Wet Grinding on Kaolin Minerals

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In the previous studies, the effects of dry grinding on the structural change of kaolin minerals have been presented[1]. It was concluded that the effect of dry grinding depends on the internal degree of crystallinity of the original kaolin mineral, and there are two processes in the structural change. One is the production of a non-crystalline material attended by disordering of the crystalline portion, and the other is the reaggregation process. At a certain period in the grinding, a zeolitic structure is formed; then finally, kaolin mineral changes into a completely amorphous substance like a silica-alumina mixed gel.

Considerable work has been done on the dry grinding of kaolinite, but comparatively little is known on the wet grinding. It was found by Shaw that the wet grinding of kaolinite causes a shearing along the cleavage plane[2]. This will lead to weakening the stacking force between kaolin unit layers. The wet grinding of kaolinite has been made heretofore using ball-mill with water or organic liquid such as benzene. Judging from the fact that wet grinding causes a shearing stress, it is obvious that a higher viscous liquid is more effective in the grinding process than the lower one. Therefore, glycerol was used in the present experiment, combined with a mechanical-mortar as it is very effective in causing a change in structure as discussed in the previous papers[1].

The purpose of this study is to know the correlation between the effect of the wet grinding and that of the dry grinding from the point of view of the degree of the crystallinity of kaolin minerals. It is hoped that this will lead to the fundamental information concerning kaolin minerals.

1) H. Takahashi, "Proc Sixth Natl. Conference on Clay and Clay Minerals", Natl. Res. Council-Natl. Acad. Sci., (in press). H. Takahashi, This Bulletin, **32**, 235, 245, 252 (1959).

2) B. T. Shaw, *J. Phys. Chem.*, **46**, 1032 (1942).

Experimental

The following kaolin minerals were investigated: Kaolinite from Mesa Alta, N. M., U. S. A.; Halloysite from Spruce Pine, N. C., U. S. A.; Halloysite from Tintic, Utah, U. S. A.. These specimens are API Standard Clay Minerals. The structural characteristics of these specimens were discussed in the previous paper[3]. Of all kaolin minerals, Mesa Alta kaolinite has the highest degree of crystallinity, of all halloysites, Spruce Pine halloysite has the highest degree of crystallinity, and Tintic halloysite has a lower degree of crystallinity than Spruce Pine halloysite.

30 g. of each original kaolin mineral was charged, mixed with 100 cc. glycerol. The mixture was wet-ground by a mechanical-mortar (15.2 cm. dia. and 8.4 cm. in depth). The specimen was taken out at intervals of 48 hours and washed with water throughly and then air-dried. The experimental specimen thus prepared was examined by X-ray, thermal and electron microscopic methods. In parallel with these examinations, its density was measured.

X-ray powder diagrams were recorded by an X-ray diffractometer (Geigerflex). Experimental conditions are as follows. Filtered Cu radiation (Cu K_α: 1.5418 Å) at 35 kV and 15 mA is used, scanning speed is 1° or 1/4° 2θ per minute, time constant is 4 seconds, receiving slit is 0.2 mm. or 0.1 mm., angular aperture 1° or 1/2° were used. The differential thermal analysis curves were recorded by the apparatus described by Sudo et al.[4]. Care was taken to pack the specimen into the sample block in a homogeneous manner and also to keep the weight of the specimen constant. The mean heating rate is 12.5°C per minute. The density was measured by pycnometer in carbon tetrachloride. The electron micrographs were obtained by the Hitachi HU-10A type Electron Microscope.

Results and Discussion

X-Ray Diffraction Studies. — X-ray diffractometer traces in the wet grinding process of kaolin minerals are given in Fig. 1. Fig. 1-a and Table I show the X-ray traces and the data of Mesa Alta kaolinite in their various stages of the wet grinding.

3) H. Takahashi, This Bulletin, **31**, 275 (1958).

4) T. Sudo et al., *J. Geol. Soc. Japan*(*Chishitu-Gaku-Zasshi*), **58**, 679 (1952).

TABLE I
POWDER DATA OF WET-GROUND KAOLINITE (MESA ALTA, N. M.)

Brindley and Robinson			Original Kaolinite		Ground 96 hr.		Ground 192 hr.		Ground 384 hr.	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
7.15	10+	001	7.14	VS	7.15	VS	7.16	VS	7.165	S
4.45	4	020	4.46	M	4.46	M	4.46	M	4.46	W
4.35	6	$1\bar{1}0$	4.35	S	4.35	M	4.36	W	4.36	W
4.17	6	$11\bar{1}$	4.18	S	4.18	M	4.18	W		
4.12	3	$1\bar{1}\bar{1}$	4.13	M						
3.837	4	$02\bar{1}$	3.84	M	3.84	W				
3.734	2	021	3.73	W	3.73	VW				
3.566	10+	002	3.57	VS	3.57	VS	3.58	VS	3.58	S
3.365	4	111	3.37	M						
3.138	2	$11\bar{2}$	3.14	W						
3.091	2	$1\bar{1}\bar{2}$	3.09	W						
2.748	2	022	2.75	W						
2.553	8	$20\bar{1}, 1\bar{3}0, 130$	2.55	S	2.56	M	2.56	M	2.56	W
2.521	4	$13\bar{1}, 1\bar{1}2$	2.53	M	2.53	W	2.53	W	2.53	VW
2.486	9	$1\bar{3}\bar{1}, 200, 112$	2.49	S	2.49	M	2.49	M	2.49	M
2.374	7	003	2.37	M	2.38	W	2.38	W	2.39	W
2.331	10	$20\bar{2}, 1\bar{3}1, 11\bar{3}$	2.33	S	2.33	S	2.34	S	2.34	M
2.284	9	$1\bar{1}\bar{3}, 131$	2.29	S	2.29	M	2.29	M	2.29	M
2.243	1	$13\bar{2}, 040$	2.24	W						
2.182	3	$1\bar{3}\bar{2}, 220$	2.18	W						
2.127	2	$02\bar{3}, 041$	2.13	W						
3.057	1	$22\bar{2}$	2.06	W						

Key to abbreviation: VS: very strong, S: strong, M: medium, W: weak, VW: very weak, br: broad, vbr: very broad.

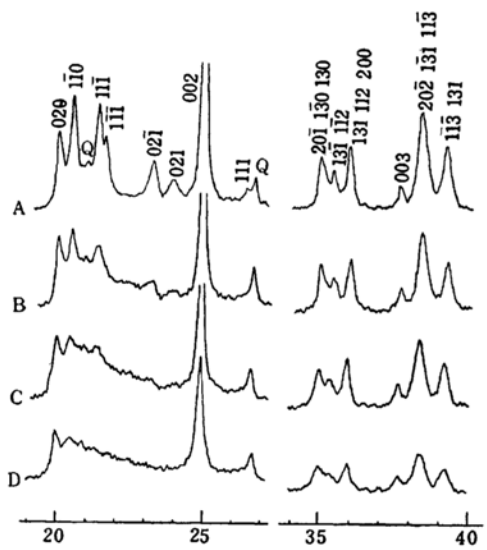

Fig. 1-a. X-ray diffractometer traces of wet-ground specimens of Mesa Alta kaolinite.
A, original kaolinite
B, ground 96 hours
C, ground 192 hours
D, ground 384 hours

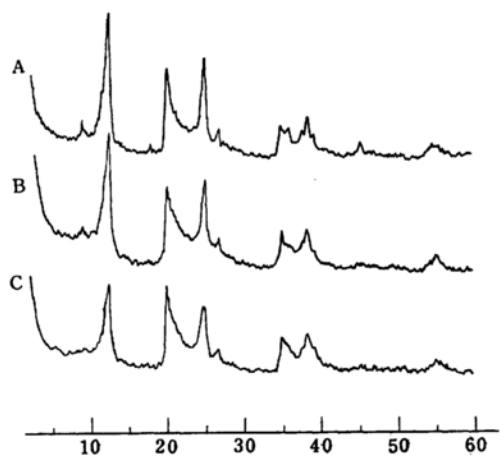

Fig. 1-b. X-ray diffractometer traces of wet-ground specimens of Spruce Pine halloysite.
A, original halloysite
B, ground 192 hours
C, ground 384 hours

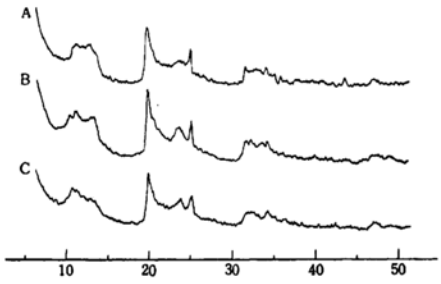

Fig. 1-c. X-ray diffractometer traces of wet-ground specimens of Tintic halloysite.

A, original halloysite
B, ground 192 hours
C, ground 528 hours

As the grinding progresses, the intensities of all reflections decrease and those of the background increase slowly. The X-ray diffraction diagram of the 48-hour-ground kaolinite is not much different from that of the original kaolinite. However, all the reflection lines become broad, $(1\bar{1}\bar{1})$ reflection becomes weak and the resolution of $(20\bar{1}, 130, 1\bar{3}0)$ reflection and $(13\bar{1}, 1\bar{1}2)$ reflection slightly fall. In the 96-hour-ground specimen, $(11\bar{1})$ and $(1\bar{1}\bar{1})$ reflections become broad, and they are hardly resolved at all with each other. The intensities of $(02\bar{1})$ and (021) reflections decrease and $(11\bar{2})$, $(1\bar{1}\bar{2})$ and (022) reflections disappear. These facts mean that the unit layers are displaced slightly in parallel to *b*-axis. In the 192-hour-ground specimen, a decrease in the intensity and a broadening of (020) and $(1\bar{1}0)$ reflections are observable, but $(02\bar{1})$ reflection can scarcely be detected. From these phenomena, it can be seen that a displacement occurs in this specimen, which is more random than the displacement by $b_0/3$ in parallel to *b*-axis. In the X-ray diagram of the 288-hour-ground specimen, the lowering in the resolution of (020) and (110) reflections is observable, but the broad $(11\bar{1})$ line can not be seen. In the X-ray diagram of the 384-hour-ground specimen, a wedge-like (02, 11) band is observable, but (003), $(20\bar{2}, 1\bar{3}1, 11\bar{3})$ and $(1\bar{1}3, 131)$ reflections resolve distinctly with one another. The structure of the 384-hour-ground specimen becomes similar to that of fireclay[5]; however, it has still more regular displacement comparing with that of fireclay. As shown in Table I, in the process of wet grinding, the value of the basal spacing grows gradually, though slightly, as the grinding progresses. This means that the local water gets into the space between the kaolin unit layers as the inter-layer water, or that the stacking of the unit layers becomes looser owing to the shearing stress. From the above results, it is clear that the structural change of kaolinite caused by wet grinding results from cleavages in the kaolin crystal.

In the case of halloysite, however, the features observed in kaolinite are not so remarkable. Figs. 1-b and -c show the X-ray traces in various stages of wet grinding of Spruce Pine halloysite and Tintic halloysite, respectively. As seen in these figures, the X-ray traces for various stages of wet grinding are only slightly different from one another. In the wet-ground specimen of Spruce Pine halloysite, all reflections become slightly broad; only the intensity of (00*l*) reflection decreases and the background increases, as the grinding progresses. In Tintic halloysite, the changes in X-ray traces due to wet grinding are similar to that of Spruce Pine halloysite. In the 528-hour-ground specimen, it is observable that the halloysite-glycerol complex is formed.

The reflection lines generally become slightly broad by wet grinding. To ascertain the broadening of the reflections, crystallite dimensions in the wet grinding process of Tintic halloysite are measured from (001) reflection and (02, 11) band[6], as reported in the previous papers[1,7]. Their values are shown in Table II.

The crysatllite dimensions thus obtained

TABLE II
CRYSTALLITE DIMENSIONS IN THE VARIOUS STAGES OF WET GRINDING OF TINTIC HALLOYSITE

Grinding time (hr.)	Crystallite dimension (Å)	
	L_c (from 001 reflection)	L_a (from 02, 11 band)
0	80	155
192	76	141
288	70	118
384	66	110
528	58	105

5) G. W. Brindley and K. Robinson, *Trans. Farad. Soc.* **42B**, 198 (1946).
6) W. L. Bragg, "The Crystalline State", I, 189 (1933); B. E. Warren, *Phys. Rev.*, **59**, 693 (1941); C. W. Brindley and K. Robinson, *Min. Mag.*, **28**, 393 (1948); C. R. Houska and B. E. Warren, *J. Appl. Phys.*, **25**, 1503 (1054).
7) H. Takahashi, This Bulletin, **32**, 17 (1959).

are, of course, not accurately real crystallite sizes but relative values. The change of the basal spacing in the process of wet grinding of halloysite is not so remarkable as that of kaolinite. This indicates that the cleavage caused by wet grinding is not very remarkable in halloysite compared with that of kaolinite. The dry grinding is in general more effective than the wet grinding in causing the structural change. However, it is observable that there is a great difference in the wet grinding effects between kaolinite and halloysite. As clearly shown in X-ray data, kaolinite is subjected to its effects more than halloysite though its degree of crystallinity is originally higher. In kaolinite, the shearing stress acts in parallel to the layer planes, as kaolinite is made of stacking of parallel unit layers. On the other hand, in halloysite, its crystal has a tubular shape, resulting from the rolling up of the unit layers[8]. So, it is hard to make cleavage by shearing stress through wet grinding. Furthermore, as halloysite has originally a two-dimensional structure; even if a small displacement takes place along the unit layers, it does not affect its X-ray diagram.

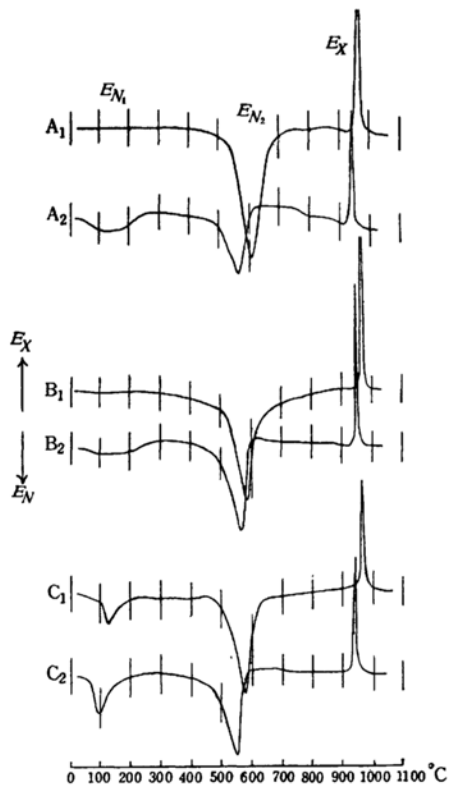

Fig. 2. Differential thermal analysis curves of wet-ground specimens of kaolin minerals.
A_1, original Mesa Alta kaolinite
A_2, ground 384 hours
B_1, original Spruce Pine halloysite
B_2, ground 384 hours
C_1, original Tintic halloysite
C_2, ground 528 hours

Differential Thermal Analysis.—Differential thermal analysis curves and data in the process of wet grinding of kaolin minerals are shown in Fig. 2 and Table III.

In ground specimens of kaolinite, the the first endothermic reaction (E_{n1}) associated with the loss of the inter-layer or adsorbed water becomes apparent and its height increases as the grinding progresses. This means that the water gets locally into the increased spaces between kaolin layers because of cleavages through wet grinding, and it becomes the interlayer water, and/or that the non-crystalline material which adsorbs some amounts of water is produced by wet grinding. For the second endothermic reaction (E_{n2}) associated with the loss of the lattice water, as the grinding progresses, the lowering in its peak temperature and the decrease in its peak height and area are observable. In the final exothermic reaction (E_x) due to the mullite nucleation, as the grinding progresses, the lowering in the peak temperature, the increase in the peak breadth and the decrease in the peak height and area are observable. However, in halloysite, these features observed in this reaction are not so remarkable compared with that of kaolinite. This fact corresponds to the fact that kaolinite is more liable to suffer the effects of wet grinding than halloysite as shown in X-ray data. That is, in halloysite, although a lowering in the peak temperature is observable, the peak breadth decreases and the peak height is either invariable or increases. These phenomena indicate that the effect of wet grinding of halloysite is nearly the same as the effect at the early stage of dry grinding[1].

Density.—In Fig. 3 is shown the density at various periods of grinding. Measurements were made after the specimens had been dried at 110°C in order to avoid the effect of the adsorbed water.

In halloysite, the density gradually decreases at first; after reaching a certain point of grinding, it rapidly decreases. On

8) T. F. Bates, F. A. Hildebrand and A. Swineford, *Am. Mineral.*, 35, 463 (1950).

TABLE III
THERMAL DATA OF WET-GROUND KAOLIN MINERALS
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

Specimen	E_{n1}			E_{n2}			E_x			
	Temp. (°C)	Height	Area	Temp. (°C)	Height	Area	Temp. (°C)	Height	Area	Breadth (°C)
Kaolinite (Mesa Alta, N.M.)										
Original	—	—	—	604	16	1080	966	39	220	5.1
Wet-Ground 384 hr.	120—170	2	230	566	13	660	947	31	190	8.4
Halloysite (Spruce Pine, N.C.)										
Original	125	1	70	583	17	1380	973	45	220	4.0
Wet-Ground 384 hr.	100—200	1	200	564	15	900	971	53	190	3.5
Halloysite (Tintic, Utah)										
Original	130	4	170	571	12	680	969	16	170	9.4
Wet-Ground 432 hr.	-110-	5	240	555	10	560	952	16	130	7.3

the other hand, in kaolinite, the decrease in the density is remarkable in the early stage of grinding, then the density slowly decreases, and finally it attains a nearly constant value. The rate of change in the density corresponds to the fact that kaolinite is more liable to suffer the effect of wet grinding than halloysite, at least in the early stage of grinding as indicated in previous sections.

The structure of kaolinite changes into a disordered structure due to cleavage caused by the wet grinding, while halloysite scarcely suffers the effect in the early stage of grinding. In a considerably long time of grinding, the structure of halloysite gradually decomposes due to fracturing and cleavage caused by grinding. This corresponds to the somewhat rapid decrease in the density.

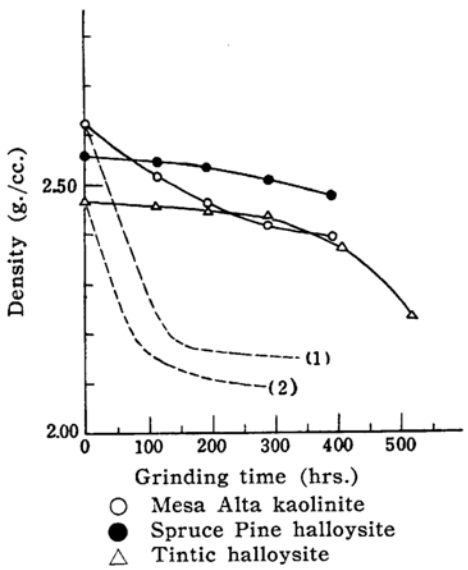

Fig. 3. Curves showing the changes of the density of wet-ground specimens of kaolin minerals with the time of grinding. (1), (2): Curves showing the changes in the process of dry grinding of Mesa Alta kaolinite and Tintic halloysite, respectively.

Electron Microscopic Studies.—The electron micrographs of some ground specimens are shown in Fig. 4.

In the early stage of grinding of kaolinite, it is seen that the edge of a kaolin crystal tends to curl. This tendency is interpreted in the light of the characteristic of the shape of kaolin unit layer by Bates et al.[8]. That is, kaolin mineral with a random displacement has generally the tubular shape like halloysite. The relation between the degree of crystallinity of a kaolin mineral and the shape of the crystal was presented in the previous paper[3]. As the grinding progresses, the shape of the kaolin crystal gradually change into a circular but platty shape. The particle size does not change remarkably. Finally, it changes into spherical aggregates of fine platty particles.

In halloysite, various shapes such as split tubular, platty, lath-shaped, cabbage-like and other variations are observable in the wet grinding process. From these phenomena, it seems that the force of wet grinding causes fracturing rather than shearing.

Mechanism of Structural Change of Kaolin Mineral due to Wet Grinding.—When kaolinite is wet-ground, the crystal

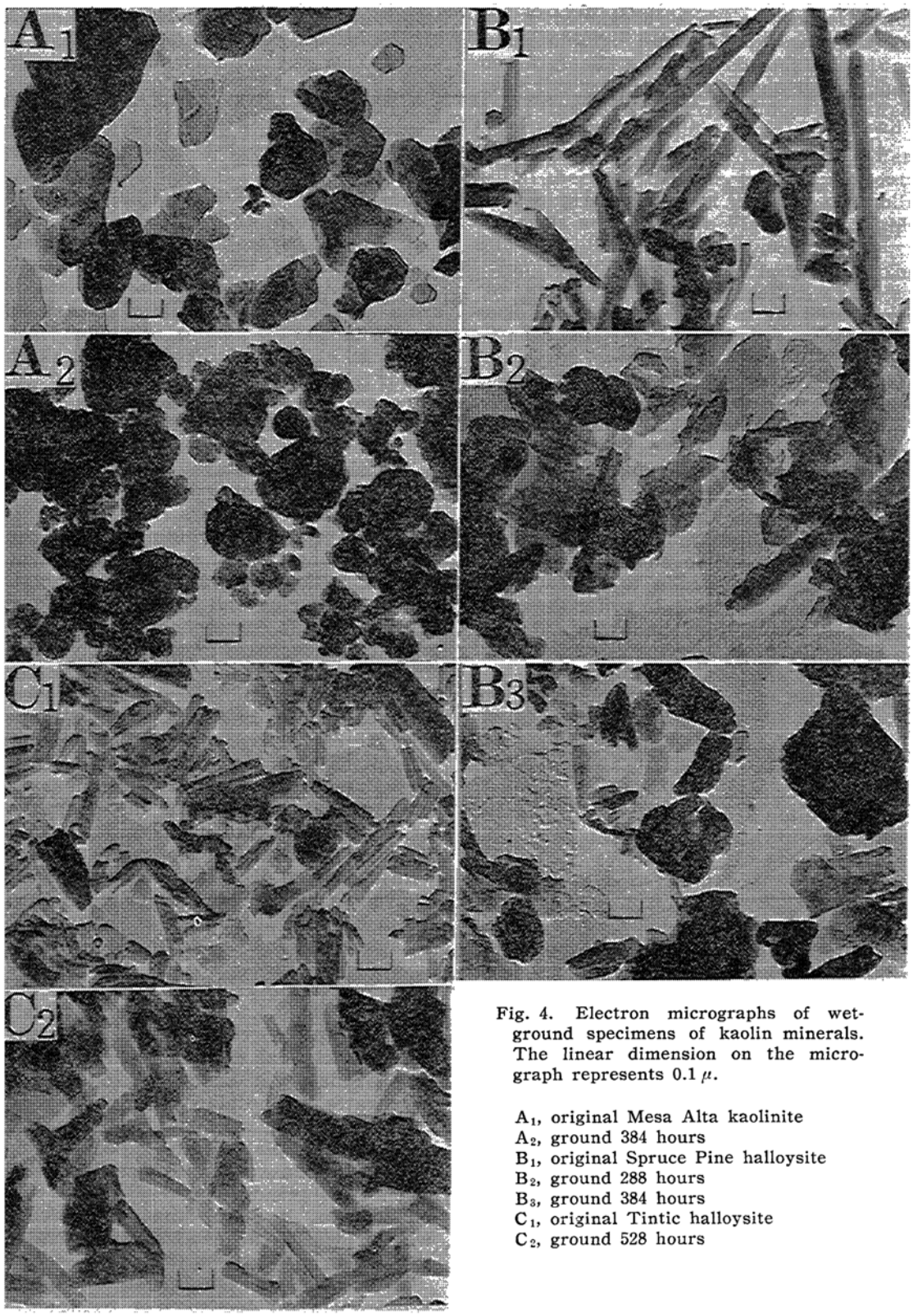

Fig. 4. Electron micrographs of wet-ground specimens of kaolin minerals. The linear dimension on the micrograph represents 0.1 μ.

A_1, original Mesa Alta kaolinite
A_2, ground 384 hours
B_1, original Spruce Pine halloysite
B_2, ground 288 hours
B_3, ground 384 hours
C_1, original Tintic halloysite
C_2, ground 528 hours

cleaves along the layer plane owing to shearing stress. In consequence, displacement of layers takes place in parallel to *b*-axis. As the grinding progresses for a long time, the structure of the original kaolinite with a triclinic in symmetry change into the more disordered structure. These displacements are remarkable in the early stage of grinding. The change of the particle shape due to wet grinding is observable as the gradual formation of fine and radial platty particles though it is not so remarkable in the early stage. When the grinding further progresses, kaolinite with a higher degree of crystallinity gradually changes into kaolin with a random displacement similar to that of halloysite.

In the early stage of grinding of halloysite, the original crystal splits and fractures owing to the fracturing force. Therefore, the change on the X-ray diagram is not so remarkable and the thermal data also indicate the same tendency. From the electron micrographs, too, it can be concluded that the force of wet grinding acts as a fracturing force, which results in splitting tubular crystal. The process of the structural change through wet grinding for the platty particle of halloysite produced by splitting is similar to that of kaolinite.

Summary

The effects of wet grinding on kaolin minerals were examined by X-ray diffraction method, differential thermal analysis, electron microscopy and density measurement. The effects of wet grinding of kaolin minerals are different from those of dry grinding, particularly at the early stage of grinding. It has been considered that the force of dry grinding acts as fracturing and cleaving forces, while the force of wet grinding acts as a weak cleaving force for kaolinite and as a weak fracturing force for halloysite in the early stage of grinding. It has been revealed that the effects of wet grinding depend on the shape of crystal in the original kaolin mineral in the early stage of grinding, and beyond a certain stage of grinding, they depend on the structural perfectness of the kaolin layer, that is, the internal degree of crystallinity of the original kaolin mineral.

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