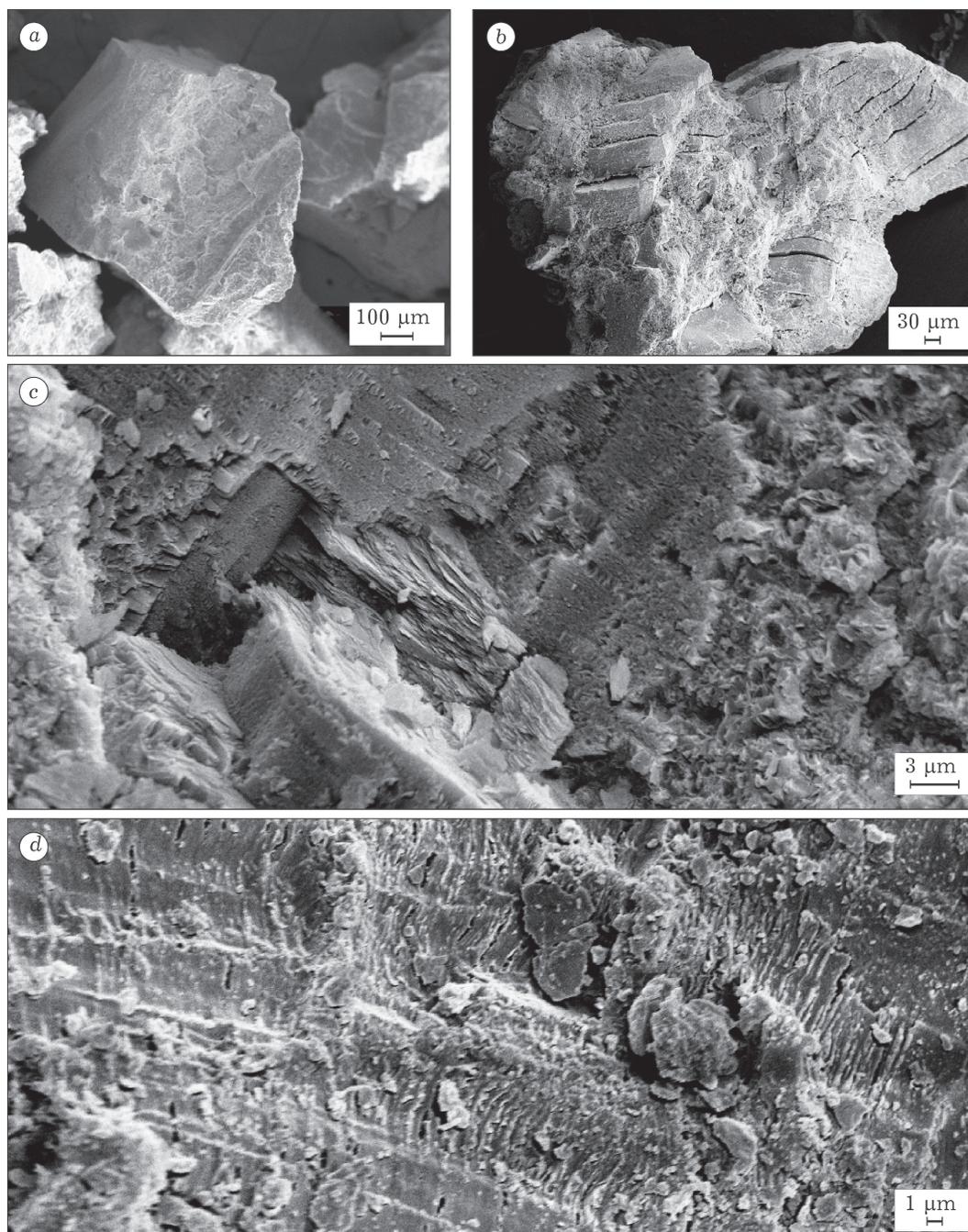


Fig. 5. Morphology of lizardite particles: *a*, *c* – initial sample; *b*, *d* – sample after thermal treatment at 650 °C.

increase in temperature could be explained by two processes occurring. The first of them is connected with the increase in the length of O–H...O bond between serpentine layers as the result of temperature expansion. The second process is characterized by the occurrence of structural deformations owing to the distortion of the shape and rotation of tetrahedrons in the plane of the lattice as well as to the subse-

quent movement of basal oxygen atoms as the result of the adaptation of tetrahedral and octahedral lattices to various types of thermal expansion. The realization sequence of the mentioned processes is different even for the polytypes of one serpentine mineral species, the difference in whose structure are insignificant. Hence, in the thermolysis of serpentine minerals with different structure either the first

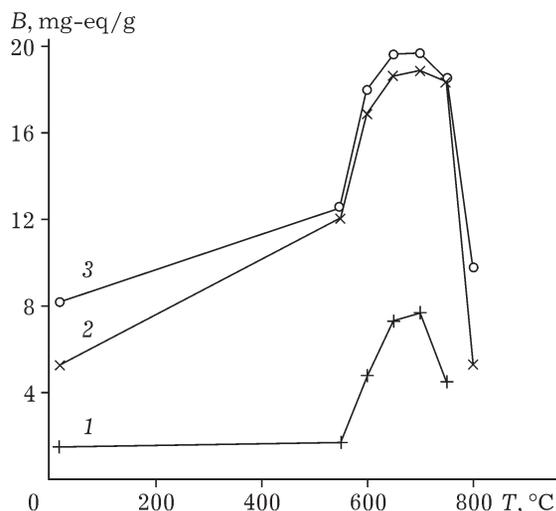


Fig. 6. Activity level (B) of antigorite (1), lizardite (2) and chrysotile (3) samples depending on the temperature of roasting.

or the second process would prevail, which represents just the explanation of the results obtained in the present work. Antigorite characterizing by the least defective structure as compared to other serpentines, as opposed to lizardite and chrysotile can compensate the influence of a temperature increase by the distortion of the lattice of the serpentine layer, with order conservation along axis c .

The stability of the antigorite structure causes the presence of separate micro-blocks with a relatively large size wherewith can be connected diffusion hindrances concerning water removal could be connected. Just antigorite transformation into forsterite according to a topotaxial mechanism with conservation of its initial form is described in [5].

The studies performed have demonstrated that the amorphization of lizardite and chrysotile proceeds much more completely as compared to antigorite; hence, in order to obtain thermally activated materials one should preferably use serpentinites containing mainly lizardite and chrysotile.

CONCLUSION

1. The behaviour of serpentine minerals under thermolysis has been investigated aiming at optimizing the technology of obtaining an active alkaline magnesia-silicate reagent. Estimation was performed concerning the amor-

phization level for different structural types of serpentine minerals with the help of XRD phase analysis, electron microscopy and chemical analysis.

2. From the data of XRD phase analysis it has been established that the common tendency for all the serpentine minerals consists in decreasing the intensity of reflections and increasing their diffuseness, as well as halo formation and background increase.

3. Micromorphological and fractographic analyses of the samples of thermally activated mineral grains has revealed the transformation of the surface, the development of its fissuring and the occurrence of friable flake neoformations.

4. Quantitative comparison of the activity level for thermally treated samples of serpentines has demonstrated that for lizardite and chrysotile a higher level of serpentine into metaserpentine transformation is observed, as compared to antigorite.

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