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DEHYDRATION ENERGY OF HALLOYSITE BY MEANS OF D. S. C. METHODS WITH THE RELATIONSHIPS OF ITS MINERALOGY AND MODES OF OCCURRENCE

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ABSTRACT

Halloysite (10Å), one species of kaolin minerals, has two different shapes under the electron microscope, such as tubular and spherical, and is formed by two various geological conditions, by hydrothermal and weathering reactions. The clay mineral has two dehydration stages, 30-120°C and 350-550°C, with transformations to metahalloysite and metakaolin. The differences of thermal properties, T. G., D. T. G. and D. S. C. methods, were investigated for five materials, three hydrothermal and two weathering specimens. The five purified materials were stored in 100% relative humidity condition, and dehydration amount by T.G., dehydration energy by D. S. C. methods were measured. In the two dehydration stages, dehydration energies 'cal/gram' for the five materials are calculated. The dehydration energies of the first stage on the five materials are nearly equal to the value of latent heat of water evaporation, and the value on one material (Dragon mine, U.S.A.) is slightly higher than that of the other materials. The values of the second stage dehydration energy for the five materials differ according to their mineralogical properties and their modes of formation. The values of hydrothermal materials are higher than that of weathering reaction materials, in the both shapes. The values of the spherical materials are higher than that of tubular ones, in the both modes of formation. These differences are caused by their crystallinity, shape of form, surface area of the fine particle, modes of occurrence, etc..

INTRODUCTION

Halloysite (10Å) has special thermal behaviors in clay mineral and kaolin mineral, such as it has two main dehydration stages with deformations of halloy-

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site to metahalloysite and metahalloysite to metakaolin. It has special mineralogical properties, such as two different forms of tubular and spherical shape under the electron microscope and different modes of formation by hydrothermal reaction and weathering reaction. The difference of dehydration in the two stages are discussed by their dehydration energies with the variations in the shape of fine perticle and the modes of formations, in this report.

EXPERIMENTAL

Purification and chemical analysis of material

Following five halloysite materials were purified by means of water washed methods and the purified materials were stored in high humidity condition of 100% relative humidity. The five purified materials were analyzed by chemically, by following methods;

SiO_2 and Al_2O_3: Gravimetry.

TiO_2: Colorimetry.

Fe_2O_3, MnO, MgO, CaO, Na_2O and K_2O: Atomic adsorption photometry.

H_2O^+ and H_2O^- : Thermogravimetry.

The results are cited in TABLE 1.

Halloysite specimens:

Formed by hydrothermal reaction: From Tawara, Gifu Pref., Ookuchi mine, Kagoshima Pref., Japan and Dragon mine, Utah, U.S.A..

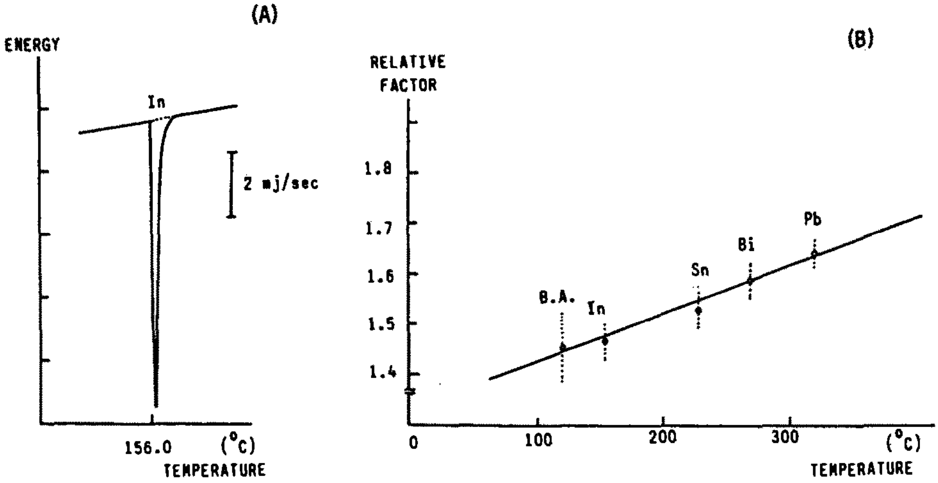
Formed by weathering reaction: From Mikuni, Kato-gun, Hyogo Pref. and Ina mine, Ina, Nagano Pref., Japan.

The specimens from Ookuchi and Ina have sphrical shape and other three ones have tubular shape.

Thermal analysis

Thermogravimetric curve (T.G. curve), differential thermogravimetric curve (D.T.G. curve), Wt. % of H_2O^+ and H_2O^- were measured by the thermobalance of "Shimadzus' Thermal Analyzer DT-30" with 10mg of the purified materials. The T.G. curves and D.T.G. curves of the purified materials from Tawara and Mikuni are shown in Fig. 2 (A), for instance. The values of Wt. % of H_2O^+ and H_2O^- in the chemical analysis are cited in TABLE 1.

Thermal energy which was used for dehydration and transformation by heat treatreatment was measured by differential scanning calorimetry, using the "Shimadzus' Thermal Analyzer DT-30" with D.S.C. attachment of "SCC-30". The results are also shown in Fig. 2 (B) on the materials from Tawara and Mikuni. Measurment of thermal energy by means of D.S.C. methods for minerals, especially for clay minerals, was rarely reported, because the temperature range for measurement is wider than that of ordinarly inorganic materials. Special methods were appli-



B.A.; benzoic acid (C_6H_5COO)

Fig. 1. Revising experiments for the D. S. C. measurment.
(A): Measurment of melting energy of In metal.
(B): Relative factors in the D. S. C. analysis.

TABLE 1

Chemical analyses of five halloysites and one kaolinite*.

Sample	Ina mine		Tawara		Mikuni		Ookuchi		Dragon	
	Wt. %	Mol.pr.	Wt. %	Mol.pr.	Wt. %	Mol.pr.	Wt. %	Mol.pr.	Wt. %	Mol.pr.
SiO_2	41.70	0.6941	41.27	0.6869	40.51	0.6742	40.63	0.6753	42.47	0.7069
TiO_2	0.24	0.0030	0.10	0.0013	0.14	0.0018	0.56	0.0070	0.12	0.0015
Al_2O_3	33.92	0.3327	34.97	0.3430	35.34	0.3466	34.09	0.3343	33.70	0.3305
Fe_2O_3	3.02	0.0190	0.20	0.0012	0.86	0.0054	3.30	0.0207	0.10_3	0.0006
MnO	0.01_6	0.0002	0.02	0.0003	tr.	------	0.00_4	0.0000_6	0.00_2	0.0000_3
MgO	0.02_7	0.0007	0.13	0.0032	0.10	0.0025	0.02_2	0.0005	0.09_6	0.0024
CaO	0.40	0.0071	0.73	0.0130	tr.	------	0.28	0.0050	0.37	0.0066
Na_2O	0.19	0.0031	0.21	0.0034	tr.	------	0.19	0.0031	0.27	0.0044
K_2O	0.33	0.0035	0.39	0.0041	0.24	0.0025	0.21	0.0022	0.07_4	0.0008
H_2O^+	10.79	0.5989	11.15	0.6177	14.07	0.7810	10.38	0.5762	10.87	0.6033
H_2O^-	9.82	0.5451	10.04	0.5562	8.66	0.4807	10.02	0.5562	11.62	0.6450
Total	100.45_3		99.29		99.92		99.68_6		99.69_5	

* Thermal reference sample, kaolinite from Suzhou White Clay mine, Suzhu, China.
(Analyzed by MINATO, 1981 - 85)

TABLE 1 (Continue)

Sample	Suzhou kaolinite	
	Wt. %	Mol.pr.
SiO_2	45.43	0.7562
TiO_2	0.02	0.0003
Al_2O_3	40.17	0.3940
Fe_2O_3	tr.	------
MnO	none	------
MgO	tr.	------
CaO	0.35	0.0062
Na_2O	0.65	0.0105
K_2O	0.26	0.0028
H_2O^+	11.98	0.6650
H_2O^-	0.96	0.0533
Total	99.73	

TABLE 2

Dehydration energy of halloysites

Locality	Dehydration 30-120°C			Dehydration 350-550°C		
	Wt.loss (mg)	D.S.C. (cal)	Energy (cal/g)	Wt.loss (mg)	D.S.C. (cal)	Energy (cal/g)
Tawara*	0.590	287	487	0.975	1002	1028
Mikuni*	1.000	480	480	0.847	798	942
Ookuchi*	1.970	930	472	0.980	1328	1355
Ina*	1.190	626	526	1.070	1013	947
Dragon**	1.230	670	544	0.990	1286	1299

* Relative factor in D.S.C.: 30-120°C -- X1.4, 350-550°C -- X1.7.

** Relative factor in D.S.C.: 30-120°C -- X0.75, 350-550°C -- X0.9

ed in this experiment. 1. Thermal standard material (purified and calcined kaolinite from Suzhou White Clay mine, Yangxi, Suzhou, China) was used in the reference side of the D.S.C. furnace. 2. Correction curves were used for relative factors at different temperatures. The curve was formed by D.S.C. mea-

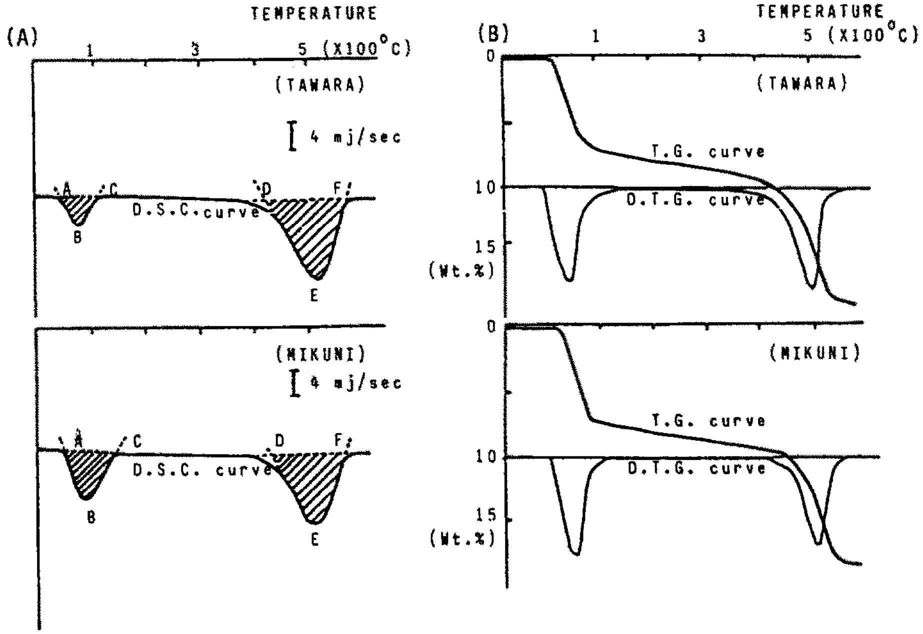


Fig 2. Thermal analysis curves of halloysites from Tawara and Mikuni.

(A): Thermogravimetric curves (T.G. curve) and differential thermogravimetric curves (D.T.G. curve). (B): Diferential scanning calorimetric curves (D.S.C. curve).

surments of standard material of benzoic acid and pure metals of In, Sn, Bi and Pb as shown in Fig. 1 (B). 3. In correction of baseline of the D.S.C. curve, same measurment was repeated after the D.S.C. measurment for the sample. The correction for the curve is obtained by drafting methods.

The measurment is carried out by following methods: Temperature range: Room temperature to 550^{0}C, Heating rate: 10^0 C/min. With N_2 gasflow condition of 30 ml/min, 10 mg of the powdered material is used. The energy is measured as areas of ABC and DEF in Fig. 2 (A) with that of In metal in Fig. 1 (A).

On the five halloysite materials, weight loss (mg) by T.G. curve and dehydration energy (cal) by D.S.C. curve are cited in TABLE 2, and also the energy per weight (cal/g) are cited in the same table.

DISCUSSIONS AND CONCLUSIONS

Dehydration energy (cal/g) at 30 - 120^{0}C, for the five materials is nearly equal for the value of the latent heat of water evaporation. The water molecules evolved at the first stage, 30 - 120°C, were weakly combined in the halloysite structure. The value of Dragon mine is higher than that of the other materials, perhaps due to its high degree of crystallinity.

Dehydration energies (Cal/g) at 350 - 550°C, for the five materials are varied in different samples, the value of Tawara, formed by hydrothermal reaction, is higher than that of Mikuni, formed by weathering reaction, both having the same tubular shape. Also, the value of Ookuchi, formed by hydrothermal reaction, is higher than that of Ina, formed by weathering reaction, both having spherical shape. For the same particle form and spherical shape, hydrothermal halloysites have higher dehydration energies than weathering halloysites. Spherical halloysites have higher dehydration values than tubular halloysites with the same mode of formation. The dehydration energy at this stage derives from degree of crystallinity, mode of formation, surface area, and particle from of the mineral. The higher value in Dragon mine is due to its higher degree of crystallinity.

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