Changes of Dynamic Properties of Some Kaolin Minerals by Heat-treatment

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In general, ceramic products are made by heating clay mineral at a high temperature in order to utilize its strength and hardness. In some cases, however, moderate abrasion as well as strength and hardness are required where clay mineral is used at the meta-stable state in the process of its structural changes, different from the general conception of ceramic products. It is therefore, important to study changes of dynamic properties of clay mineral when it is heated at a relatively low temperature region, and this study aims at clarifying the characteristics of the results of heat-treatment in air-tight and carbon dioxide atmosphere.

Mutual relationship between changes of dynamic properties, densities and structures of some kaolin minerals was investigated when they were heated in a closed vessel. On the dynamic properties, the Young's modulus and bending strength, and on the physical properties, bulk density and density were measured.

At the same time, the relationship between changes of dynamic properties and structures was partly tested by X-ray diffraction method. The results of Kibushi-clay heated in a closed vessel were compared with the results when it was heated in the open air.

Samples.—The following kaolin minerals were used in this study: Shidare-Kibushi clay from Shidare, Gifu, Japan; Yagusa-Kibushi clay from Yagusa, Aichi, Japan; Naegi-Kaolin from Naegi, Gifu, Japan; and Hongkong-Kaolin from Hongkong.

By the X-ray diffraction method, any of them excepting Hongkong-Kaolin is a kaolin mineral of fireclay type[1] and contains a small quantity of quartz in spite of being elutriated. Shidare-Kibushi clay contains a small quantity of organic matter as an impurity. Hongkong-Kaolin is halloysite with a high crystallinity[2]. The results of chemical analysis of the four samples which have been elutriated are shown in Table I.

In differential thermal analysis curves of all samples, the endothermic peak was reached due to the loss of inter-layer water between 100 and 200°C and to the loss of structural water between 400 and 500°C. The exothermic peak was reached at about 950°C corresponding to the structural change to mullite.

TABLE I
CHEMICAL ANALYSIS OF SOME KAOLIN MINERALS

Component	Shidare-Kibushi	Yagusa-Kibushi	Naegi-Kaolin	Hongkong-Kaolin
SiO_2	48.76	50.29	47.48	46.78
TiO_2	0.77	0.23	0.01	tr.
Al_2O_3	34.53	33.13	37.59	35.62
Fe_2O_3	1.50	2.10	0.40	0.46
MnO	0.00	tr.	0.00	tr.
CaO	0.27	0.24	0.11	0.81
MgO	0.20	0.64	0.02	0.63
K_2O	0.34	1.51	1.61	1.16
Na_2O	0.19	0.58	0.16	1.11
Ig·Loss	13.43	11.40	12.45	13.27
Total	99.99	99.82	99.83	99.84

All samples were elutriated, roll-milled with a proper amount of water and extruded into rods of about 3.5 mm. in diameter by a press. Each sample prepared as mentioned above was dried at 100°C in a drying oven for 24 hours. The samples were heated in an air-tight graphite crucible, the temperature of which is raised by 5°C per minute in an electric furnace with siliconit heaters, and then they were cooled down naturally in the crucible taken out of the furnace after having constantly been heated therein at a given temperature for an hour. In the case of heat-treatment in the open air, samples were heated in a porcelain crucible with many holes under the same conditions as in the case of the air-tight crucible. The temperatures of heat-treatment in both cases were 500, 800, 900, 1000, 1050, 1100, 1150, 1200 and 1250°C.

Experimental

Young's Modulus. — Young's modulus was measured in a cramp-free state by loading at a non-fixed end. It was calculated by the following equation[3]:

$$\text{Young's modulus} = (4l^3/\pi a^4 e)\,P/3$$

where l, distance between the fixed point and the loaded point=10 cm.; P, load=980 dynes; a, radius of sample (cm.); and e, length of strain (cm.).

1) G. W. Brindley and K. Robinson, *Trans. Faraday Soc.*, 42B, 198 (1946).
2) G. Honjo and K. Mihama, *Acta Cryst.*, 7, 511 (1954), and H. Takahashi, This Bulletin, 31, 275 (1958).
3) Y. Tani, "Experimental Elasticity", (Iwanami Koza) V. F. 30 (1939).

TABLE II
BULK DENSITY OF SOME KAOLIN MINERALS

Temp. °C	Shidare-Kibushi		Yagusa-Kibushi	Naegi-Kaolin	Hongkong-Kaolin
100	1.72	open	1.92	1.86	1.68
500	1.64	1.58	1.88	1.78	1.63
800	1.64	1.61	1.80	1.72	1.55
900	1.72	1.76	1.95	1.88	1.63
1000	1.74	1.82	2.04	1.92	1.65
1050	1.86	2.03	2.37	2.14	1.74
1100	2.02	2.49	2.43	2.31	1.88
1150	2.34	2.46	2.43	2.44	2.13
1200	2.37	2.45	2.08	2.50	2.15
1250	2.44	2.39	—	—	—

TABLE III
DENSITY OF SOME KAOLIN MINERALS

Temp. °C	Shidare-Kibushi		Yagusa-Kibushi	Naegi-Kaolin	Hongkong-Kaolin
100	2.629	open	2.629	2.61	2.58
500	2.537	2.505	2.598	2.59	2.57
800	2.572	2.574	2.577	2.56	2.58
900	2.591	2.687	2.685	2.66	2.61
1000	2.672	2.695	2.716	2.68	2.66
1050	2.670	2.699	2.671	2.70	2.67
1100	2.675	2.688	2.647	2.66	2.68
1150	2.651	2.654	2.684	2.64	2.69
1200	2.662	2.669	2.613	2.66	2.69
1250	2.637	2.653	—	—	—

TABLE IV
YOUNG'S MODULUS ($\times 10^{11}$ dyne/cm^2)

Temp. °C	Shidare-Kibushi		Yagusa-Kibushi	Naegi-Kaolin	Hongkong-Kaolin
100	0.525	open	—	—	—
500	1.66	1.78	1.88	1.75	1.02
800	1.63	2.01	2.34	2.00	1.10
900	2.19	2.98	3.25	2.65	1.47
1000	2.52	3.58	4.40	2.83	1.56
1050	3.68	4.82	5.00	3.44	2.01
1100	4.85	5.91	5.92	5.08	2.85
1150	5.75	6.80	6.20	5.78	4.50
1200	6.05	7.18	5.92	6.53	4.27
1250	6.62	6.00	—	—	—

TABLE V
BENDING STRENGTH (g./mm^2)

Temp. °C	Shidare-Kibushi		Yagusa-Kibushi	Naegi-Kaolin	Hongkong-Kaolin
100	1300	open	1620	1490	470
500	2320	5140	2660	3260	1050
800	5100	6490	6950	5990	2570
900	5950	7970	8210	8110	3840
1000	7030	7720	8960	7720	4240
1050	8360	8130	12600	9040	6000
1100	10770	12900	17690	11130	6860
1150	12030	12920	17670	14600	9770
1200	13800	13350	11390	17500	9300
1250	14600	12600	—	—	—

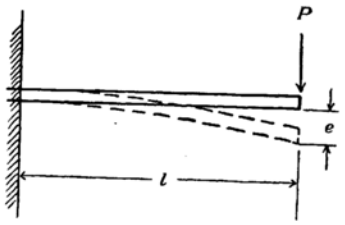


Fig. 1. Measuring procedure of Young's modulus.

Bending Strength. — Although a bending strength does, in an exact sense, not always mean a physical value, it is practically used as a breaking strength in industries. By supporting a sample on two knife edges, continuously loading on the middle of the sample and reading the weight of the load just breaking the sample the bending strength was calculated by the following equation[4]:

$$\text{bending strength} = 8Pl/\pi d^3$$

where P, weight of load just breaking the sample (g.); l, distance between two supporters 60 mm. and d, diameter of sample (mm.).

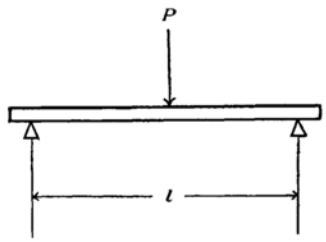


Fig. 2. Measuring procedure of bending strength.

Density. — The sample was ground into a powder finer than 200-mesh and its density was measured by a picnometer in mono-chlorbenzene at 25°C.

Results

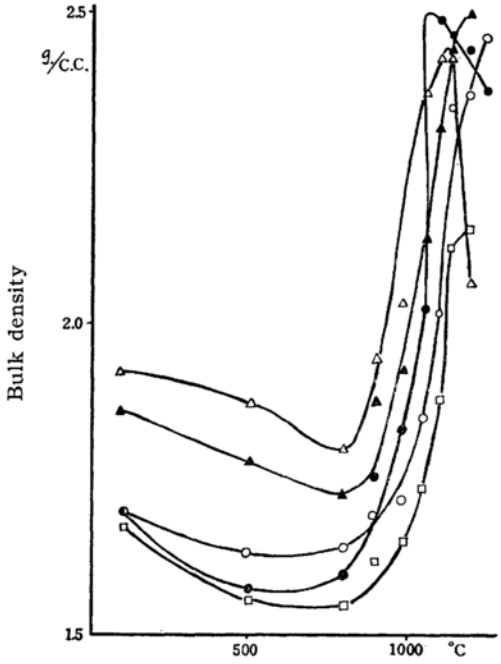
Bulk Density.—The value of bulk density is shown in Table II and Fig. 3, and there is the minimum point at about 800°C in each curve, except that the temperature corresponding to the minimum point of bulk density of Shidare-Kibushi clay heated in the open air moves down to about 500°C and its maximum point appears at about 1150°C.

Density.—As shown in Table III and Fig. 4, there is a minimum point between 500 and 800°C and a maximum point at about 1000°C in each curve of the density. Beyond 1000°C the density decreases gradually.

Young's Modulus.—As shown in Table IV and Fig. 5, the Young's modulus increases rapidly beyond 800°C and a maximum value is shown between 1100 and 1200°C.

Bending Strength.—As shown in Table V and Fig. 6, beyond 800°C the bending strength increases gradually and beyond 1000°C, it increases

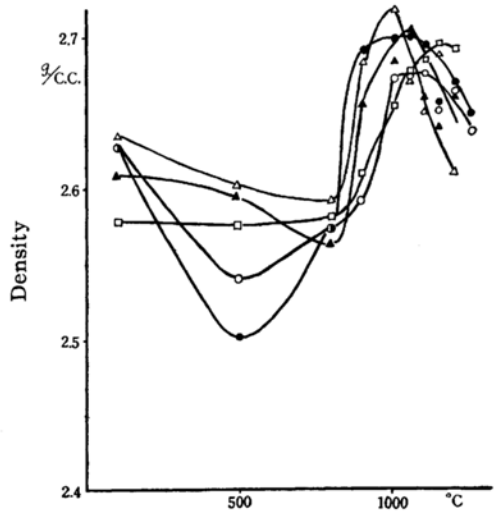
4) Japanese Industrial Standard (JIS), S-6005, 4 (1955).



Treated temperature

Fig. 3. Curves showing the changes of bulk density in the various stages of heat-treatment.

○ Shidare-Kibushi
● Shidare-Kibushi (open)
△ Yagusa-Kibushi
▲ Naegi-Kaolin
□ Hongkong-Kaolin



Treated temperature

Fig. 4. Curves showing the changes of density in the various stages of heat-treatment.

○ Shidare-Kibushi
● Shidare-Kibushi (open)
△ Yagusa-Kibushi
▲ Naegi-Kaolin
□ Hongkong-Kaolin

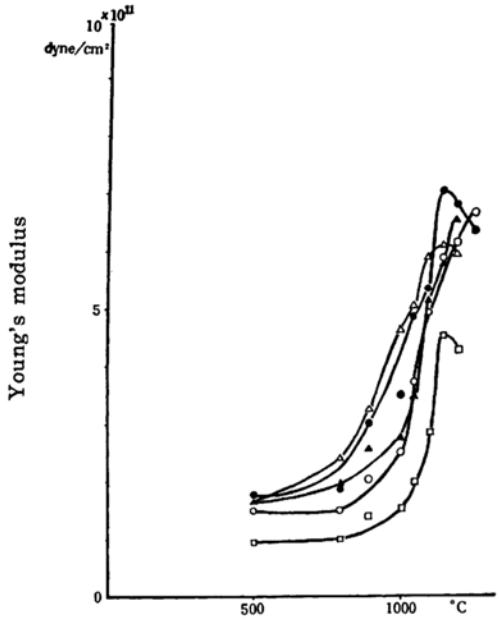


Fig. 5. Curves showing the changes of Young's modulus in the various stages of heat-treatment.
- ○ Shidare-Kibushi
- ● Shidare-Kibushi (open)
- △ Yagusa-Kibushi
- ▲ Naegi-Kaolin
- □ Hongkong-Kaolin

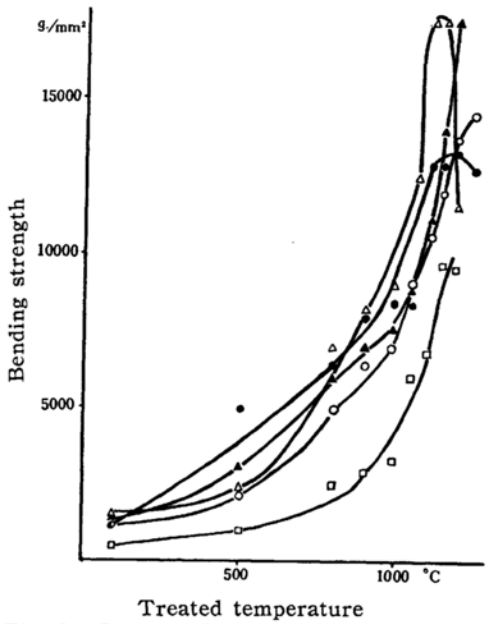


Fig. 6. Curves showing the changes of bending strength in the various stages of heat-treatment.
- ○ Shidare-Kibushi
- ● Shidare-Kibushi (open)
- △ Yagusa-Kibushi
- ▲ Naegi-Kaolin
- □ Hongkong-Kaolin

rapidly. In both cases, there are maximum values and, after reaching the maximum values, it decreases rapidly.

Discussion

Even clay minerals, which belong to the same "kaolin" group, differ from one another according to their kinds in regard to the bending strength and Young's modulus. There are many factors, for example, particle sizes, structural characteristics, impurities, etc., which influence the dynamic properties of kaolin minerals.

As only four samples were experimented with in regard to their dynamic properties, it is difficult to discuss and to relate the results of their dynamic properties with the results of chemical analysis. The effects of the impurity contained in kaolin mineral on the dynamic properties are studied now and their results will be reported in future.

In this paper, some relationships between the dynamic properties and the structural characteristics are discussed. The changes of the dynamic properties by heat-treatment beyond a certain temperature are not continuative but are abrupt. In the heat-treated specimens of Yagusa-Kibushi clay, for example, the bending strength increases to only 2000 g./mm² between 800 and 1000°C and as much as 8000 g./mm² between 1000 and 1100°C, but decreases rapidly between 1100 and 1200°C. Also, the Young's modulus and even density take a similar tendency. These phenomena seem to be attributed to the changes of crystal structures in clay minerals. Therefore, those causes which affect the changes of dynamic properties may be due to the following:

1. Change of plasticity of kaolin mineral by heating at an early stage.
2. Change of crystal structure of kaolin mineral and transformation of its macrostructure caused by the change of crystal structure by heating at a later stage.
3. Sintering.

Now, the value expressed by percentage which is obtained by dividing a bulk density by a density is called "filling ratio". The dynamic properties and the filling ratio will be discussed. As shown in Table VI and Fig. 7, the minimum value of filling ratio appears, generally speaking at the temperatures between 500 and 800°C. The changes of the filling ratio

TABLE VI
FILLING RATIO (PERCENTAGE)

Temp. °C	Shidare-Kibushi		Yagusa-Kibushi	Naegi-Kaolin	Hongkong-Kaolin
100	65.3	open	73.9	72.0	65.2
500	64.4	63.2	71.8	68.2	63.3
800	64.0	62.6	70.0	67.2	60.2
900	66.2	65.8	72.5	70.7	63.9
1000	65.2	67.7	74.9	71.7	62.1
1050	70.0	75.2	88.8	79.3	65.0
1100	75.5	92.5	91.7	86.8	72.5
1150	88.0	92.5	90.5	91.6	79.2
1200	89.0	91.8	82.7	93.8	80.6
1250	92.6	90.2	—	—	—

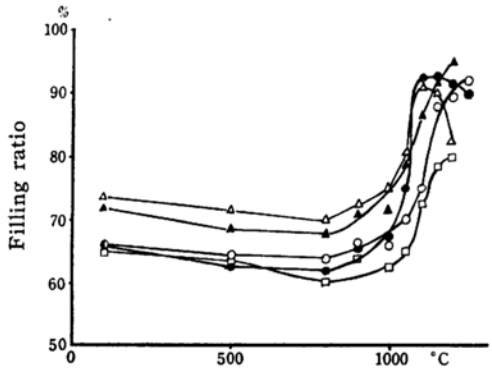


Fig. 7. Curves showing the changes of filling ratio in the various stages of heat-treatment.
○ Shidare-Kibushi
● Shidare-Kibushi (open)
△ Yagusa-Kibushi
▲ Naegi-Kaolin
□ Hongkong-Kaolin

may be due to the following. In the early stage of heating, the sample loses interlayer water. At the temperatures between 500 and 800°C, it has the minimum filling ratio, because it becomes porous owing to the loss of structural water while the shrinkage caused by sintering does not keep pace with it. Beyond 800°C, it is in the state of "meta-kaolin" and its filling ratio is recovered gradually between 800 and 1000°C, because the shrinkage by sintering is larger than the loss of structural water.

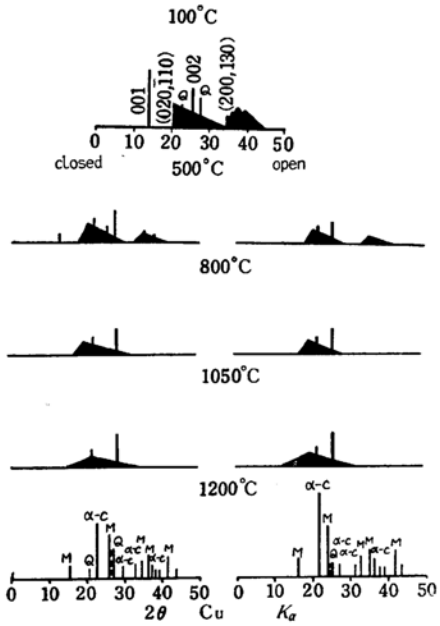
The Young's modulus changes a little until it reaches 800°C, but as soon as the temperature exceeds 800°C, the Young's modulus begins to increase in company with filling ratio. This indicates that the Young's modulus increase is accompanied by the sintering. The filling ratio increases rapidly beyond 1000°C which may be due not only to the sintering but also to the commencement of the structural changes of the kaolin minerals[5]. This rapid increase of the filling ratio has influence on the bending strength and the Young's modulus.

The temperature at which crystallization begins varies a little according to the kinds of kaolin mineral. That is to say, in the case of Yagusa-Kibushi clay, the Young's modulus begins to increase just beyond 1000°C, but in the case of Shidare-Kibushi clay and Naegi-Kaolin, it does at higher temperature. In the case of Hongkong-Kaolin, it begins to increase rapidly beyond 1050°C. However, when the temperature of heat-treatment rises up to a certain point along with the development of crystallization, the filling ratio does not increase but begins to decrease and, at the same time, the bending strength and the Young's modulus also are inclined to decrease. This may be explained as follows.

In the case of Shidare-Kibushi clay, the filling ratio continues to increase until 1250°C together with the bending strength and Young's modulus, which may be caused, to a great extent, by the sintering and the commencement of crystallization. Crystals of mullite and α-cristobalite do not yet grow at 1050°C, but they appear at 1200°C. In the case of Yagusa-Kibushi clay, the Young's modulus increases rapidly beyond 1000°C, and reaches the maximum value between 1100 and 1200°C. However, at 1200°C the Young's modulus apparently starts to decrease according to the decrease of the filling ratio. Moreover, the characteristics of the sample heated at 1200°C shows a distinguished expansion in diameter.

X-ray diffraction data will be discussed below. As shown in Fig. 8, in the case of Shidare-Kibushi clay, mullite begins to

5) W. F. Bradley and R. E. Grim, *Am. Mineral*, **36**, 182 (1951).



M: mullite, α-c: α-cristobalite, Q: quartz

Fig. 8. Schematic drawings of the X-ray diffractometer traces of heat-treated specimens of Shidare-Kibushi clay.

grow at about 1050°C. At about 1200°C, the crystallization to mullite is distinguishable and the quartz of impurity changes to α-cristobalite. Therefore, it is considered that when this clay begins to crystallize and its filling ratio increases rapidly owing to sintering, both the bending strength and the Young's modulus increase together. However, when the crysrallizations to mullite and α-cristobalite are remarkable, cracks grow along the crystals, and therefore, the filling ratio and bending strength together with the Young's modulus are reduced.

The difference between the heat-treatment in a closed vessel and in the open air will be discussed. In general, Kibushi clay changes at the lower temperature when heated in the open air. This may be clearly seen from the X-ray diffraction diagrams of the heat-treated specimens of Shidare-Kibushi clay shown in Fig. 8. That is, in the heat-treatment in a closed vessel, two reflections, (001) and (002), are clearly left at 500°C although their intensities are weaker, while in the heat-treatment in the open air, the reflections are thoroughly extinguished at the same temperature. The X-ray diffraction diagram of the 1100°C heat-treated specimen in the open air is almost exactly similar to that of the specimen heated at 1200°C in a closed vessel.

Summary

When kaolin mineral is heat-treated at a relatively low temperature region, its density has the minimum value between 500 and 800°C and the maximum at about 1000°C.

The value of dynamic properties of kaolin mineral increases slightly until about 800°C but increases rapidly beyond 1000°C to reach the maximum value. Then, the value is inclined to decrease rapidly beyond the temperatures, at which the maximum value is yielded. Similarly, the filling ratio also has the minimum value at about 800°C and increases rapidly beyond 1000°C to reach the maximum value. This indicates that when kaolin mineral is heat-treated at a relatively low temperature region, its dynamic properties have a close relation with its filling ratio. It is considered that these phenomena are due not only to the sintering of clay mineral by heat-treatment but also to the structural changes as shown in X-ray diffraction data.

The changes of dynamic and physical properties and of the structures of kaolin mineral heated in a closed vessel take place later than those heated in the open air. It may be due to the fact that the oxidation of the organic matters contained in kaolin mineral is oppressed in a closed vessel.

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