Journal of Thermal Analysis, Vol. 45 (1995) 481-489

EFFECT OF DEGRADATION OF MONTMORILLONITE BY VIBRATION GRINDING ON THE DTA CURVES IN THE RANGE 20–1500°C

V. Š. Fajnor and L'. Kuchta

Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University,
Mlynská Dolina, 842 15 Bratislava, Slovak Republic

(Received December 8, 1994; in revised form March 14, 1995)

Abstract

The effect of vibration grinding on the DTA curves of montmorillonite isolated from the most important locality of bentonite in the Slovak Republic (Jelšovy potok, Middle Slovakia) was studied in the temperature range 20–1500°C. Interpretation is offered for 6 endothermic and 3 exothermic peaks. vibration grinding modified the course of dehydration of the mineral, suppresses the 'dehydroxylation' peak at 700°C, enables the crystallization of high-temperature quartz, cristobalite and cordierite at lower temperatures in comparison with unground natural montmorillonite. Vibration grinding slows down the crystallization of mullite which – unlike quartz, cristobalite and cordierite – does not belong to high-temperature phases of Cheto-montmorillonite. The order in which these high-temperature phases occur is not influenced by vibration grinding.

Keywords: differential thermal analysis, high-temperature phases, montmorillonite, vibration grinding

Introduction

The ceramic properties of kaolinite can be improved when the mineral is ground for several hours or days in a ball mill, but when this mineral is ground in a vibration mill, less than 1 h is sufficient [1, 2]. Even within the first few minutes of vibration grinding significant changes can be observed while during grinding in a ball mill these changes did not occur even after several hours [3]. Complete destruction of the crystal structure of kaolinite was first described by Kelley and Jenney [4]. Long-time grinding of montmorillonite in a ball mill was studied for the first time probably by Bloch [5]. He found that the crystal structure of the mineral was completely destroyed after 700 h of grinding. According to B. Èíæel *et al.* [6, 7] a few hours of vibration grinding of montmorillonite was sufficient to diminish X-ray diffraction line intensities and at the same time

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

significant changes occurred in the DTA curves in the temperature interval 20 to 1150°C.

The aim of this work was to study the effect of vibration grinding of montmorillonite on the character of DTA curves in the temperature range 20 to 1500°C with respect to the high-temperature reactions of this mineral.

Experimental

The fraction of montmorillonite with particles below 2 μm was isolated from the water suspension of bentonite from Jelšovy potok (Middle Slovakia) – the most important bentonite locality in Slovakia [8].

The following formula was calculated from chemical analysis results:

$$\mathrm{Me}^{\mathrm{II}}_{0.52}\ [\mathrm{Si}_{7.59}\mathrm{Al}_{0.41}][\mathrm{Al}_{3.06}\mathrm{Fe}_{0.34}\mathrm{Mg}_{0.63}]\mathrm{O}_{20}(\mathrm{OH})_4\cdot n\mathrm{H}_2\mathrm{O}$$

Part of Si atoms in tetrahedral sites is substituted by Al atoms (5%) and part of Al atoms in the octahedral sites by Fe atoms (8%) and mainly by Mg atoms (16%). Due to these heterovalent substitutions, octahedral and tetrahedral layers are negatively charged and the charge is balanced by the exchangeable cations Mg^{2+} and Ca^{2+}.

It was proved by X-ray phase analysis (vertical goniometer Philips, CuK_α radiation and Ni filter) that the isolated montmorillonite was monomineral.

The samples were ground in the laboratory vibration mill VM-4 (Czechoslovak production). The grinding mechanism, which is revolved by electric motor (1100 watts, 930 r.p.m), consists of a cylindrical steel container (10.7 cm inner diameter) in which a steel ring (8 cm diameter) and a steel cylinder (4.2 cm diameter) are concentrically placed. The samples in amounts 40–50 g were dried at a temperature of 60°C before grinding. The times of grinding were 5, 30, 60, 120 and 180 min.

Thermal analyses were performed with a Derivatograph Q-1500 D (MOM Budapest, Hungary) under the following conditions: weight of samples: 310 mg; heating rate: 15 deg·min^{-1}; reference material: α-$\mathrm{Al}_2\mathrm{O}_3$; crucible: corundum; atmosphere: air, static.

To enable the interpretation of DTA curves in the high temperature region (1000–1500°C), samples placed in a platinum boat were annealed for two hours in a tube furnace. Temperatures of isothermal heating were 850, 900, 1000, 1100, 1200 and 1300°C. Annealed samples were crushed in an agate mortar and X-rayed in the range of 5–60° 2Θ.

Results and discussion

DTA curves of montmorillonite samples are presented in Fig. 1. The strong nearly symmetric double endothermic peak at temperatures 150 and 200°C is characteristic of the DTA curves of natural (not ground) montmorillonite (Fig. 1a). This double peak is caused by dehydration of montmorillonite – it means the release of water adsorbed at the surface of the mineral and of water molecules coordinating exchangeable cations Ca^{2+} and Mg^{2+}.

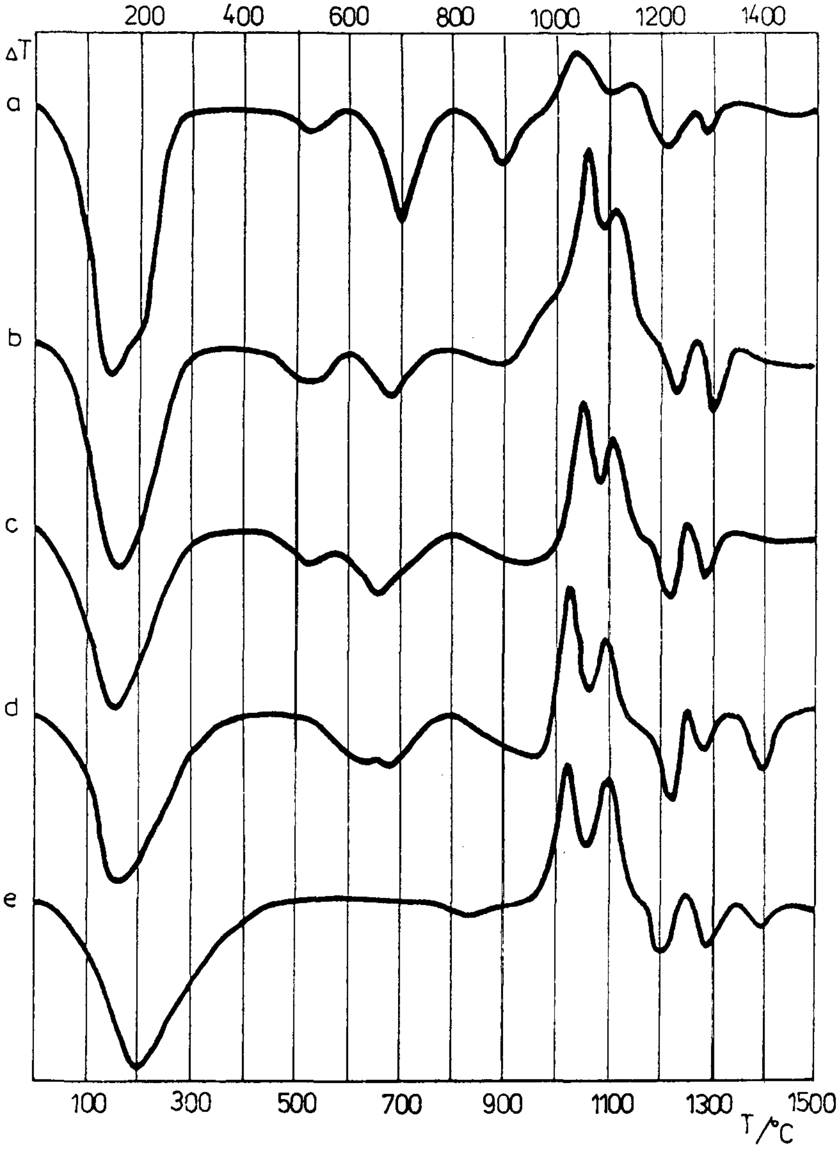

Fig. 1 DTA curves of montmorillonite (a - unground sample, b - sample ground for 0.5 h, c - sample ground for 1 h, d - sample ground for 2 h, e - sample ground for 3 h), obtained at a heating rate of 15 deg·min^{-1} and with a sample weight of 310 mg

Dehydroxylation of this mineral proceeds in two steps. Maxima of the corresponding endothermic peaks are at 530 and 700°C. The second peak at 700°C is distinct and symmetrical. The next endothermic peak in the DTA curve (Fig. 1a) of 900°C is due to the degradation of the crystal structure of dehydrated montmorillonite. When the temperature rises above 1000°C, two broad exothermic peaks appear in the DTA curve with maxima at 1040 and 1145°C. Both peaks are probably due to the crystallization of the high-temperature phases. Before a temperature of 1500°C is attained, two other endothermic peaks occur in the DTA curve with maxima at 1210 and 1285°C (which are probably caused by decomposition of the high-temperature phases of motmorillonite) and an exothermic peak with maximum at 1265°C (crystallization of a new high-temperature phase). From the temperature difference 140°C between the first exothermic peak and the preceding endothermic peak (T_m=900°C) it can be concluded that the studied montmorillonite does not belong to the high-temperature type Wyoming nor to the Cheto type, although it is nearer to the Cheto type [9–11]. According to Brigatti and Poppi [12] there is a certain region of chemical composition in which a montmorillonite may belong either to the Wyoming-type or to the Cheto-type.

A thirty-minute vibration grinding of montmorillonite caused changes in the DTA curves (Fig. 1b). Significant decrease in size of particle aggregates and preferenced orientation of crystals to the one plane, revealed by scanning electron microscopy [13], leads to an easier release of water from the sample and the originally double endothermic peak becomes a single peak at 165°C. The first dehydroxylation peak (T_m=555°C) becomes broader and the height of the second dehydroxylation peak (T_m=690°C) decreases, which means that vibration grinding facilitates dehydroxylation of this mineral. The broadening and decreasing of the endothermic peak at 900°C indicate degradation of the crystal structure of montmorillonite. The first exothermic peak becomes sharper and the second one is shifted towards lower temperatures (T_m=1120°C). The area of both these exothermic peaks increased. The third exothermic peak is sharper than that of the unground sample. The temperature interval between the maxima of the first two peaks, which was 105°C before grinding, decreased to 55°C after a 30 min grinding. The temperatures of the endothermic peaks were shifted towards higher values (from 1210 to 1230°C and from 1285 to 1305°C). An exothermic peak between them at 1270°C became higher.

After 60 min of vibration grinding all changes in the DTA curve were deepened (Fig. 1c). The temperature of the maximum of the third exothermic peak stabilized at 1260°C.

A qualitative change occurred in the DTA curve after 120 min of vibration grinding (Fig. 1d). The two endothermic peaks connected with dehydroxylation of the mineral were nearly overlapped and in the high-temperature region a new endothermic peak occurred at 1400°C. This peak would probably occur for samples ground for shorter time at temperatures higher than 1500°C.

There are several features characteristic of the DTA curve of the sample ground for 180 min (Fig. 1e):

- the extraordinary broad endothermic peak with maximum at 200°C,
- total disappearance of dehydroxylation peaks,
- the shift of the endothermic peak connected with degradation of the crystal structure of montmorillonite anhydride from 900 to 840°C,
- two distinct exothermic peaks with maxima at 1015 and 1100°C with approximately identical height and area,
- the third exothermic peak at 1260°C,
- and the last three endothermic peaks at 1210, 1295 and 1395°C.

When unground montmorillonite was isothermally heated at 850°C, the most intense diffraction (d=0.342 nm) of high-temperature quartz appeared (Fig. 2). Two traces of diffractions of spinel $MgAl_2O_4$ also appeared (d=0.286 and d=0.243 nm) as well as the traces of another diffraction of high-temperature quartz (d=0.185 nm). These values for quartz are higher than those of pure quartz, indicating a solid solution of quartz and $MgAl_2O_4$ with a very small proportion of spinel. Therefore, the quartz phase observed was called Q_{ss} [13].

In the X-ray diffraction pattern of the vibration-ground sample heated at the same temperature (measured in the range 5–60° 2Θ) there are five diffractions of high-temperature quartz (d=0.443, 0.342, 0.222, 0.185 and 0.160 nm) but there appear neither the diffractions of pure spinel nor those of the other crystal phases (Fig.2).

The further prolongation of vibration grinding (1, 2 and 3 h) did not cause any distinctive changes in the X-ray diffraction pattern of the samples heated at 850°C for 2 h. The high-temperature quartz was the only crystalline phase in all cases (Fig. 2c). It was the first high-temperature phase of montmorillonite that appeared during the heating. The course of its crystallization has been described in detail by Kranz and Čičel [15].

When montmorillonite was heated for 2 h at 900°C, the X-ray diffraction pattern exhibited nine diffractions of the high-temperature quartz (d=0.443, 0.342, 0.255, 0.230, 0.222, 0.205, 0.185, 0.171 and 0.160 nm), two very weak diffractions of spinel and one high-intensity diffraction of cristobalite.

By gradual vibration grinding (from 0.5 h to 3 h) the diffractions of high-temperature quartz and two very weak diffractions of spinel were not changed but the intensity of the most intense diffraction of cristobalite increased and two other lines appeared (d=0.318 nm and d =0.251 nm).

The authors of the high-temperature classification stated that in the case of montmorillonite of the Cheto-type the first exothermic peak in the DTA curve can be ascribed to the formation of high-temperature quartz [9]. The results presented in this work are in accord with this because the temperature of crystallization of the high-temperature quartz from vibration-ground montmorillonite decreased simultaneously with the decrease of the maximum of the first exothermic peak. It is likely that the second exothermic reaction is caused by the formation of cristobalite. Vibration grinding of montmorillonite accelerates the formation of cristobalite probably because of a preferred destruction of the octahedral layer.

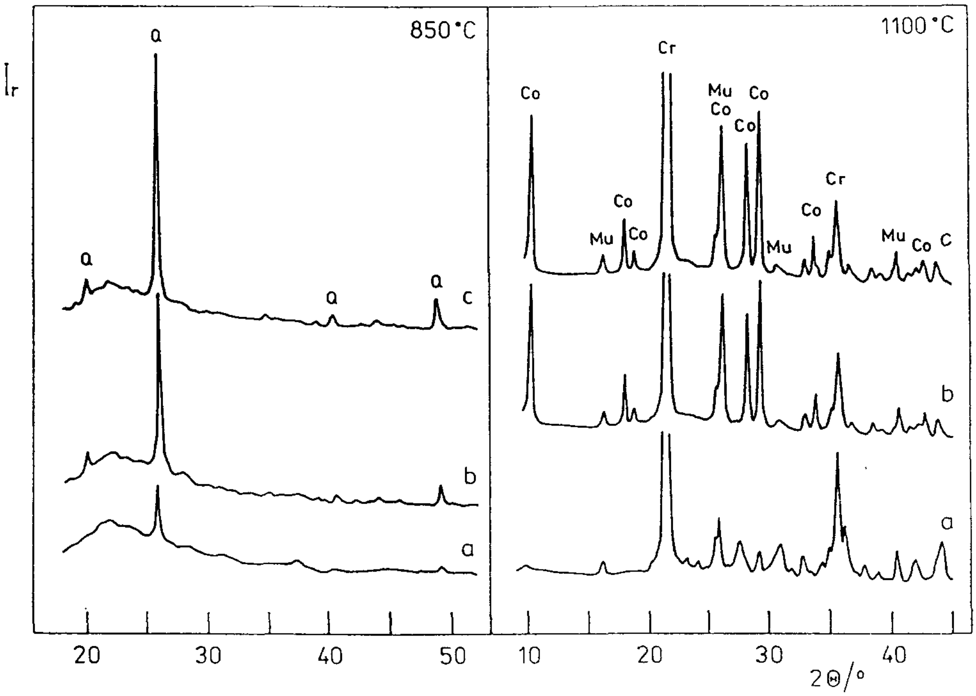

Fig. 2 X-ray patterns of unground montmorillonite (a), montmorillonite ground for 0.5 h (b) and montmorillonite ground for 3 h (c), annealed at 850 and 1100°C (Co - cordierite, Cr - cristobalite, Mu - mullite, Q - quartz)

After annealing at 1000°C diffractions of cristobalite, mullite, spinel and the most intense diffraction of anorthite (d=0.318 nm) appeared in the X-ray diffraction pattern of all studied samples. The intensities of diffractions of the particular high-temperature phases were not affected by vibration grinding.

The diffraction pattern of an unground sample annealed at 1100°C showed only diffractions of cristobalite and mullite (Fig. 2a), but no diffractions of cordierite were observed. Diffractions of spinel disappeared and the intensity of the only anorthite diffraction decreased. The thirteen distinctive diffractions of new high-temperature phases, cordierite, appeared in the diffraction patterns of samples ground for more than 0.5 h (Fig. 2c). Diffractions of anorthite were not distinguished any more. The duration of grinding did not affect the diffraction patterns.

Based on the finding that the third exothermic peak in the DTA curves became more intensive we can assume that it is due to the crystallization of cordierite. Since the diffractions of spinel for the unground sample (1100°C) disappeared but cordierite still had not crystallized we can also assume that the endothermic peak in the DTA curve at 1210°C is due to the degradation of the crystal structure of spinel. We can also assume that the degradations of anorthite and cordierite manifest themselves by an endothermic peak at 1300°C because for vibration ground samples, after crystallization of cordierite, the anorthite disappeared. It is surprising that the degradation of montmorillonite by vibration grinding facilitates crystallization of cordierite at the relatively low temperature of 1100°C (Fig. 2b, c).

The X-ray diffraction patterns of samples annealed at 1200°C do not differ from one another. The most intense diffractions belong to cordierite and the less intense ones to mullite. On all patterns there are three diffractions of high-temperature cristobalite, although the first diffraction is overlapped by the diffraction of cordierite. The spacings of these three diffractions correspond exactly neither to alpha nor to beta cristobalite, so it is not the pure high-temperature cristobalite that was formed by recrystallization of pure high-temperature quartz.

In the diffraction patterns of an unground sample annealed for 2 h at 1300°C, distinctive diffractions of mullite and cristobalite can be observed. The diffractions of cordierite are hardly observable, which can be explained by the fact that the endothermic peak at 1300°C is accompanied by the disappearance of cordierite.

The mullite diffractions on the corresponding diffraction patterns of vibration-ground samples are considerably weaker so we can say that vibration grinding suppresses crystallization and formation of mullite. There are either none or just traces of cordierite diffractions in the X-ray diffraction patterns. The fact that samples ground for 2 or 3 h exhibit the diffractions of cristobalite, is rather surprising. The appearance of another endothermic peak in the DTA curves of those samples (1400°C) could be explained by the disappearance of cristobalite. It is also possible that the peak represents the melting of the samples.

Conclusions

The DTA curves in the high-temperature range and formation of crystalline high-temperature phases of the studied montmorillonite (isolated from the bentonite from Jelšovy potok, Middle Slovakia) permit the conclusion that this montmorillonite is nearer to the high-temperature type Cheto. Unambiguous assignment to the Cheto type cannot be made because of formation of the high-temperature phase, mullite, that is typical for the Wyoming type. There is also a relatively small temperature difference between the first exothermic peak in the DTA curve and the preceding endothermic peak (140°C).

The vibration grinding of montmorillonite (after 3 h of grinding the sample is totally amorphous) changes completely the DTA curve in the whole temperature range studied (20–1500°C).

Grinding modifies the dehydration process, causes gradual extinction of dehydroxylation peaks in the DTA curve and enables the crystallization of the high-temperature quartz, cristobalite and cordierite at lower temperatures than in unground montmorillonite. On the other hand, grinding probably makes crystallization of mullite more difficult.

Vibration grinding of the studied montmorillonite causes unambiguously an acceleration of the formation of the high-temperature phases of the Cheto type. Till now we have not found sufficient theoretical explanation for this phenomenon.

The formation of quartz is the first step of the high-temperature changes of this montmorillonite. Further on cristobalite together with spinel, and anorthite are formed and at the end of the process cordierite is formed. The order of the high-temperature phase formation is not affected by vibration grinding, but the amorphization of the montmorillonite affects considerably the temperature of the formation of high-temperature phases.

References

1 W. Hiller, Silikattech., 21 (1970) 89.
2 J. Wiegmann and G. Kranz, Silikattech., 8 (1957) 520.
3 R. Schrader, T. Haase, G. Knesche, H. J. Kutzer, H. Hennek, E. Kuntzsch, E. Schaar and S. Schrickel, Silikattech., 21 (1970) 196.
4 W. P. Kelley and H. Jenney, Soil. Sci., 4 (1936) 367.
5 J. M. Bloch, Bull. Soc. Chim. France, 17 (1950) 774.
6 B. Číčel and G. Kranz, Clay Minerals, 16 (1981) 151.
7 B. Číčel, I. Novák and R. Lazar, Silikáty, 22 (1978) 347.
8 I. Kraus, Z. Hroncová, S. Horsky and A. Mihalič, Mineralia Slovaca, 21 (1989) 525.
9 R. E. Grim and G. Kulbicki, Amer. Mineralogist, 46 (1961) 1329.
10 V. Š. Fajnor and J. Masár, Proc. Thermanal 76 – High Tatras 1976, SVŠT, Bratislava 1976, p. 5.
11 V. Š. Fajnor and J. Masár, Geologica Carpathica, 30 (1979) 489.
12 M. F. Brigatti and L. Poppi, Clay Minerals, 16 (1981) 81.
13 I. Novák, B. Číčel, D. Jakubeková and D. Frtalová, Silikáty, 26 (1982) 15.
14 G. Kranz, J. Wiegmann and B. Číčel, Proc. 10th Conf. on Clay Mineralogy and Petrology – Ostrava 1986, KU Prague 1988, p. 39.
15 G. Kranz and B. Číčel, Silikattech., 36 (1985) 38.

Zusammenfassung — Im Temperaturbereich 20–1500°C wurde der Effekt von Vibrationsmahlen auf DTA-Kurven von Montmorillonit untersucht, welches aus den bekanntesten Bentonit-

Vorkommen der Slowakischen Republik (Jelšovy potok, Mittelslowakei) isoliert wurde. Für 6 endotherme und 3 exotherme Peaks wurde eine Interpretation vorgeschlagen. Vibrationsmahlen verändert den Weg der Dehydratation des Minerals, unterdrückt im Vergleich zu ungemahlenem natürlichen Montmorillonit den "Dehydroxylierungs"-Peak bei 700°C und ermöglicht die Kristallisation von Hochtemperatur-Quarz, Cristobalit und Kordierit bei niedrigeren Temperaturen. Vibrationsmahlen verlangsamt die Kristallisation von Mullit, welches – im Gegensatz zu Quarz, Cristobalit und Kordierit – nicht zu den Hochtemperatur-Phasen von Cheto-Montmorillonit gehört. Die Reihenfolge, in der diese Hochtemperatur-Phasen vorkommen, wird durch Vibrationsmahlen nicht beeinflußt.