Thermal Effects of Some Kaolin Minerals. I. Kaolinite and Kibushi-clay

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All kaolin minerals are made of aluminosilicate layers in their crystal structures. However, there are imperfections in the mode of stacking of unit layers, and this leads to variety in the structure of kaolin minerals[1]. The different properties which are found among kaolin minerals are due to there being many kinds of characteristic factor in each mineral. Of such factors, the most important one is the structural perfection or imperfection, that is, the degree of crystallinity including the stacking disorder.

It is well known that a kaolinite transforms into mullite through heat-treatment at 950~1000°C[2]. Investigations on the structural change of kaolin minerals with heat-treatment have been made chiefly in a temperature region higher than 950°C. However, little investigation has been done in regard to the effect of heat-treatment in the relatively low temperature region.

The course of the transformation of a kaolinite into mullite involves two major structural changes. One is a structural change due to the loss of the adsorbed water. The other is a structural change caused by the loss of the lattice water. In this paper, the fundamental information regarding the change in the structure of kaolinite with heat-treatment, in the relatively low temperature region, are presented, through X-ray diffraction method, differential thermal analysis and particularly using these together with density measurement.

Experimental

Twenty samples of kaolinte and kaolin mineral of fireclay type were used in this study. In studying these samples continuous disordering was observed among different samples. For the structural changes of kaolinite and kaolin mineral of fireclay type through heat-treatment, the structural changes of the following three samples are generally representative of the whole. Three of the samples mentioned above are as follows; Kaolinite from Mesa Alta, N.M., U.S.A.; Kaolinite from Drybranch, Geor., U.S.A.; Kibushi-clay from Shidare, Gifu, Japan. Two of the kaolinite samples are the API Standard Clay Minerals; Kibushi-clay is a kaolin mineral of fireclay type. The structural characteristics of these samples have been discussed in the previous paper[3]. The original samples were powdered and sieved through 250 mesh. The heat-treatment was made in an electric furnace under the ordinary atmosphere, keeping at a given temperature for an hour.

The X-ray powder diagrams were recorded by the X-ray diffractometer (Geigerflex). Experimental conditions were as follows. Filtered Copper radiation ($CuK\alpha$: 1.5418 Å) at about 35 kV and 15 mA was used; scanning speed was 1° or 1/4° 2θ per minute; time constant was 4 seconds; receiving slit was 0.2 mm or 0.1 mm; angular aperture was 1° or 1/2°.

The differential thermal analysis curves were obtained by the apparatus described by Sudo et al.[4]. Care was taken to pack a specimen into the sample block in the homogeneous manner and also to keep the weight of the specimen constant. The mean heating rate is 12.5°C per minute.

The density of the specimens was measured by a pycnometer in carbon tetrachloride. It was made in the original state after it had been dried at 110°C in order to avoid the effect of the adsorbed or interlayer water.

Results and Discussion

X-ray Diffraction Studies.—X-ray diffractometer traces for heat-treated kaolinite and Kibushi-clay are given in Figs. 1 and 2, respectively.

In the traces of Mesa Alta kaolinite, which are observed in the X-ray diagram before it is heat-treated at 400°C, an increase in the intensity of reflection, particularly (001), and the reduction in the line breadth are most remarkable. In the 545°C heat-treated specimen, the intensity of all reflections, particularly (001) reflections, sharply decreases. In this specimen,

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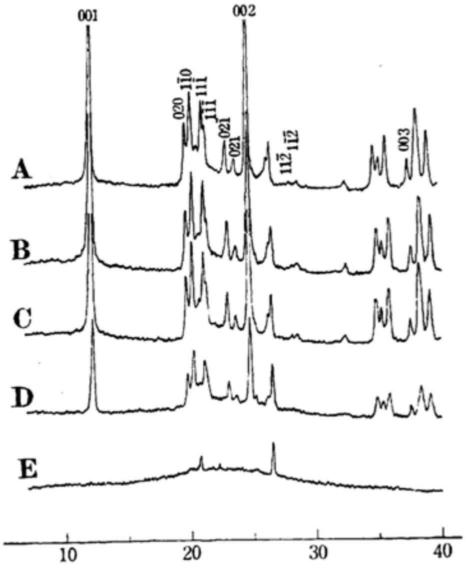
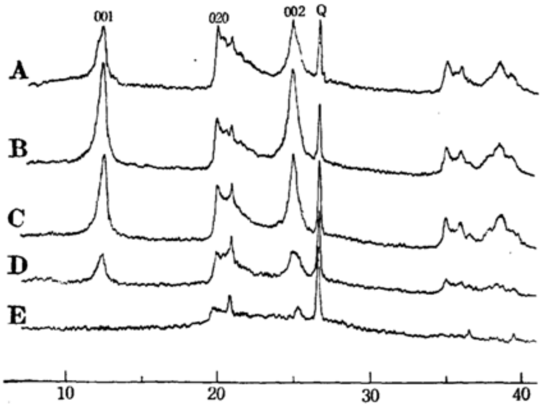
[4] T. Sudo et al., *J Geol. Soc. Japan* (*Chishitsu-Gaku-Zasshi*), **58**, 116 (1952).



Degrees 2θ Cu K_α

Fig. 1. X-ray diffractometer traces of heat-treated specimens of kaolinite (Mesa Alta, N.M.).
A, original kaolinite
B, treated at 200°C
C, treated at 400°C
D, treated at 545°C
E, treated at 700°C



Degrees 2θ Cu K_α

Fig. 2. X-ray diffractometer traces of heat-treated specimens of Kibushi-clay.
A, original clay
B, treated at 200°C
C, treated at 400°C
D, treated at 545°C
E, treated at 700°C

the ($11\bar{2}$) reflection of 3.14 Å spacing, which is weak in the original state, the ($1\bar{1}\bar{2}$) re-reflection of 3.09 Å spacing disappear, and the ($11\bar{1}$) and the ($1\bar{1}\bar{1}$) reflections are not resolved from each other. In the process up to this stage, the values of the interplanner spacings of all the reflections remain almost unchanged. In the 700°C heat-treated specimen, all reflections disappear, the original regular kaolin structure is entirely broken, and only a very diffuse and weak band is observable.

The structural transformation of Dry-branch kaolinite through heat-treatment follows practically the same process as that of Mesa Alta kaolinite. In the 545°C heat-treated specimen, its X-ray diagram indicates that the structure is in remarkably disorder in comparison with the 545°C heat-treated specimen of Mesa Alta kaolinite. The lattice water is lost, in this case, at a lower temperature than in the case of Mesa Alta kaolinite. This fact means that the velocity of the disintegration of the kaolinite structure attending the loss of the lattice water is related to the degree of crystallinity of the original mineral.

In Kibushi-clay, it is revealed in the light of X-ray traces that it has also the two elements of the progress and lowering of crystallinity as in the case of kaolinite. The progress of crystallinity of Kibushi-clay is remarkable up to 400°C heat-treatment. The lowering of crystallinity begins also at a low temperature as compared to that of kaolinite. In Kibushi-clay, its basal spacing slowly decreases with the rising of heat-treatment. This means that it is due to the loss of the inter-layer water which exists sporadically in this clay. In other words, it is because this clay originally contains the inter-layer water in its structure. This proves certainly that Kibushi-clay is low in crystallinity.

Differential Thermal Analysis.—Fig. 3 shows the differential thermal analysis curves in the process of heat-treatment of kaolinite. Table I shows the thermal data obtained from these curves.

In Mesa Alta kaolinite, as can be supposed, no endothermic reaction associated with the loss of the inter-layer water is observed. For the endothermic reaction (E_n) associated with the loss of the lattice water, the reduction in the area under the peak is not so remarkable between its original and 200°C heat-treated specimen; however, a slight reduction due to the loss of the lattice water becomes broad. In the 400°C heat-treated specimen, the area of this reaction reduces a little, and so does its height. In the 545°C heat-treated specimen, the area reduces con-

Table I

Thermal data of heat-treated specimens of kaolinite

Sample	Treated temp.	E_n Temp. at peak	E_n Height of peak	E_x Temp. at peak	E_x Height of peak	E_x Breadth of peak
Kaolinite	original	604°C	16	966°C	39	5.1°C
(Mesa Alta,	200°C	598	14	964	41	4.8
N.M.)	400	593	11	964	44	4.2
	545	543	9	962	50	4.7
	700	—	—	962	63	5.0
Kaolinite	original	592	20	964	41	4.8
(Drybranch,	200	588	16	962	44	3.5
Geor.)	400	572	10	962	49	3.4
	545	559	3	963	58	3.9
	700	—	—	960	62	4.1

Table II

Thermal data of heat-treated specimens of kibushi-clay

Treated-temperatre	E_{n1} Temp. at peak	E_{n1} Height of peak	E_{n2} Temp. at peak	E_{n2} Height of peak	E_x Temp. at peak	E_x Height of peak	E_x Breadth of peak
original	130°C	1	574°C	14	945°C	13	10.5°C
200°C	120	1	572	12	943	14	10.3
400	120	1	570	12	944	13	10.5
545	—	—	561	5	944	14	10.4
700	—	—	—	—	942	18	9.6

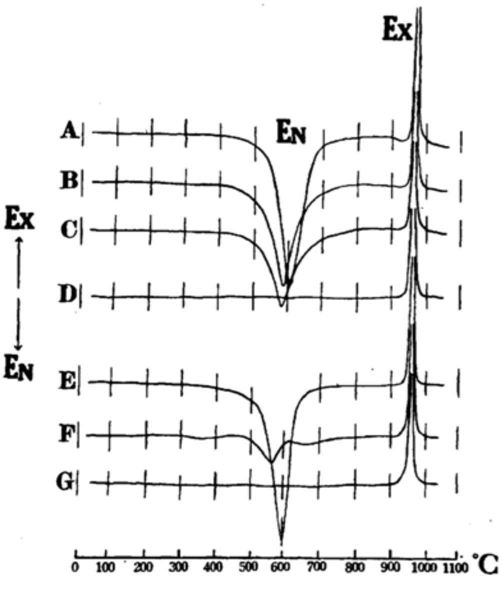


Fig. 3. Differential thermal analysis curves of heat-treated specimens of Mesa Alta and Drybranch kaolinite.
A, original Mesa Alta kaolinite
B, treated at 200°C
C, treated at 545°C
D, treated at 700°C
E, original Drybranch kaolinite
F, treated at 545°C
G, treated at 700°C

siderably. This means that the loss of the lattice water has considerably increased. In the 700°C heat-treated specimen, this endothermic reaction completely disappears.

Drybranch kaolinite behaves in a manner similar to Mesa Alta kaolinite. However, in the 545°C heat-treated specimen, the area of the endothermic reaction is small as compared with the 545°C heat-treated specimen of Mesa Alta kaolinite. This means that the crystallinity of its original sample is slightly lower than that of Mesa Alta kaolinite.

The final exothermic reaction (E_x) is due to the mullite nucleation. It is seen that the peak shifts slightly to the lower temperature side as the treated temperaturerises, and the peak height slowly increases. In the 700°C heat-treated specimen, the peak is considerably higher as compared with that of the original sample. From this fact, in spite of the fact that the X-ray diagram indicates that this state is amorphous, the rearrangement of ions is slowly occurring in the metakaolin matrix for the mullite nucleation. Generally, the breadth the exothermic reaction is defined as the breadth of temperature between the beginning point and the end point. However, as these points are not so clear, in this study, the breadth at the point of the half value of the peak height is taken as the breadth of the peak. The breadth of the peak thus defined is considered to indicate the sharpness of the mullite nucleation. This breadth slightly reduces as the heat-treatment temperature rises. After reaching the minimum value, it increases again. Any definite conclusion can hardly be made from this phenomenon, however.

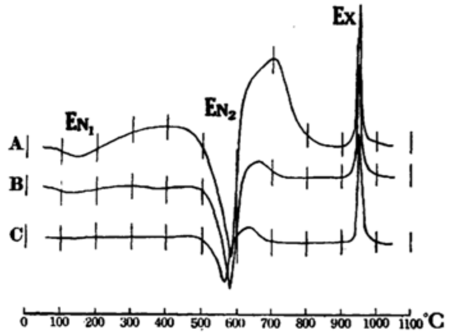


Fig. 4. Differential thermal analysis curves of heat-treated specimens of Kibushi-clay.

A, original clay
B, treated at 400°C
C, treated at 545°C

Fig. 4 shows the differential thermal analysis curves taken in the process of heat-treatment of Kibushi-clay and Table II gives data obtained from these curves. In the original sample, a weak endothermic reaction appears, associated with the loss of adsorbed or inter-layer water. In the 200°C and 400°C heat-treated specimens, the presence of weak but clear endothermic reaction is still observable. This might be due either to the fact that, after the heat-treatment it adsorbs water vapor so rapidly from the atmospheric air, or to the fact that the inter-layer water still remains even after the heat-treatment. The presence of such reactions in the heat-treated Kibushi-clay indicates that the degree of crystallinity of this clay is low. Similar phenomena are also observable in halloysite with a lower degree of crystallinity. For the endothermic and the exothermic reactions, the features in the variation of these reactions are similar to those of kaolinite, but these features are more pronounced.

Density.—The change in the density with the heat-treatment is shown in Fig. 5. The density changes to a maximum through heat-treatment, then it falls and reaches the minimum value at the point where the lattice water is lost, finally it increases again rapidly. It can be seen that the higher the crystallinity is, the lower is the temperature correspoding to the maximum value on the density curve, and the higher is the temperature corresponding to the minimum value. This is correlated with the fact that as the internal degree of crystallinity is lower, the lattice water is lost at a lower temperature. The fact that the density of Kibushi-clay sharply increases in the early stage of heat-treatment is due to the presence of organic substance in it. The organic substance is slowly carbonized and oxidized through heat-treatment, and it is released as carbon dioxide. This corresponds to the fact that size of a broad exothermic reaction which appears just byond 600°C on the differential thermal analysis curve becomes smaller and smaller as the heat-treatment temperature rises.

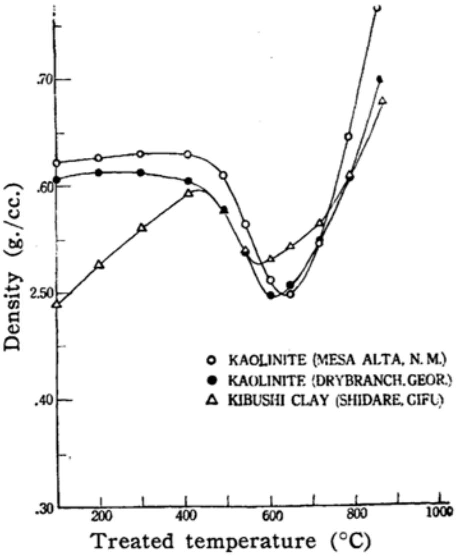


Fig. 5. Curves showing the changes of the density with the treated temperature.

The minimum value of density where the lattice water is lost, has no relation to the degree of crystallinity in either the kaolinite or the fireclay. Past the minimum point, the density increases almost in a straight line. The curve is steeper as the degree of crystallinity of the original sample is higher. It is evident that the rearrangement of ions is occurring in the lattice of the metakaolin state prior to the mullite nucleation after the loss of lattice water. It is supposed that the stronger the structure of the original sample is, the faster and more perfect is the rearrangement of ions for the mullite nucleation.

Mechanism of Structural Change of Kaolinite and Kibushi-clay with Heat-Treatment.—The crystallinity of kaolin minerals consists of two elements as described in the previous paper[3], that is the degree of crystallinity in stacking of layers, and the internal degree of crystallinity in each layer. In the heat-treatment process of kaolinite and Kibushi-clay, there are two opposite processes. In the structural change of these clays in the early stage of heat-treatment, a minute water adsorbed on the surface of its crystallite or existing between micelles which is not detectable by th thermal curve, is lost gradually, and from this fact, it can be considered that its apparent crystallite size increases owing to the aggregation of several neighbouring crystallites. The apparent crystallite size becomes larger than that of the original crystallite. This tendency is remarkable particularly along the direction of *c*-axis which is perpendicular to the layer plane. Also the value of the density increases and the progress of the crystallinity is observable. In the next stage, the loss of the lattice water in the kaolin mineral takes place. At the beiginning of this reaction, the kaolin mineral transforms suddenly to metakaolin, and this lead to the amorphous structure in the X-ray diagram. In the metakaolin state which is realized prior to the mullite nucleation from the metakaolin, no observable indication for the structural change can be seen in the X-ray diagram. However, it is evident that, in the metakaolin structure, the rearrangement of ions takes place for the mullite nucleation. The rate of rearrangement depends on the crystallinity of the original sample. The higer the original crystallinity is, the more perfect is the rearrangement, and the more clearly can the mullite nucleation be seen. Compared with Kibushi-clay, in kaolinite the rearrangement proceeds more remarkably.

Summary

The structural change of kaolinite and Kibushi-clay with heat-treatment in the relatively low temperature region has been studied. It has been found that there are generally three processes, and that the structural change depends on the degree of crystallinity of the original samples.

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