

Studies of Montmorillonite Mechanochemically Decomposed at Different Water Contents

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Abstract

Clay minerals, as e.g. montmorillonite, abundantly exist in the slip zones such as earthquake faults and landslides. Water contents are an important factor for controlling slip behavior, since montmorillonite contains a considerable amount of water molecules compared with other clay minerals. Here, a series of mechanochemical milling experiments were conducted for montmorillonite at the water contents ranging from 0% to 800%. Decomposition occurs at the water contents below 25% and above 600%, which are well correlated with the consistency limits of montmorillonite reported so far, *i.e.* shrinkage/plastic and liquid limits, respectively. Montmorillonite is found to be effectively decomposed into amorphous materials at the water contents below the shrinkage/plastic limit. In the region of water content between shrinkage/plastic and liquid limits, decomposition cannot be achieved solely by the mechanochemical treatment. At the water contents higher than the liquid limit, decomposition is again started. The present work demonstrates that the degree of decomposition can be of usefulness for speculating how the water molecules behave in the slip zones in nature.

Keywords

Montmorillonite-Water System, Slip Zone, Fault, Milling, Amorphous Material, Consistency Limits

1. Introduction

Clay minerals abundantly exist in the slip zones such as earthquake faults and landslides. They are expected to play a significant role in fault lubrication due to the low frictional strength [e.g., [1] [2]]. Smectite group is of particular importance owing to a high capacity of interlayer water expanding the basal spacing under wet conditions [3] [4] [5]. Clay-water system changes its physical state drastically from solid to liquid states via semi-solid and plastic states with in-

creasing water content. The critical water contents at these transitions are known as consistency limits (Atterberg limits), *i.e.* shrinkage, plastic, and liquid limits [6].

Amorphous ultrafine particles have been found in a number of clay rich fault planes, which are considered to be the mechanochemically-decomposed products during seismic slip [7] [8] [9] [10]. Hirono *et al.* [11] recently proposed that the amorphous ultrafine particles remaining at the fault slip planes could be an indicator of the seismic activity. As for the landslide, Okawara *et al.* [12] predicted that the amorphous materials in the slip zone arise from a paleo-slip. In nature, the slip planes contain a considerable amount of water, largely influencing decomposition behavior as well as the slip properties.

Since 1950's, mechanochemical milling experiments have been conducted for clay minerals, especially for kaolinite [e.g., [13] [14]] and montmorillonite [e.g., [15] [16]], mainly from an industrial point of view. Here, X-ray diffraction (XRD) has been exclusively employed focusing on the crystal structures before and after milling treatments under pressure and temperature. Structural evolution of minerals caused by mechanochemical milling has been thus predicted based on the results of XRD, which is well documented in the literatures [17]. It has not been yet fully understood as to how water contents have an influence on decomposition behavior. Therefore, we performed the mechanochemical milling experiments for montmorillonite as a representative of smectite group at different water contents in this study. Decomposition behavior in the vicinity of consistency limits is highlighted based on the results of X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM), and Fourier transform infrared (FT-IR) spectroscopy.

2. Materials and Methods

2.1. Materials and Sample Preparation

Starting material is montmorillonite (JCSS-3101; Na-montmorillonite from Tsukinuno, Yamagata Prefecture, NE Japan) provided by Japan Clay Science Society. The representative chemical formula is

$\text{Na}_{0.474}(\text{Al}_{1.570}\text{Mg}_{0.322}\text{Fe}_{0.103})(\text{Al}_{0.117}\text{Si}_{3.883})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ with a small amount of quartz as impurity. The structural, physical and chemical characteristics are described elsewhere [18].

2.2. Milling Treatment

Mechanochemical milling was performed using a planetary ball mill system (Fritsch P6) employing a bowl-ball set made of tungsten carbide. The inner volume of the bowl is 45 ml and the diameter of the milling ball is 5 mm. 180 pieces of milling ball were put into the bowl together with deionized water and the air-dried montmorillonite so that the water/montmorillonite weight ratios were 0%, 25%, 50%, 100%, 200%, 400%, 600%, and 800%. A ball/(powder + water) volume ratio was approximately 1 to 1. The milling treatments were done with the main disc rotational speed of 400 rpm for 0.5 hour, 3 hours, and 12 hours.

2.3. Analytical Methods

The products after mechanochemical milling were air dried and gently powdered in an agate mortar for XRD experiments and FT-IR spectroscopy. For FE-SEM observations, the powder was suspended in deionized water and a minute quantity of the suspension liquid was dropped on a silicon wafer with micro syringe, and air dried. XRD patterns were obtained using Rigaku RINT-1200 (40 kV and 20 mA with CuK α radiation) with software JADE6 (Materials Data, Incorporated). Corundum (α -alumina, High Purity Chemicals Co. Ltd.) was added up to 20 wt% of the run product as an internal standard before XRD analysis. FE-SEM (Hitachi SU-8020) was conducted with the acceleration voltage of 1.5 kV and 2.0 kV. FT-IR spectra were obtained using a spectrometer (Nicolet iS 5, Thermo Fisher Scientific) with diamond ATR attachment.

3. Results

Figure 1 shows XRD patterns observed for the samples milled at the water contents of 0% and 25% for 3 hours, at 50%, 400%, 600%, and 800% for 12 hours together with that of starting material. XRD peaks of montmorillonite denoted

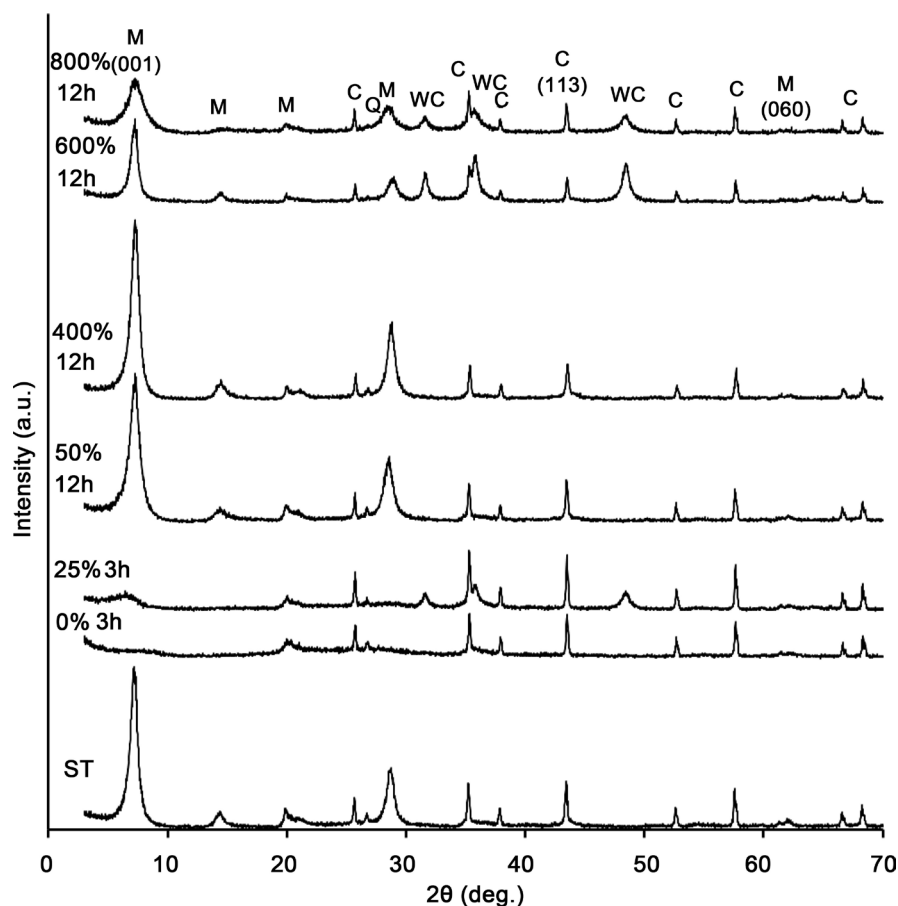


Figure 1. XRD patterns observed for the samples milled at the water contents of 0% and 25% for 3 hours, at 50%, 400%, 600%, and 800% for 12 hours together with that of starting material (ST). The characters M, C, Q, and WC indicate montmorillonite, corundum, quartz and tungsten carbide, respectively.

as M disappear for the sample milled under the dry condition (0%), whereas significant decreases in the peak intensities are seen at 25%, 600%, and 800%. Furthermore, XRD peaks arising from not only 00n (basal reflections) but also 060 peaks disappear with the increases of background around 25 degrees, which is presumably caused by the formation of silicate rich amorphous materials. On the contrary, the XRD patterns do not show remarkable changes at 50, 100, 200, and 400%. XRD peaks arising from quartz denoted as Q appear regardless of the water contents as well as milling time. The peaks of tungsten carbide at 600% and 800% are due to contamination from the milling bowl and balls.

The degree of mechanochemical decomposition can be more quantitatively discussed with the peak intensities of montmorillonite 001 relative to the corundum 113 peaks as shown in **Figure 2**. The peak intensities rapidly decrease at the water contents of 0% and 25%, whereas no significant decreases are observed in the range of water content from 50% to 400%. Again, they begin to decrease at the water contents of 600% and 800%. The present XRD demonstrate the following sequential process for mechanochemical decomposition for montmorillonite. The crystal structures of montmorillonite are effectively decomposed at the smaller water contents ranging from 0% and 25%. The decomposition hardly occurs at the water contents of 50%, 100%, 200%, and 400% even after long milling treatment with 12 hours. The crystal structure of montmorillonite begins to

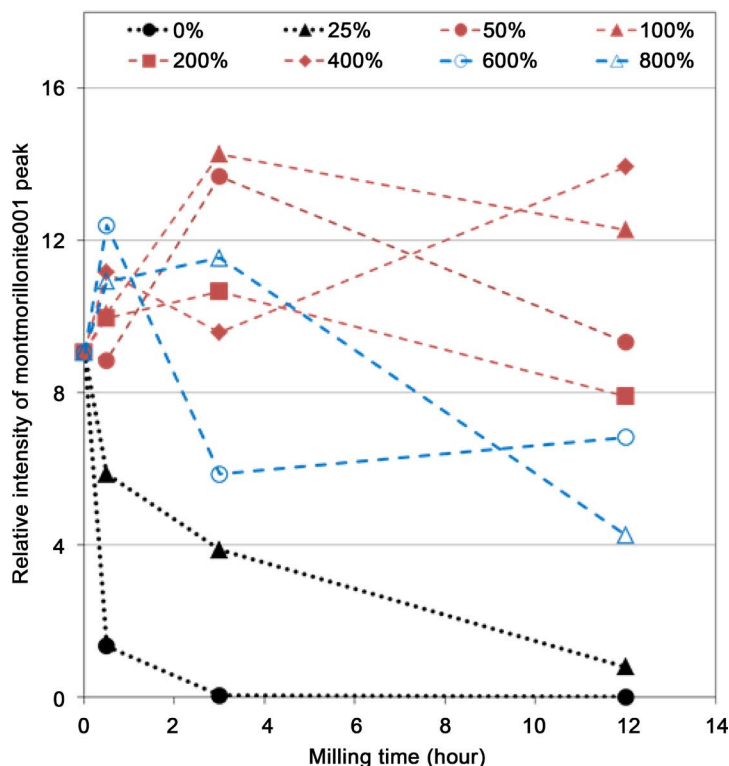


Figure 2. Peak intensities of montmorillonite 001 relative to the corundum 113 peaks as a function of milling time for the samples milled at the water contents of 0% (black solid circles), 25% (black solid triangles), at 50% (red solid circles), 100% (red solid triangles), 200% (red solid squares), 400% (red solid diamonds), 600% (blue open circles), and 800% (blue open triangles).

decompose when the water content is increased up to above 600%. An appearance of inflection point at 3 hours is probably caused by an orientation preference dominated due to strong impact before 3 hours.

Figure 3 shows FE-SEM images of (a) starting material, (b) milled at the water content of 0% for 3 hours, (c) milled at 25% for 3 hours, (d) milled at 50% for 12 hours, (e) milled at 600% for 12 hours, (f) milled at 800% for 12 hours. The starting material exhibits the thin flaky shape of about 1 micrometer (see **Figure 3(a)**). Upon milled at 0% for 3 hours, the flaky shape is not preserved forming the agglomeration with the fine particles of less than 100 nm (**Figure 3(b)**). The flaky-shape particles still remain when the sample is milled at 25% for 3 hours, however, they are partially fragmented indicating tiny globules on the surface of particles (**Figure 3(c)**). The flaky particles are clearly seen for the sample milled at the water content of 50% for 12 hours, indicating no significant change is caused by milling (see **Figure 3(d)**). The SEM images for the samples milled at 100% for 12 h, at 200% for 12 h, and at 400% for 12 h are similar to that at 50% for 12 hours, and are thus not shown here. The flaky particles with tiny globules of about a few tens nm again appear upon milling at 600% and 800% for 12 hours, which is in consistent with the XRD results.

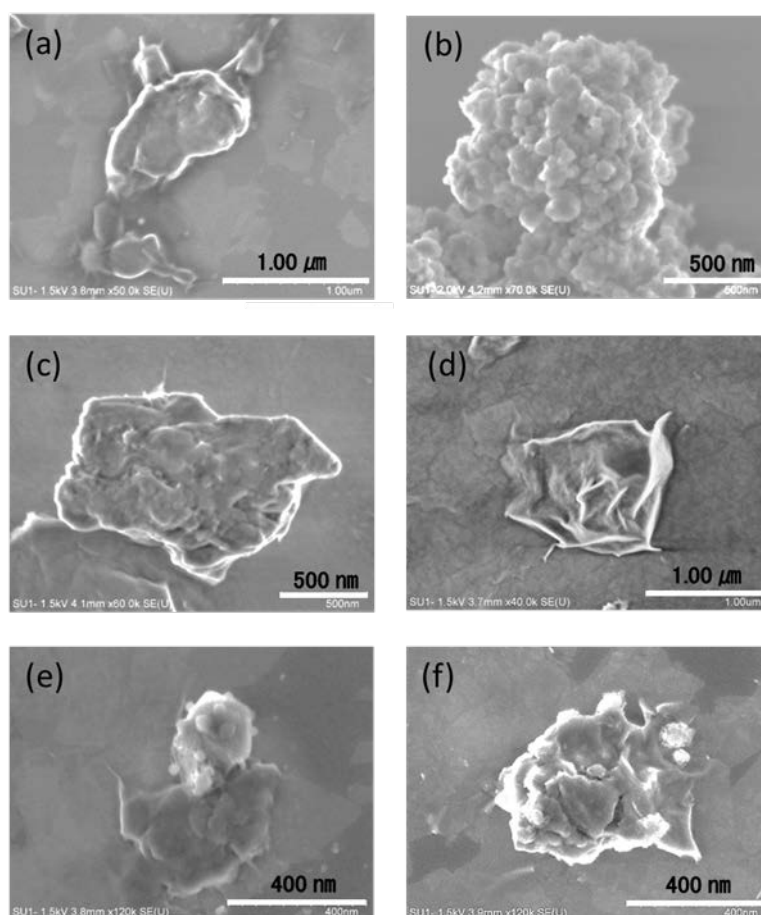


Figure 3. FE-SEM images observed for the samples of (a) starting material, milled at (b) 0% for 3 hours, (c) 25% for 3 hours, (d) 50% for 12 hours, (e) 600% for 12 hours, and (f) 800% for 12 hours.

Figure 4 shows the results of FT-IR spectroscopy, where the peaks of molecular H_2O and OH vibration observed for the samples milled at the water contents of 0% for 3 hours (red solid line), at 25% for 3 hours (brown solid line), 50% for 12 hours (green solid line), 600% for 12 hours (light blue solid line), and 800% for 12 hours (blue solid line) are presented together with that of starting material (black solid line). The starting material exhibits a sharp OH vibration peak at the wave number of $\sim 3600\text{ cm}^{-1}$, the intensity of which is higher than that of broad molecular H_2O vibration peak at $\sim 3400\text{ cm}^{-1}$. In contrast to that, the peak intensities of OH vibration decrease for the samples milled at the water content of 0% and 25% for 3 hours, signifying the decomposition of OH associated region. The peak of OH vibration recovers for the sample milled at 50% for 12 hours. The FT-IR data for the samples milled at 100% for 12 hours, at 200% for 12 hours, and at 400% for 12 hours are similar to that at 50% for 12 hours, and are thus not shown here. The peak intensities of OH vibration relatively decrease for the samples milled at 600% and 800% for 12 hours.

4. Discussion

It is known that montmorillonite possess a 2:1 layered structure with two-

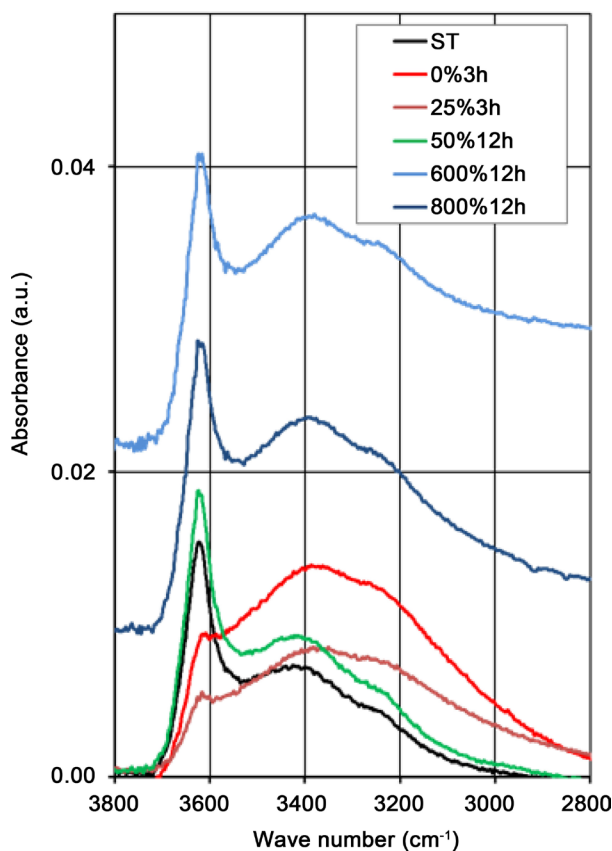


Figure 4. FT-IR spectra of molecular H_2O and OH vibrations obtained for the samples milled at the water contents of 0% for 3 hours (red solid line), at 25% for 3 hours (brown solid line), 50% for 12 hours (green solid line), 600% for 12 hours (light blue solid line), and 800% for 12 hours (blue solid line) together with that of starting material (black solid line).

dimensional (2D) nanosheets consisting of tetrahedral sheets and octahedral sheets. Basically, the O^{2-} and Si^{4+} are located at the vertices and the central site of the tetrahedron, respectively. The vertices of the octahedron are occupied by O^{2-} and OH^- groups, whereas metallic elements, such as Al, Mg and Fe atoms, are located at the central site. The diminishing of the peaks arising from 060 diffraction and OH vibration in the XRD and FT-IR data, respectively, thus provide the information that the octahedral sheets are locally decomposed.

As consistently revealed by the XRD experiments, FE-SEM observations, and FT-IR spectroscopy, montmorillonite is effectively decomposed at the low water contents 0% and 25%. The tendency at the lower water contents below 25% are in agreement with those observed for saponite, one of smectite group minerals, under the dry condition [19] and for montmorillonite at the water content of 10% [20]. The crystal structure of montmorillonite maintains without yielding the amorphous materials at the water contents ranging from 50% to 400%. Decomposition again begins at the higher water contents above 600%. It is thus inferred that the degree of decomposition transits at the water contents at 25% and 600%. The consistency limits of montmorillonite are accepted as ~10%, 54 ~ 98%, and 290% ~ 710% for the shrinkage, plastic, and liquid limits, respectively [6]. The transition of decomposition degree at 25% and 600% observed in the present work corresponds to the shrinkage/plastic and liquid limits, respectively.

At the water content of 25%, the basal spacing of Na-montmorillonite expands to 18 Å, which amounts to three interlayer water [21]. On the one hand, the basal spacing of 12 Å is expected for the starting material, which corresponds to the one interlayer water state. Considering that one interlayer water is roughly estimated to be 9 wt% [18], three interlayer water amounts to 27 wt%. Under this condition, water molecules exclusively exist in the interlayer spaces, by which montmorillonite could act as a solid material. It is thus expected that impact energy is sufficiently given to montmorillonite in the milling bowl enough to decompose into amorphous materials. This is supported from the analytical results of frictional properties for montmorillonite-based gouge at the hydration states (dry (<4.5 wt%), 1 layer (6.7 - 8.7 wt%), 2 layer (10.6 - 16.0 wt%) and 3 layer (>16.0 wt%)) [22]. At the water contents ranging from 50% to 400%, montmorillonite-water system as plastic gel paste is formed, in which the impact energy could be dissipated without decomposing montmorillonite. This is evidenced from similar SEM images for the samples milled at 50% for 12 hours, 100% for 12 h, at 200% for 12 h, and at 400% for 12 h. At the water contents above 600%, the gel state is suppressed yielding an increase in the impact energy. Decomposition is thus again started, which is evidenced from the contamination of tungsten carbide.

As mentioned before, the water contents in the slip zones largely influences the slip properties. The water contents in the natural faults and landslide slip zones are normally considered to be below the liquid limit, since clay minerals flow out under water rich conditions. When the water content is below the shrinkage/plastic limit, montmorillonite can be easily decomposed to be amor-

phous materials. On the contrary, montmorillonite cannot be decomposed solely by the mechanochemical treatment at the water content above the shrinkage/plastic limit. The water contents in the slip zones in nature can be thus monitored by the degree of decomposition in montmorillonite.

The slip zones in nature could contain not only montmorillonite but also other minerals such as quartz, feldspars, micas, kaolinite, and etc. These minerals have different physical properties and also influence the slip properties. It is however emphasized here that the slip and shearing properties approach pure montmorillonite at the fraction higher than ~30% [23] [24]. A considerable amount of water can be present in the slip zone at the higher liquid limits, where montmorillonite is decomposed as demonstrated in the present work.

5. Conclusion

Clay minerals, as e.g. montmorillonite, abundantly exist in the slip zones such as earthquake faults and landslides. Water contents are an important factor for controlling slip behavior, since montmorillonite contains a considerable amount of water molecules compared with other clay minerals. Here, mechanochemical milling experiments were systematically conducted for montmorillonite in the wide water content region from 0% to 800%. The decomposition behavior was discussed based on the results of XRD experiments, FE-SEM observations, and FT-IR spectroscopy. Mechanochemical decomposition occurs at the water contents below 25% and above 600%. It was found that the degree of decomposition transits at the water contents of 25% and 600%. The critical water contents of 25% and 600% observed here are well correlated to the shrinkage/plastic and liquid limits, respectively. At the water contents below the shrinkage/plastic limit, montmorillonite is effectively decomposed into amorphous materials. In the region of water content between shrinkage/plastic and liquid limits, montmorillonite is hardly decomposed exclusively by the mechanochemical treatment. Decomposition is again started at the water contents higher than the liquid limit. The present work demonstrates that the degree of decomposition can be of usefulness for speculating how the water molecules behave in the slip zones in nature and could extend to the field study.

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