Coexistence States of Iron in Synthesized Iron-bearing Allophane (Al_2O_3-SiO_2-Fe_2O_3-H_2O System)

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A sharp exothermic peak at 980°C, which is found characteristic of allophane in its differential thermal analysis, shifted to the lower-temperature side and broadened as the iron content in the iron-coprecipitated samples increased. In the case of the iron-mixed samples, however, this exothermic peak did not shift, and a new broad exothermic peak, which was ascribed to hydrated ferric oxide, appeared. The crystallization processes in the heat-treated samples were found to depend on the coexistence state and the quantity of the iron. The dimensions of a unit cell of the mullite, crystallized at 1200°C from the iron-coprecipitated samples, varied with the iron content. The iron-mixed samples, however, showed little change in their cell dimensions. It is concluded that there are two states of the coexistence of iron in the allophanes. In one of them, iron ions form solid solutions of the allophane, *i.e.*, as an iron-allophane. In the other, iron is in the mixture as the hydrated ferric oxide. The maximum amount of iron in the solid solution was estimated to be 5 wt% in the iron-allophane.

An allophane is an amorphous or low-crystalline mineral, and its main components are silica, alumina, and water. Its chemical formula may be generally expressed as $1\text{-}2SiO_2\cdot Al_2O_3\cdot 5H_2O$. The allophane is considered not to be a simple mixture of a hydrated aluminum oxide gel and a silicic-acid gel.[1,2] The natural allophanes usually contain iron. The natural iron-bearing allophane dose not always show the same properties. It has, therefore, been suggested that there are two states of the coexistence of iron in the soil-allophane.[3]

In this work, the coexistence states of iron in the synthesized iron-bearing allophanes were studied by means of differential thermal analysis and X-ray powder diffractometry on heat-treated samples.

Experimental

Materials. The iron-coprecipitated samples were prepared in the following manner:[4] a mixed solution of aluminum sulfate, sodium silicate,[5] and ferric sulfate was boiled at a specified acidity of pH 5.4—6.0 obtained by adding hexamethylenetetramine. The gel thus coprecipitated was washed by decantation and then air-dried for three weeks. The iron-mixed samples were also prepared by mixing the synthesized allophane, free from iron, and the hydrated ferric-oxide gel in order to compare the properties of the iron-coprecipitated samples. The colors of the iron-coprecipitated and the iron-mixed samples were yellow and light-purplish red respectively.

Procedure. The X-ray powder diffractograms of the samples were taken with a Geigerflex, Model D-3F, Rigaku Denki Company, while the differential thermal analysis was carried out with equipment designed in our laboratory.

The sample, in a quartz tube, was heated for five hrs in an electric furnace at 800, 900, 1000, 1100, and 1200°C respectively. The firing-products were identified and their relative amounts were estimated by using the diffraction peaks at (210) and (120) of the mullite, those at (104) and (110) of the hematite, that at (440) of the silico-alumina spinel, and that at (101) of the cristobalite. The unit-cell dimensions of the mullite, one of the firing products, was calculated by using the diffraction peaks at (230), (121), and (201) of the mullite.

TABLE 1. CHEMICAL COMPOSITIONS OF COPRECIPITATED AND MIXED SAMPLES

Sample		Chemical composition, wt%					Molar ratio $\frac{SiO_2}{Al_2O_3}$	Molar ratio $\frac{SiO_2}{Al_2O_3+Fe_2O_3}$
		SiO_2	Al_2O_3	Fe_2O_3	$H_2O(\pm)$	Total		
	32[a]	30.04	29.48	tr.	40.66	100.18	1.73	——
Coppted	C32-1[a]	26.00	28.95	1.34	43.32	99.61	1.52	1.48
	C32-2	26.54	27.66	1.98	43.86	100.04	1.63	1.56
	C32-3	25.51	26.89	2.80	44.33	99.53	1.61	1.52
	C32-5	23.74	25.15	5.14	46.25	100.28	1.60	1.42
	C32-8	21.34	23.75	7.93	46.98	99.94	1.55	1.28
	C32-10	21.68	21.62	10.41	46.68	100.39	1.70	1.30
Mixed	M32-3	28.73	28.20	3.05	40.02	100.00[b]	1.73	1.62[b]
	M32-5	27.93	27.41	5.00	39.66	100.00[b]	1.73	1.55[b]
	M32-10	25.84	25.36	10.10	38.71	100.00[b]	1.73	1.38[b]

a) The numerical symbol "32" denotes the rough molar ratio of silica/alumina in the sample to be 3:2, while the numerical postscript "1", for example, denotes the rough iron content in the sample (here, 1 wt%).
b) Calculated.

1) G. Brown, *Clay Mineral Bull.*, **2**, 294 (1955).
2) J. Ossaka, "Advances in Clay Science," Vol. 2, ed. by S. Iwao, Gihodo, Tokyo (1960), p. 339.
3) S. Iwai, J. Ossaka, and M. Kasai, unpublished study.
4) J. Ossaka, S. Iwai, M. Kasai, T. Shirai, and S. Hamada, *Nippon Kagaku Zasshi*, **90**, 1288 (1969).
5) The sodium silicate solution was prepared by dissolving the melt of silica melted with sodium hydroxide.

Results

The chemical compositions of the samples are given in Table 1.

The silica/alumina ratios in the samples did not agree with the original ratios of the components in the solutions. The former were almost always smaller than the latter.[6]

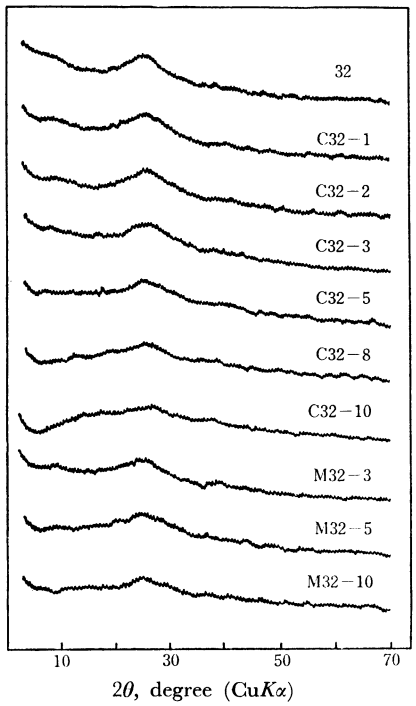

Fig. 1. X-Ray powder diffraction patterns.

The X-Ray Powder Diffractometry and the Differential Thermal Analysis of the Samples. Figure 1 shows the X-ray powder diffraction patterns. All the samples were identified as amorphous or lower crystalline materials, since there were few sharp peaks. However, a very broad peak was observed at approximately 25° (2θ; Cu$K\alpha$) in the iron-coprecipitated samples with a smaller amount of iron.

The DTA curves are shown in Fig. 2. All the samples showed the broad endothermic peak in the range from 100°C to 200°C and the exothermic peak at approximately 900°C, a position which was characteristic of the allophane. The exothermic peak observed in the iron-coprecipitated samples shifted from 980°C to 860°C and broadened as the iron content increased. On the contrary, the exothermic peak observed in the iron-mixed samples did not shift and did not broaden in spite of the change in the iron content, while the very broad exothermic pattern, which was assigned to the hydrated ferric oxide, was observed in the range from 300°C to 500°C. Although the iron-coprecipitated samples containing less than 5 wt% of iron showed only allophane-characteristic DTA curves, the broad exothermic peak due to the hydrated ferric oxide was observed when the iron content was above 5 wt%.

6) J. Ossaka, "Advances in Clay Science," Vol. 3, ed. by S. Iwao, Gihodo, Tokyo (1961), p. 225.

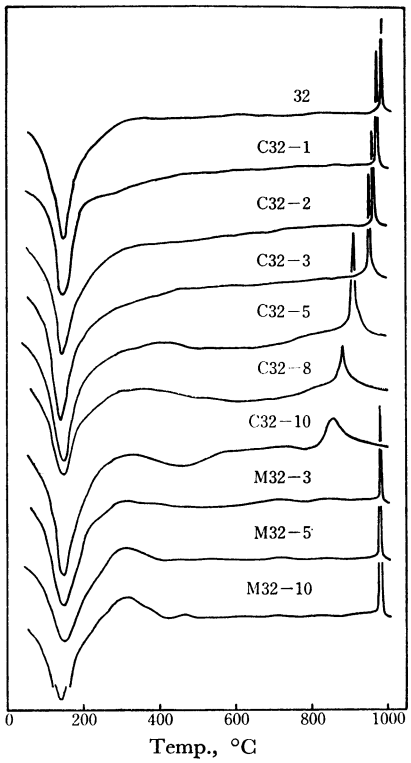

Fig. 2. DTA curves.

The Variation in Firing-products in the Samples during the Heat-treatment. The crystalline phases formed in the heat-treated samples at 800, 900, 1000, 1100, and 1200°C respectively were examined by means of the X-ray powder diffractometer. Although the final product of the heat treatment was the mullite, the crystallization process was found to vary, depending on the condition of the original samples (Fig. 3). The crystal-

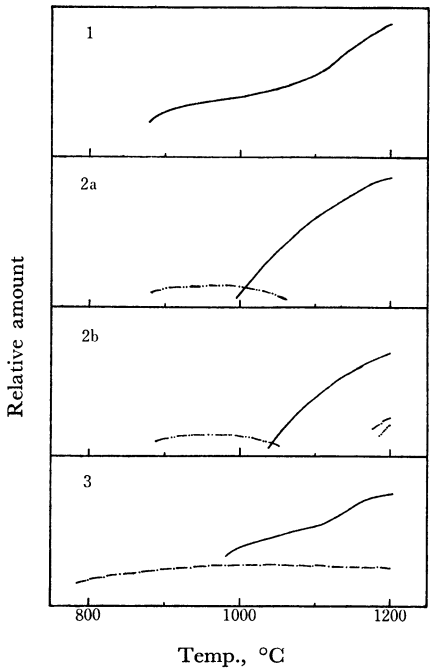

Fig. 3. Types of crystallization processes.
——— Mullite -·-·-·- Silico-alumina spinel
-·-·-·- Hematite ····· Cristobalite

lization processes may be classified into three types, as is shown in Fig. 3. It can be seen from Fig. 3 that the crystallization processes depend on the content and the coexistence state of the iron, while the silica/alumina ratio did not affect the crystallization process. The crystallization of all the iron-mixed samples belonged to the 3-type process, even if the iron content was only 3 wt%. The crystallization process of the iron-coprecipitated samples was found to be of the 1 or 2 type. The crystallization process of the iron-coprecipitated samples with less than 3 wt% iron was the same as that of the iron-free allophane, while those above 3 wt% were transformed into the mullite through the silico-alumina spinel phase. However, the hematite and the cristobalite phases were observed at 1200°C when the samples contained more than 8 wt% of iron. A clear difference between the crystallization processes of the iron-coprecipitated and the iron-mixed samples was also found in the DTA analysis.

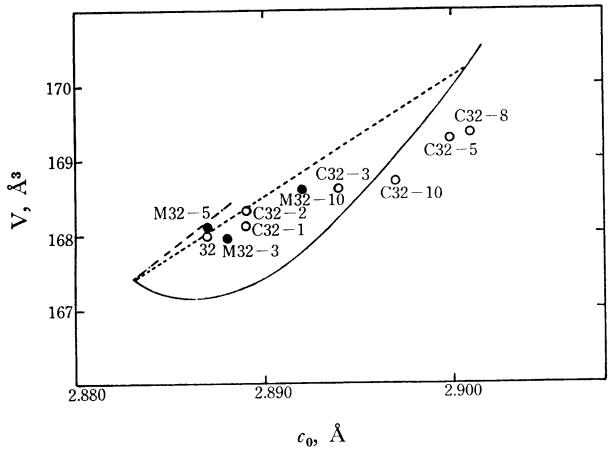

Fig. 4. Relationship between c_0 and V of crystallized mullite at 1200°C.
-·-·-·- iron free mullites[6]
——— iron and titanium-bearing mullites.
····· iron bearing mullite[11]

The Unit-cell Dimensions of the Mullite Formed in the Samples. The values of c_0 and the unit-cell volume, V, of the mullite which was formed in the heat-treated samples at 1200°C for five hrs were estimated from the X-ray powder diffractograms. The relationship between c_0 and V is shown in Fig. 4. The c_0 and V values of iron-free mullite varied with the silica/alumina ratios.[7] Therefore, the variation in the cell dimensions in the mullite with the quantity of iron was examined by comparing samples with the same original ratio of silica/alumina. The c_0 and V values of the mullite crystallized from the iron-coprecipitated samples increased with an increase in the iron content, while the c_0 and V values for the iron-mixed samples were nearly equal to those for the iron-free allophane except for the M32-10 sample. A clear difference in the cell dimensions was observed between the two types of samples.

Discussion

The exothermic peak at approximately 900°C in the differential thermal analysis on silica-alumina gel was explained as originating from the formation of γ-alumina[8] or mullite.[9,10] However, the X-ray analysis favored the conclusion that the formation of the mullite was mainly responsible for this peak in the present experiment.

It was found, in the case of the iron-coprecipitated samples with more than 3 wt% of iron, that the transformation to the mullite occurred through the intermediate stage of the formation of the silico-alumina spinel, while the iron-coprecipitated samples with less than 3 wt% of iron were transformed directly into the mullite, as with the iron-free allophane. The existence of the silico-alumina spinel as a metastable phase in the mullite was found in the course of the crystallization of heat-treated kaolinite by Brindley and Nakahira.[11]

The iron-mixed samples were converted into hematite with little change in their cell dimensions. Therefore, it can be said that the silica-alumina gel reacted in some degree with the hydrated ferric oxide, but formed a solid solution only with difficulty. Agrell and Smith,[7] and Murthy and Hummel[12] pointed out that the cell dimensions increased considerably with an increase in the iron content in the solid solution of the mullite, while the silica/alumina ratio in the mullite hardly influenced the cell dimensions. The large change in the cell dimensions of the mullite which was found when the iron content of the sample was varied indicates the formation of a solid solution of the mullite with iron. Agrell and Smith[7] also reported that there was 2 wt% of iron in a solid solution of the mullite, while the hematite was found, besides the solid solution of the mullite, when 5 wt% of iron was present in the sample. In the present study, it can be concluded, as in Fig. 4, that the solid solution of the mullite with iron is formed when the iron content is less than 5 wt%.

These facts support the idea that iron is contained as a solid solution of the allophane, *i.e.*, that it is the iron-allophane, when the amount of iron in the coprecipitated samples, is less than 5 wt%, while a part of the iron takes the form of the hydrated ferric oxide when its quantity is larger than 5 wt%.

7) S. O. Agrell and J. V. Smith, *J. Amer. Ceram. Soc.*, **43**, 69 (1960).

8) H. Insley and R. H. Ewell, *J. Res. Nat. Bur. Stand.*, **14**, 615 (1935).

9) V. J. Wiegman, C. H. Horte, and I. Sücker, *Silikat. Tech.*, **9**, 358 (1958).

10) T. Demadiuk and W. F. Cole, *Nature*, **181**, 1400 (1958).

11) G. W. Brindley and M. Nakahira, *J. Amer. Ceram. Soc.*, **42**, 311 (1959).

12) M. K. Murthy and F. A. Hummel, *ibid.*, **43**, 267 (1960).