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HIGH-TEMPERATURE PHASES OF MONTMORILLONITE SYNTHETIZED FROM THE OXIDES $SiO_2-Al_2O_3-MgO-CaO$

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The high-temperature (950 – 1500°) changes in synthetic montmorillonite of relatively simple chemical composition, studied by X-ray diffraction analysis, infrared spectroscopy and electron microscopy, are described. It was found that this montmorillonite belongs to the Wyoming type and the high-temperature phases involve cristobalite, mullite, anorthite and spinel. Only mullite crystallized from this sample on heating for two hours at 1500°.

The paper deals with the detailed study of the high-temperature changes in synthetic montmorillonite of simple chemical composition. According to the DTA curve, in the temperature region 900-1100° this synthetic montmorillonite can be considered as of Wyoming type in the classification of Grim and Kulbicki [1]. The main high-temperature phases which crystallize above 900° from this type of montmorillonite are mullite and cristobalite [1, 2].

In comparison with samples of natural montmorillonite of Wyoming type, this sample does not contain any iron. Hydrothermal synthesis of this montmorillonite, as well as its physico-chemical characteristics and thermal study, are described in [3].

Experimental

Samples of the investigated mineral were heated for two hours at temperatures from 950 to 1500° in a Marsh furnace. Temperature was followed by a Pt/Pt – Rh (10%) thermocouple which was inserted directly into the sample. The samples were measured, after cooling, with a Philips vertical goniometer (CuKα, Ni filter). Infrared spectra of samples prepared in nujol mulls were recorded with a Spectromaster (Grubb Parsons) in the range 400 – 1175 cm^{-1}. Electron micrographs were made with a BS 242 microscope (Tesla, Czechoslovakia) with an acceleration potential of 60 kV and a direct magnification of 2500×. The resulting magnification of 7000× was achieved by photographic means.

In the X-ray pattern of the sample heated at 900° no diffraction lines were observed. After heating at 950°, diffraction lines of cristobalite, mullite, anorthite and spinel appeared. The most intense diffraction line was that of cristobalite,

followed by the doublet of mullite and another diffraction line of cristobalite. As for anorthite and spinel, only the first (the most intense) line appeared.

In the case of heating at 1000° the intensity and the number of diffraction lines of all high-temperature phases of synthetic montmorillonite were increased. A similar situation was observed after heating of the sample at 1050°.

At 1100° the heights of the most intense diffraction lines of anorthite and mullite were equal, but at higher temperatures the intensities of the diffraction lines of anorthite and spinel rapidly decreased.

After heating of the sample at 1200°, only a single diffraction line of spinel appeared. Diffraction lines of anorthite disappeared within the range 1200–1300° and the diffraction lines of cristobalite disappeared within the range 1300–1400°. When the sample was heated at 1500°, only diffraction lines of mullite were observed.

The dependence of the heights of the most intense diffraction lines of cristobalite (d_{220} = 0.25 nm), mullite (d_{210} = 0.338 nm), anorthite (d_{040} = 0.318 nm) and spinel (d_{311} = 0.242 nm) on the temperature of heating is given in Fig. 1.

Study of the infrared spectrum of the sample heated at 1000° (Fig. 2) shows a certain transition between the X-ray-amorphous product of decomposition of the crystal structure of montmorillonite (900°) and well-crystallized high-temperature phases (1100°).

At 1100° the infrared spectrum is characterized by absorption bands with maxima at 1090, 785, 620 and 470 cm^{-1}, corresponding to cristobalite [4]. The absorption band with maximum at 575 cm^{-1} can be assigned to mullite and the band centered at 945 cm^{-1} to spinel [4].

After two-hour heating at 1200° the absorption bands assigned to cristobalite did not change appreciably. The intensity of band of mullit increased and the intensity of the band of spinel decreased (Fig. 2).

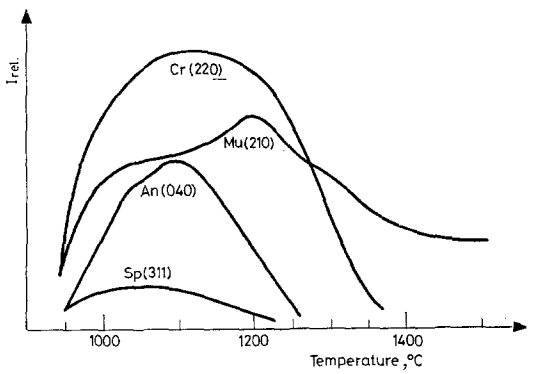

Fig. 1. Dependence of the height of the most intense diffraction lines of high-temperature phases of montmorillonite on temperature (Cr – cristobalite, Mu – mullite, An – anorthite, Sp – spinel)

At 1300° the intensity of the absorption band centered at 570 cm^{-1} and assigned to mullite increased slightly. A more distinct change in the infrared spectrum occurs after heating of the sample at 1400°. Except for the absorption band with maximum at 620 cm^{-1}, almost all the absorption bands of cristobalite as well as the band of spinel disappeared.

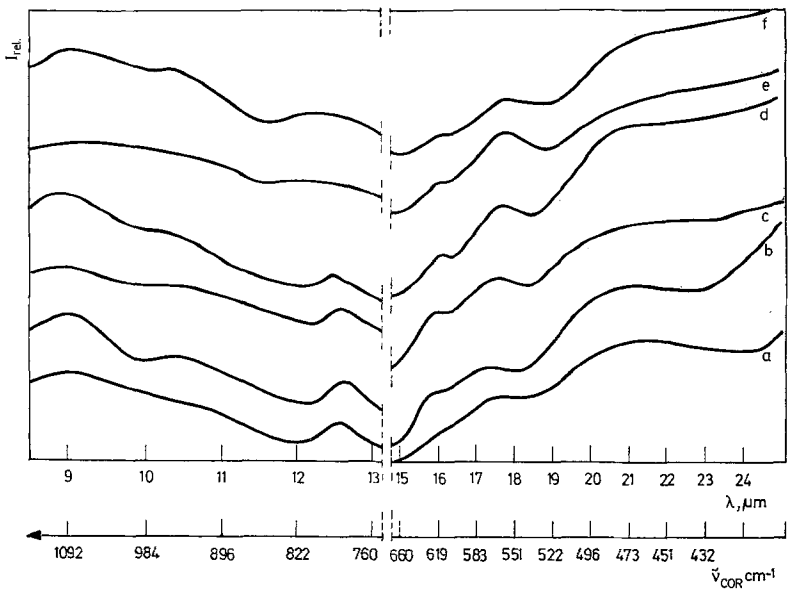

Fig. 2. Infrared spectra of montmorillonite samples after heating at 1000 °C (a), 1100 °C (b), 1200 °C (c), 1300 °C (d), 1400 °C (e) and 1500 °C (f)

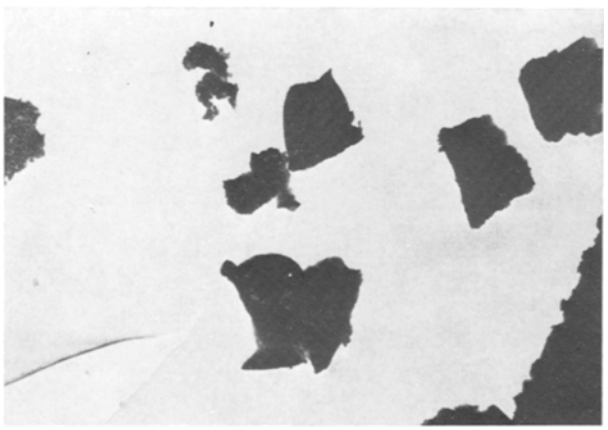

Fig. 3. Electron micrograph of a sample of montmorillonite after heating at 1000 °C; magnification 7000×

At 1500° the sample of synthetic montmorillonite melted. After cooling of the melt the absorption bands with maxima at 1090, 950, 800, 620 and 555 cm^{-1} appeared. This infrared spectrum will be interpreted in the discussion.

Development of the high-temperature phases of the synthetic montmorillonite was also investigated by the method of electron microscopy. Prior to measurements, samples were powdered in an agate mortar.

In the electron micrographs of the sample heated at 1000° the morphology of the particles shows that they were mechanically treated. Glass-like formations with sharp edges are evident, but crystals of high-temperature phases cannot be observed (Fig. 3). The situation is similar in the case of the sample heated at 1100°. The morphology of the particles of the sample heated at 1200° shows that in this

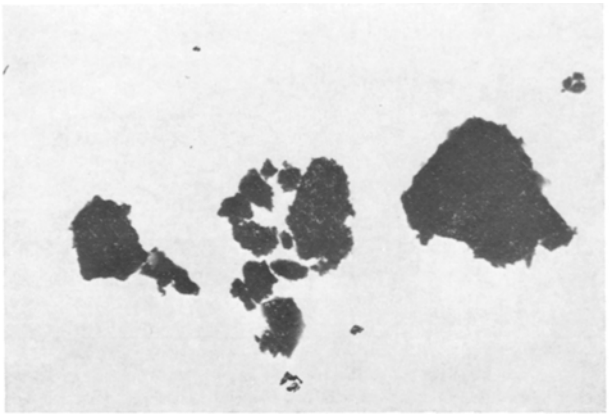

Fig. 4. Electron micrograph of a sample of montmorillonite after heating at 1200 °C; magnification 7000×

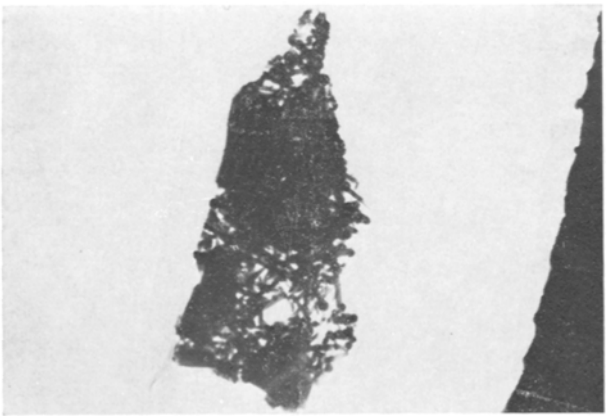

Fig. 5. Electron micrograph of a sample of montmorillonite heated for eight hours at 1200 °C and then etched with a 3 per cent solution of HF; magnification 7000×

case a certain recrystallization occurred, as the electron micrographs reveal particles smaller then 0.5 μm besides the aggregates 5 – 8 μm in size (Fig. 4).

In the electron micrographs of the sample heated at 1300°, only greater particles having sharp edges and conchoidal fracture appeared, 3 – 7 μm in size. The morphology of the particles also shows the features of mechanical treatment. After heating at 1400° and 1500° the morphology of the investigated samples was not changed. The crystalline high-temperature phases (cristobalite, mullite, anorthite and spinel) were thus not observed using electron microscopy.

Therefore, the question arose as to whether the time of heating (2 hours) is sufficient for formation of high-temperature phases visible using electron microscopy. For this reason the sample of synthetic montmorillonite was heated for eight hours at 1200°, but even after this time no formation of high-temperature phases of montmorillonite was observed in the electron micrographs.

Owing to these negative results, an attempt was made to destroy partially the glass-like surface of the particles, by etching with a 3 per cent solution of hydrofluoric acid for two minutes.

In the electron micrographs, distinct needle-like crystals of mullite and spherical formation of cristobalite appeared (Fig. 5). This chemical treatment of the sample heated for two hours at 1200° showed that both main high-temperature phases of montmorillonite of Wyoming type are well crystallized after this period of heating. The found identity of the X-ray patterns of samples heated for two and eight hours is in agreement with this observation.

Discussion

The infrared spectra of samples heated at 1000, 1100 and 1200° (Fig. 2) and their electron micrographs (Figs 3 – 6) demonstrate that the high-temperature phases of the synthetic montmorillonite are formed gradually and more slowly than results from the X-ray measurements (Fig. 1). Crystallization of mullite, cristobalite, anorthite and spinel proceeds in a glass melt.

Electron micrographs of the sample heated at 1200° show that at this temperature a certain change occurs (Fig. 4). From the increased intensity of the absorption band with maximum at 570 cm^{-1} in the infrared spectrum (Fig. 2) from the reduced absorption bands of cristobalite and as from the results of X-ray measurements given in Fig. 1, it follows that this high-temperature change is due to the formation of additional mullite and to the beginning of disappearance of cristobalite. The fact that prologation of the time of heating (from 2 to 8 hours) has no effect on the course of the X-ray patterns, the infrared spectrum and the character of the morphology of the particles in the electron micrographs, can be regarded as evidence that a two-hour heating is quite sufficient for the high-temperature changes of montmorillonite to occur.

It was found that from the point of view of infrared spectroscopy the most important high-temperature phase of synthetic montmorillonite of Wyoming type is cristobalite, followed by mullite, and the presence of spinel can also be observed.

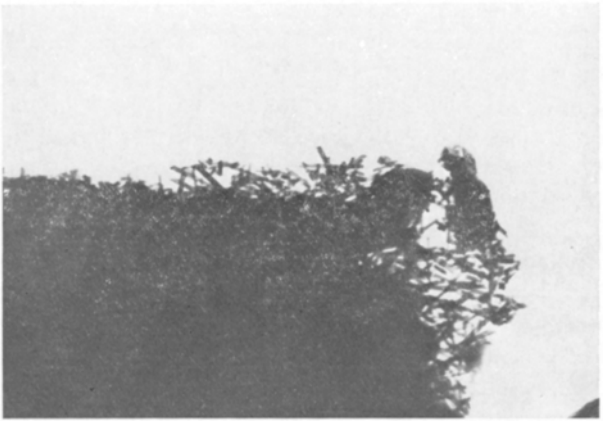

Fig. 6. Electron micrograph of a sample of montmorillonite heated for two hours at 1200 °C and then etched with 3 per cent HF; magnification 8000×

As regards electron microscopy, where it is necessary to observe samples etched by hydrofluoric acid, the most important high-temperature phase of this montmorillonite is mullite, followed by cristobalite. Rarely, crystals of spinel were also observed.

In the temperature range 1300–1500° the results obtained by the applied methods are different. Electron micrographs do not show very considerable changes in morphology and size of particles of the sintered and even the molten sample. According to the X-ray data, cristobalite disappears in this temperature range and mullite remains. This conclusion is supported by the infrared spectra (Fig. 2). However, the course of the infrared spectrum of the sample heated for two hours at 1500° demonstrates the repeated formation of cristobalite, or another modification of SiO_2, besides unchanged mullite.

It can be emphasized that the high-temperature changes of synthetic montmorillonite of Wyoming type proceed analogously to those of natural montmorillonite of this high-temperature type, in spite of the fact that the synthetic montmorillonite is produced from only five oxides (SiO_2, Al_2O_3, MgO, CaO and H_2O), while the natural one usually involves ten oxides [2, 3, 5].

References

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ZUSAMMENFHSSUNG — Die durch Röntgendiffraktionsanalyse, Infrarotspektroskopie und Elektronenmikroskopie untersuchten Hochtemperatur (950—1500°) — Änderungen in synthetischem Montmorillonit verhältnismässig einfacher chemischer Zusammensetzung werden beschrieben. Es wurde gefunden, daß dieser Montmorillonit dem Typ Wyoming angehört und, daß die Hochtemperaturphasen Cristobalit, Mullit, Anorthit und Spinell enthalten. Aus dieser Probe kristalliesierte bei zweistündigem Erhitzen auf 1500 °C nur Mullit.

Резюме — С помощью рентгенодифракционного анализа, ИК спектроскопии и электронной микроскопии изучены высокотемпературные изменения (950—1500°) синтетического монтмориллонита относительно простого химического состава. Найдено, что этот монтмориллонит относится к типу Вайоминг, а его высокотемпературные фазы включают кристобалит, муллит, анортит и шпинель. При нагревании монтмориллонита в течении 2 часов при 1500° кристаллизуется только муллит.