Thermal Effects of Some Kaolin Minerals. II. Halloysite

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In the preceding part of this series, studies were made on the structural changes of kaolinite and kaolin mineral of fireclay type with heat-treatment in the relatively low temperature region with respect to the degree of the crystallinity[1].

In the early stage of heat-treatment, the progress of the crystallinity is remarkable. It is mainly due to the loss of the adsorbed water. In the next stage, there occurs the lowering of crystallinity due to the break of the kaolin structure resulting from the loss of the lattice water. In the following stage, the rearrangement of ions for the mullite nucleation becomes remarkable, though the X-ray diagram indicates that this state is an amorphous structure.

Halloysite is composed of the same structural units as those of kaolinite, but the stacking of almino-silicate layers is in almost entirely disorder and generally contains the inter-layer water between unit layers. The crystallinity of halloysite, except a certain type of halloysite[2,5], is lower than that of kaolinite. And, it was also found by Brindley and Robinson that the theory of the reflection for a random layer lattice is applicable to the structure of halloysite[3]. The change in the structure of halloysite owing to the loss of the inter-layer water, was studied in details by Brindley and Goodyear[4].

In this paper, the structural changes of halloysite with heat-treatment in the relatively low temperature region, are presented, through X-ray diffraction method, differential thermal analysis and the density measurement from the point of view of the degree of crystallinity of kaolin minerals and are compared with those of kaolinite.

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[1] H. Takahashi, This Bulletin, **31**, 1031 (1958).

[2] G. Honjo and K. Mihama, *Acta Cryst.*, **5**, 511 (1954).

[3] G. W. Brindley and K. Robinson, *Min. Mag.*, **28**, 393 (1948).

[4] G. W. Brindley and J. Goodyear, ibid., **28**, 407 (1948).

[5] H. Takahashi, This Bulletin, **31**, 275 (1958).

Experimental

Twelve samples of halloysite with the various degrees of crystallinity were used in this study. From the point of view of the degree of crystallinity in halloysite, the following four samples are generally representative for the structural changes through heat-treatment. Four samples mentioned above are as follows; Halloysite from Spruce Pine, N. C., U. S. A.; Halloysite from Bedford, Ind., U. S. A.; Halloysite from Tintic, Utah, U. S. A. and Shichinoe-clay from Shichinoe, Aomori, Japan.

These samples, except for Shichinoe-clay, are the API Standard Clay Minerals. Of all kinds of halloysite used in this study, Shichinoe-clay has the lowest degree of crystallinity. The structural characteristics of these samples have been discussed in the previous paper5), and those of Shichinoe-clay was also discussed by Sudo6). The method of preparation of the experimental specimens and the experimental conditions of all measurements are the same as those in kaolinite and Kibushi-clay.

Results and Discussion

X-ray Diffraction Studies.—Fig. 1 shows the X-ray diffractometer traces of heat-treated specimens of Tintic halloysite. As shown in these traces, the reflections which correspond to hydrated halloysite disappear owing to the loss of the inter-layer water when heat-treated, and it changes into a dehydrated halloysite. With the rise of the treated temperature, the intensity of all reflections increases and (001) reflection becomes sharp to 400°C. In the 545°C heat-treated specimen, the reflections which are apparent in the original sample are not observable, but only a wedge-like background. In the 700°C heat-treated specimen, only a very diffuse and indistinct band is observable. In Tintic halloysite, it is considered that the crystallinity progresses up to 400°C. This is because the residual inter-layer water which exists sporadically between the kaolin layers is lost with the rise of treated temperature, which causes the arrangement of kaolin unit layers to be ordered. Past 400°C, the structure of halloysite begins to disintegrate due to the gradual disappearance of the lattice water. Then the lattice water completely vanishes. Therefore, its crystallinity drops. The X-ray diagram shows also that the rate of change in the heat-treated specimens of other halloysites is similar to that of Tintic halloysite. The only difference is that the loss of lattice water occurs at a lower temperature according to the order of crystallinity of the original sample. The temperature which eliminates the lattice water is the highest in Spruce Pine halloysite and lowest in Shichinoe-clay. This is quite natural in the light of the thermal data.

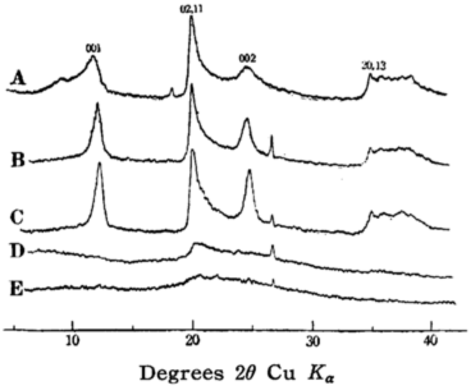

Fig. 1. X-ray diffractometer traces of heat-treated specimens of Tintic halloysite.
A, original halloysite
B, treated at 200°C
C, treated at 400°C
D, treated at 545°C
E, treated at 700°C

It is known by Brindley that halloysite has a pseudo-hexagonal form in symmetry and has a two-dimensional like structure3). To the two-dimensional structure, Warren's theory is applicable7). This theory has been applied to various kinds of substance8), particularly to amorphous carbon in the process of graphitization9). The structure of halloysite is more complex than that of amorphous carbon in in the chemical composition and the crystal structure. So, it is very dangerous to apply this theory entirely to halloysite. However, the values obtained by the application of this theory should have some relation with the real values to some extent. For this reason, the crystallite dimensions were obtained from the broadening of (001) and (02, 11) reflection lines. There are two elements determining the broadening of the reflection line. One is the crystallite size, and the other is the lattice distortion. Accordingly, to obtain the real crystallite size from the line broadening, the factor of the lattice distortion must be eliminated10). However, the

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6) T. Sudo, *Clay Min. Bull.*, **2**, 96 (1954).

7) B. E. Warren, ***Phys. Rev.***, **59**, 693 (1941).

8) E. Aruja, ***Nature***, **154**, 53 (1944).

9) J. Biscoe and B. E. Warren, ***J. App. Phys.***, **13**, 364 (1942). H. Akamatu et al., This Bulltin, **29**, 574 (1956).

10) C. R. Houska and B. E. Warren, ***J. App. Phys.***, **25**, 1503 (1954).

increase of the line breadth correlates the fact that the lattice distortion becomes remarkable and that the crystallite size becomes reduced. These two facts mean a lowering in the crystallinity. Therefore, the crystallite sizes thus obtained indicate the relative degree of crystallinity rather than the real crystallite sizes. Consequently, the crystallite sizes are not the real crystallite sizes, but the values are proportional to the real crystallite sizes. However, the real crystallite sizes of halloysite are not much different from the values thus obtained, which are probably, approximate values. This fact was also described in the separate paper11). The crystallite dimension along the direction of the c-axis (L_c) was measured by the Bragg's equation12) and the crystallite dimension parallel to the layer plane (L_a) was measured by Warren's equation7).

$$L_c=\frac{0.9\,\lambda}{\beta_c\cos\theta}\quad\text{(Bragg's equation)}$$

$$L_a=\frac{1.84\,\lambda}{\beta_a\cos\theta}\quad\text{(Warren's equation)}$$

λ: wave length (Cu K_α: 1.5418 Å)
θ: diffraction angle (degree)
β: half value of breadth (radian)

In these measurements, quartz was used for a correction substance for the instrumental broadening of the reflection line.

Kaolin minerals generally change in their shapes and physico-chemical properties according to the structural characteristics. Kaolin minerals have two kinds of crystallinity; that is, one is the internal crystallinity and the other is the crystallinity in the stacking of layers5). Therefore, these two kinds of crystallinity must be considered. So, the ratio of the intensity of (001) reflection to that of (02,11) band is measured. This term seems to indicate somewhat the order of the crystallinity of halloysite samples. The original samples of halloysite, except for Spruce Pine halloysite, are partially hydrated halloysite. In Fig. 2 is shown the schematic drawing of the X-ray diagram of the partially hydrated halloysite. In Fig. 2, the intensity ratio was obtained by the following equation4).

$$\text{Intensity ratio}=\frac{I_{(001)}+\dfrac{I_{H(001)}}{4}}{I_{(02,11)}}$$

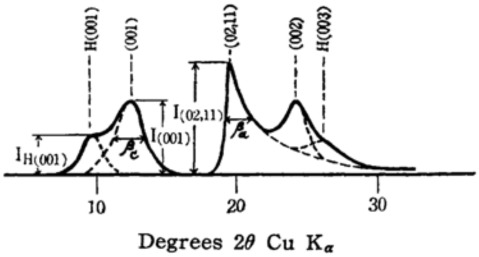

Fig. 2. Schematic drawing of the X-ray diagram of the partially hydrated halloysite.

Fig. 3 shows the change of the spacings of (001) and (02,11) reflections, the crystallite dimensions and the intensity ratios with heat-treatment. Figs. 3-A, -B, -C and -D show the data for four samples of halloysite.

On the crystallite dimensions, L_c-dimension increases with the rise of the treated temperature; when the regularity along the direction of c-axis disappears, L_c-dimension sharply decreases. L_a-dimension, in the partially hydrated halloysite, reaches a maximum value, it then decreases slowly, and then sharply decreases, In Spruce Pine halloysite, L_a-dimension curve has no maximum point perhaps owing to the original sample being dehydrated halloysite. The increase of L_c-dimension with heat-treatment, is caused by the progress of regularity along the direction of c-axis because of the loss of the inter-layer water, while the decrease in L_a-dimension is due to the fracturing of kaolin layers.

As for the change of the intensity ratio, the value increases and reaches a maximum point with the rise of treated temperature, and then sharply decreases. The value of the intensity ratio is larger as the crystallinity is higher. This means that the higher the crystallinity of halloysite is, the higher is the regularity along the direction of c-axis. From the value of the intensity ratio, it is understood that Spruce Pine halloysite has very high crystallinity. The maximum value in the change of the intensity ratio is considered to indicate the degree of crystallinity of halloysite. In the hydrated halloysite with very low crystallinity, found in Japan, the results are reverse to those so far described, as far as the intensity ratio is concerned. This is for the reason that there is a remarkable disorderliness in the kaolin layers6).

As for the changes in spacing, the spacing of (001) reflection slowly reduces

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11) H. Takahashi, "Proc. Sixth Natl. Coference on Clay and Clay Minerals", Natl. Acad. Sci.-Natl. Res. Council, U.S.A. (in Press).

12) W. L. Bragg, "The Crystalline State", Vol. I, p. 189 (1933).

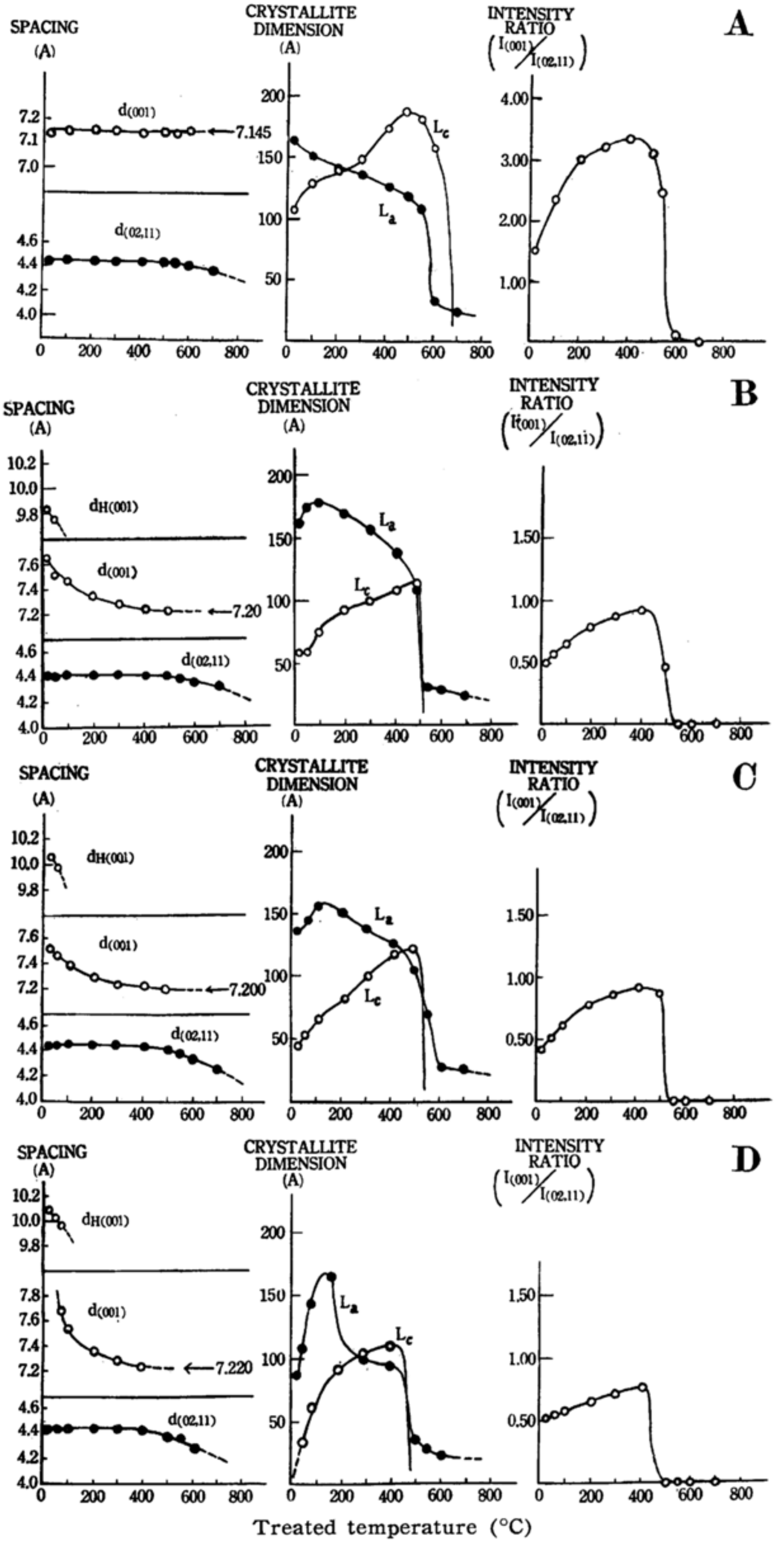

Fig. 3. Curves showing the changes of the spacing of (001) and (02, 11) reflections, the crystallite dimensions and the intensity ratios with the heat-treated temperature.

A, Spruce Pine halloysite C, Tintic halloysite
B, Bedford halloysite D, Shichinoe halloysite

with the loss of the inter-layer water until it reaches a nearly constant value. This maintained value seems to indicate the order of the crystallinity in halloysite. The spacing of (02,11) band decreases sharply with the loss of lattice water. This corresponds to the disintegration of the kaolin structure.

Differential Thermal Analysis.—The differential thermal analysis curves of some specimens with heat-treatment are shown in Fig. 4, and Table I shows the thermal data obtained from these curves.

In the heat-treated specimens of halloysite except for Spruce Pine halloysite, the endothermic reaction (E_{n1}) associated with the loss of the inter-layer or adsorbed water is observable even in the 400°C heat-treated specimen of halloysite. This might be due to the fact that after the heat-treatment it adsorbs water vapor so rapidly from the atmospheric air. This phenomenon corresponds to the crystallinity of the original sample in the low stage.

In the endothermic reaction (E_{n2}) caused by the loss of the lattice water in Spruce Pine halloysite, the peak height and area of this reaction reduce in the 545°C heat-treated specimen. And in the 700°C heat-treated specimen, this reaction is unobservable. In the 545°C heat-treated specimen of Shichinoe-clay, this reaction disappears. This means that the structure

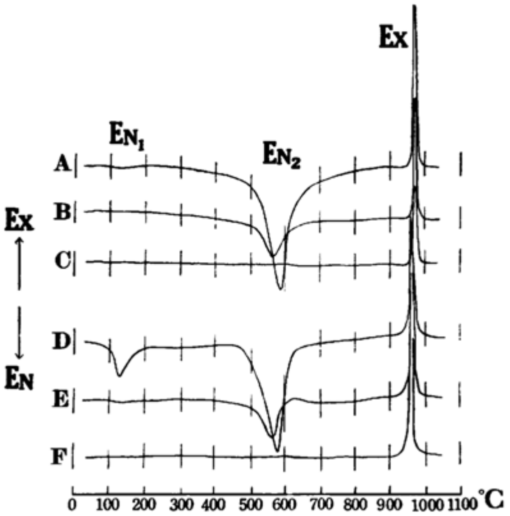

Fig. 4. Differential thermal analysis curves of heat-treated specimens of Spruce Pine and Tintic halloysite.
A, original Spruce Pine halloysite
B, treated at 545°C
C, treated at 700°C
D, original Tintic halloysite
E, treated at 545°C
F, treated at 700°C

TABLE I
THERMAL DATA OF HEAT-TREATED SPECIMENS OF HALLOYSITE
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

Specimen	Treated-temp.	E_{n1}		E_{n2}		E_x		
		Temp. at peak	Height of peak	Temp. at peak	Height of peak	Temp. at peak	Height of peak	Breadth of peak
Halloysite	original	125°	1	583°	17	973°	45	4.0°
(Spruce Pine, N. C.)	200°	—	—	581	17	971	46	3.4
	400	—	—	573	15	969	48	2.2
	545	—	—	555	5	968	51	3.4
	700	—	—	—	—	967	52	3.6
Halloysite	original	125	2	574	16	970	34	4.5
(Bedford, Ind.)	200	120	1	574	16	969	32	4.2
	400	120	1	574	14	967	32	4.7
	545	—	—	563	6	966	30	4.8
	700	—	—	—	—	964	38	5.1
Halloysite	original	130	4	571	12	969	16	9.4
(Tintic, Utah)	200	115	2	570	15	963	24	4.3
	400	115	1	565	13	965	34	4.2
	545	—	—	558	4	964	30	4.9
	700	—	—	—	—	959	46	5.2
Halloysite	original	129	6	550	12	885	7	23.4
(Shichinoe, Aomori)	200	115	2	546	13	885	8	23.4
	400	125	1	543	9	886	9	25.6
	545	—	—	—	—	883	12	26.6
	700	—	—	—	—	881	12	27.0

of Shichinoe-clay disintegrates at a lower temperature as compared with that of Spruce Pine halloysite. This fact corresponds to the fact that the original sample of Shichinoe-clay has the lowest degree of crystallinity of all the halloysite samples used in this study.

In the exothermic reaction (E_x) associated with the mullite nucleation, the features of this reaction are the same as those of kaolinite. That is, the peak temperature tends to lower, though very slightly, and the peak height gradually increases with the rise of treated temperature.

In the 700°C heat-treated specimen, the peak height is large as compared with that of the original sample. This fact seems to indicate that in the metakaolin state, the rearrangement of ions takes place for the mullite nucleation though this state is amorphous from the X-ray diagram. Therefore, the heat-treatment accelerates the rearrangement of ions for the mullite nucleation. As a result, the peak height of the exothermic reaction increases. The peak breadth of this reaction reduces with the rise of the heat-treatment, and attains a minimum value, and then slightly increases again.

Density.—In Fig. 5 are shown the changes of the density of halloysite specimens with heat-treatment. Measurements were made on dried specimens.

The rate of change in the density are very similar to those of kaolinite and Kibushi-clay described in the preceding part of this study. The density increases at first with the rise of treated temperature, and reaches a maximum point; then it falls suddenly and maintains the minimum value. Past the minimum point in the density curve which corresponds to the disappearance of the lattice water, the density increases sharply and straight. The curve is steeper as the crystallinity of the original sample is higher. The same phenomena were also observable in kaolinite and Kibushi-clay.

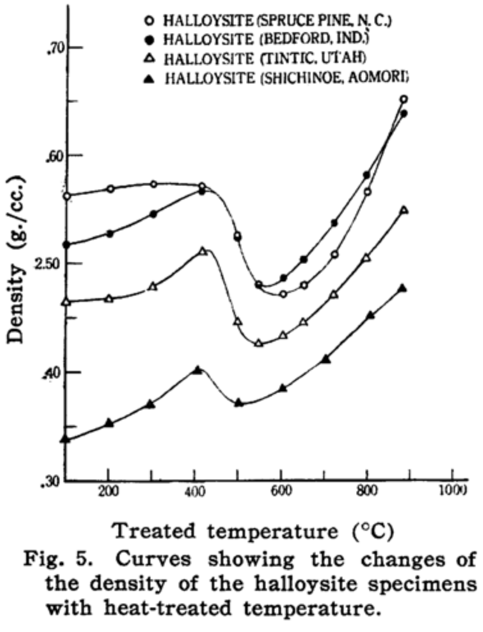

Fig. 5. Curves showing the changes of the density of the halloysite specimens with heat-treated temperature.

When the inclinations in the density curves of kaolinite and ordinary halloysite are compared, that of kaolinite is larger than that of the other.

Therefore, past the minimum point on the density curve, it is considered that the inclination of the density curve of kaolin mineral is corrected to the degree of crystallinity of the kaolin mineral, particularly to the internal degree of crystallinity. This indicates that the rearrangement of ions occurs in the metakaolin state, despite of the fact that the structure is amorphous by the X-ray diagram, and that the stronger the structure of the original sample is, the faster and more perfect is the rearrangement of ions. The mullite nucleation is more remarkable as the crystallinity of the original kaolin mineral is higher.

Mechanism of Structural Change of Halloysite with Heat-treatment.—In the heat-treatment process of halloysite, there are three steps of the structural change with respect to the degree of crystallinity. In the first process, crystallites in one neighborhood aggregate as the inter-layer water vanishes gradually, and so the apparent crystallite size and the value of the density increase and its crystallinity therefore progresses. This tendency is remarkable particularly along the direction of *c*-axis. In the second process, the hydroxyl ions oriented with the metal ions are cut out and dehydrated, and then kaolin changes into metakaolin. The density decreases suddenly in this stage. As the result, the crystallinity owing to the disintegration of the structure of halloysite. Past this stage, the structure of halloysite becomes amorphous. However, the value of the density of all kinds of halloysite sharply increases with the rise of treated temperature similar to that in kaolinite. The higher the crystallinity is, the larger is the proportion of the increase of the density in all kaolin minerals. This fact shows that even in this amorphous state, the rearrangement of ions for the mullite nucleation occurs. The higher the original crystallinity is, the more perfect is the rearrangement.

Summery

The structural change of halloysite with heat-treatment in the relatively low temperature region has been studied, and was compared with those of kaolinite and Kibushi-clay. There are three processes, same as in the case of kaolinite. The first process is accompanied by the loss of the inter-layer and adsorbed water, and the second process by the loss of the lattice water. In the third process, which is an amorphous state corresponding to the metakaolin state, the rearrangement of ions takes place for the mullite nucleation. The rate of the structural change depends on the degree of crystallinity of the original kaolin mineral.

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