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THERMAL DECOMPOSITION OF ALUMINIUM HYDROXIDES TO ALUMINAS

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ABSTRACT

The thermal decomposition of crystalline and gelatinous aluminium hydroxides to alumina has been investigated by thermogravimetry, differential thermal analysis, x-ray diffraction study and infrared spectrophotometry.

INTRODUCTION

It has been reported by many investigators that the thermal transformation of various aluminium hydroxides yields a number of aluminas being a transition stage in a process leading ultimately to α-alumina (ref.1). The present author has studied the thermal transformation of crystalline (hydrargillite, bayerite, boehmite and diaspore) (refs.1-5) and gelatinous aluminium hydroxides (amorphous and pseudoboehmite) (refs.5-7) to α-alumina. This work is therefore undertaken to obtain further information on the thermal decomposition of aluminium hydroxides to aluminas.

EXPERIMENTAL

Crystralline aluminium hydroxides

Four kinds of hydrated alumina are well known at present: hydrargillite (gibbsite) and bayerite as alumina trihydrates; boehmite and diaspore as alumina monohydrates. In addition one more alumina trihydrate (nordstrandite) has been proposed for hydrated alumina (refs.8,9).

The following materials were used as specimens for hydrargillite and bayerite (refs.1,3,4,10): Hydrargillite-I and II (H-I,II) were precipitated form sodium aluminate solution (molar ratio Na_2O/Al_2O_3 = 1.70 in 3.5 M NaOH) by seeding decomposition with hydrargillite-I and bayerite-II, respectively at 30 °C; Bayerite-I and II (B-I,II) were precipitated from sodium aluminate solutions by interaction with a stream of carbon dioxide with 1 and 4 $dm^3 min^{-1}$, respectively, at 30 °C. The results for the distribution of particle size in specimens H-I,II and B-I,II measured by means of an Andreasen pipette indicated that the particle size becomes smaller in the order B-I, H-I, B-II and H-II. Microscopical examination showed that the particles of H-I and B-I are mostly single ones, while in

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H-II and B-II they are agglomerates of fine particles below 1 μ. Nordstrandite (N) was prepared as follows: amorphous aluminium hydroxide precipitated from aqueous solution of aluminium chloride on addition of sodium hydroxide solution at pH 7.5 was aged in aqueous solution of hexamine (~10 %) for about a month at 50 °C (ref.12). Boehmite (Bö) was prepared hydrothermally from hydrargillite for 2 hr at 200 °C (refs.2,11). Diaspore (D) is a natural deposit in Yonago, Nagano, Japan, containing SiO_2 and Fe_2O_3 in 4.60 and 0.7 %, respectively.

Gelatinous aluminium hydroxides

The following materials were used as specimens for gelatinous aluminium hydroxides: the precipitates from aqueous solutions containing aluminium chloride or nitrate on addition of sodium hydroxide solutions at various pH, from sodium hydroxide solutions by reaction with hydrochloric acid and from aqueous solutions containing aluminium chloride and urea on heating. The resulting gelatinous precipitates consist of amorphous aluminium hydroxide (A), pseudoboehmite (Bo) and intermediate boehmite (Bó) (ref.13), crystallized more than pseudoboehmite, indicating the particular increase in the intensity of x-ray diffraction peak at the plane(200), as indicated in Table 1 which gives the condition of preparation and the crystallographic composition, examined by x-ray diffraction.

TABLE 1
Gelatinous precipitate from aqueous solutions of aluminium on addition of alkalies

Specimen No.	Condition of preparation							Crystallographic composition[a]
	Precipitation					Ageing		
	Aq. soln. of Al	Added alkali	Rate of addition of alkali (ml/min)	Temp. (°C)	pH	Temp. (°C)	Time (hr)	
G1	1 M $AlCl_3$	3 M NaOH	5	25	4.5	25	24	A
G2	1 M $AlCl_3$	3 M NaOH	5	25	6	25	24	A
G3	1 M $AlCl_3$	3 M NaOH	5	25	8	25	24	A
G4	1 M $AlCl_3$	3 M NaOH	5	25	6	—	—	A
G5	1 M $Al(NO_3)_3$	3 M NaOH	5	25	6	25	24	A
G6	$Na[Al(OH)_4]$[b]	3 M HCl	50	25	6	25	24	A
G7	0.1 M $AlCl_3$	0.9 M $(NH_2)_2CO$	—	95	—	95	5	A
G8	1 M $AlCl_3$	3 M NaOH	50	50	9	50	24	Bo
G9	1 M $Al(NO_3)_3$	3 M NaOH	50	50	9	50	24	Bo
G10	$Na[Al(OH)_4]$[b]	3 M HCl	50	70	9	70	1	Bo
G11	0.02 M $AlCl_3$	0.9 M $(NH_2)_2CO$	—	95	—	95	24	Bó

a) A, Bo and Bó represent amorphous aluminium hydroxide, pseudoboehmite and intermediate boehmite, respectively.
b) Molar ratio $[Na_2O]/[Al_2O_3]$ of 1.80 at 3 M NaOH

Instrumental measurements

These materials were examined by TG and DTA, and aluminium hydroxides and their thermally decomposed products by x-ray diffraction and infrared spectrophotometry as described previously (ref.14). The decomposition products were prepared by heating the samples at stated temperature for 2 hr after heating up to the temperature at a rate of 5 °C min^{-1} under atmospheric pressure. The TG and DTA were carried out on an automatic recording thermobalance and DTA apparatus, made by the Agne Research Centre, using platinum-platinum/rhodium thermocouples, and partly a Shinku-Riko Co., Ltd. Model TGD-1500RH-P differential thermobalance, equipped with infrared heater. For the measurement of diiferential thermal electromotive force, α-alumina was uaed as a reference material. The specimen in 100-120 mg was heated at a rate of 5 °C min^{-1} under atmospheric pressure. In the DTA at higher temperature, the material derived from the specimens preheated for 2 hr at the selected temperatures (700 °C for hydrargillite, 600 °C for bayerite, boehmite and intermediate boehmite, 500 °C for pseudoboehmite and 400 °C for amorphous aluminium hydroxide) were weighed in 300-450 mg.

RESULTS AND DISCUSSION

Thermal decomposition of alumina hydrates and thermal transformation of anhydrous alumina to α-alumina

The view (ref.1) has been accepted until quite recently that the hydrated aluminas except diaspore are thermally transformed to stable α-alumina through boehmite and γ-alumina. Recently, however, it was reproted by many observers that thermal transformation of the various hydrated aluminas yields a number of crystalline variations of aluminas which are transition stages in a process leading ultimately to α-alumina (ref.1). From these results it is deduced that these are two essential stages: 1) the formation of virtually anhydrous alumina; 2) the transformation of this product to α-alumina. The thermal decomposition of hydrargillite is of importance because of its industrial production, and it has been studied by many investigators since its thermal transformation is more complicated than that of bayerite, boehmite or diaspore. Many investigators have described the intermediate aluminas designated as χ, γ, δ, δ_1, κ, κ', η, θ, ε and ρ.

Thermal decomposition of alumina trihydrates. The curves of TG and DTA for hydrargillite-I,II and bayerite-I,II are illustrated in Fig.1. Table 2 gives the x-ray results for the thermal decomposition products of the specimens. The infrared spectra show the following absorptions: for hydrargillite, the OH stretching band at 3700-3300 cm^{-1}, the OH bending bands at 1020 and 965 cm^{-1} and the Al-OH broad band centered around 795 and 735 cm^{-1}; for bayerite, the OH stretching band at 3700-3400 cm^{-1}, the OH bending modes at 1020 and 975 cm^{-1}, and the

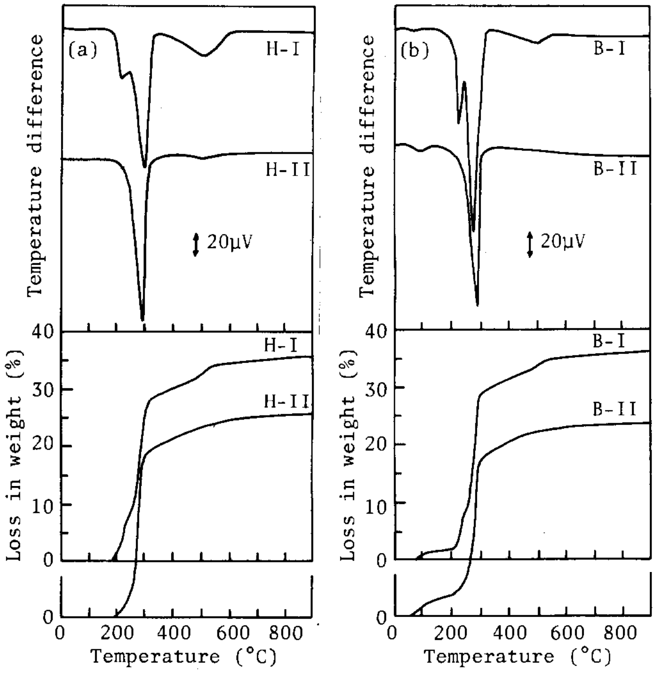

Fig.1. TG and DTA curves of hydrargillite-I, II (H-I,II) and Bayerite-I, II (B-I,II). (a) H-I,II; (b) B-I,II

Al-OH vibration around 770-720 cm^{-1}. These absorption bands disappear completely during dehydroxylation of the specimens (refs.3,4).

Hydrargillite is classified as the types I and II according to the hydration behaviour (Fig.1(a)): The DTA curves exhibit three endothermic reactions at 210, 300 and 510 °C for hydrargillite-I (coarse), and an endothermic one at 295 °C for hydrargillite-II (fine), and these reactions occur at the points near the change of the shape in the TG curve. The weight-loss at 100 °C is in 35.6 % for types I and II, consisting with the theoretical loss in weight of alumina trihydrate. The products at the endothermic peaks in the DTA curves indicate that hydrargillite-I dehydrates to a mixture of boehmite and hydrargillite at 210 °C, of boehmite and λ-alumina at 300 °C, to λ-alumina at 510 °C, and that hydrargillite-II dehydrates directly to λ-alumina at 295 °C. As reported previously (ref. 1), the formation of boehmite during the dehydration depends on the effect of water vapour pressure. When the particles of sample are coarse, the periphery of the particle approximates to the state included by the saturated water vapour, and boehmite is formed on the surface. This phenomenon is not observed with fine particles, in the form of agglomerates. In this case, the structure of boehmite formed during the dehydration is identified with that of boehmite obtained by the hydrothermal treatment, but it appears that the former boehmite is a poor crystallite. Thus, if we denote the boehmite formed during the dehydration of hydrargillite as a boehmite´, the dehydration of hydrargillite is

TABLE 2
X-ray diffraction results of the products derived from aluminium hydroxides heated at various temperatures

Temp. (°C)	Phase detected						
	H-I	H-II	B-I	B-II	N	Bö	D
200	H+Bö	H	B+Bö	B	N	Bö	D
300	Bö+λ	λ	η+Bö	η	η	Bö	D
400	Bö+λ	λ	η+Bö	η	η	Bö	D
500	λ	λ	η	η	η	γ	α+D
600	λ	λ	η	η	η	γ	α
700	λ	λ	η	η	η	γ	α
800	λ	λ	η+θ	η+θ	η+θ	γ	α
900	λ+κ	λ+κ	θ	η+θ	θ+η	δ	α
1000	κ+θ	κ+θ	θ	θ	θ	θ+δ	α
1100	θ+κ+α	κ+θ	θ	θ	θ+(α)[a]	δ+α	α
1200	α+θ	κ+θ+α	α+θ	θ+α	θ+α	α+θ	α
1300	α	α	α	α+θ	α	α	α

a) Parenthesis indicates a small amount.

expressed in the following processes:

Hydrargillite-I → λ-alumina; hydrargillite-II → λ-alumina.
↘ boehmite' ↗

The dehydration behaviour of bayerite resembles that of hydrargillite, and bayerite is also signified as the types I and II (Fig.1(b)). Bayerite-I (coarse) dehydrates to a mixture of boehmite and bayerite at 225 °C, of boehmite and η-alumina at 275 °C, to η-alumina at 505 °C, while bayerite-II (fine) dehydrates directly to η-alumina at 285 °C. At 1000 °C, the weight-losses for type I and II are in 35.9 and 33.6 %, respectively, in agreement with the theoretical value of alumina trihydrate. Hence it is expected that the dehydration process of bayerite is given as follows:

Bayerite-I → η-alumina; bayerite-II → η-alumina
↘ boehmite″ ↗

in which a boehmite″ is designated in comparison with boehmite' for the dehydration process of hydrargillite.

Furthermore the x-ray diffraction results (Table 2) for the products derived from hydrargillite and bayerite, heated at various temperatures, indicate that the thermal transformation of anhydrous alumina to α-alumina proceeds as follows: for hydrargillite-I and II, λ→κ→θ→α; for bayerite-I and II, η→θ→α. Their DTA curves (Fig.2) exhibit the exothermic reactions due to the transformation of θ-alumina to α-alumina at 1290 and 1280 °C for hydrargillite-I and II, respectively, and at 1230 °C for bayerite-I and II.

The thermal transformation of hydrargillite to α-alumina has been studied by many workers. Stumpf *et al* (ref.15) reported that the thermal transformation proceeds through the stages boehmite, χ-, γ-, κ-, θ- and α-alumina. Thibon *et al*

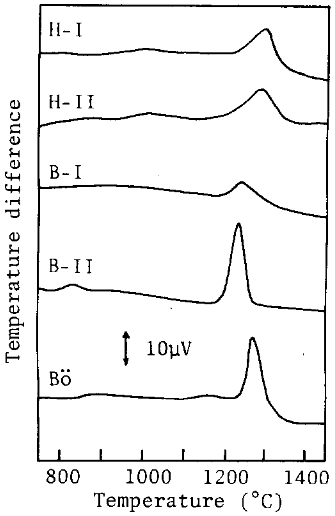

Fig.2. DTA curves of the materials derived from hydrargillite-I,II (H-I,II), bayerite-I,II (B-I,II) and boehmite (Bö), preheated at 700, 600 and 600 °C, respectively.

(ref.16) suggested that the calcination of hydrargillite at successively higher temperatures yields boehmite, κ′-, κ- and α-alumina, although the boehmite is not formed from hydrargillite with a very high specific surface. Prettre *et al* (ref.17) proposed that the course of the thermal decomposition of hydrargillite goes to boehmite, η+κ′-, κ- and α-alumina. According to Alexanian (ref.18), the sequence was boehmite, γ-, δ-, κ- and α-alumina. Glemser *et al* (ref.19), on the other hand, indicated that the thermal transformation of hydrargillite occurs in the sequence boehmite, ε-, κ- and α-alumina. Torkar *et al* (ref.20) maintained that hydrargillite is thermally decomposed via boehmite, χ-, κ- and α-alumina. Further Velisar *et al* (ref.21) proposed the thermal sequence of boehmite, γ-, κ +θ- and α-alumina for hydrargillite.

In contrast, Brown *et al* (ref.22) assumed a dual transformation in the thermal decomposition of hydrargillite, heated successively to higher temperatures or for some hours at certain definite temperatures as represented by the following scheme:

$$\begin{tikzcd}
\text{Hydrargillite} \arrow[r, "300^\circ\text{C}"] \arrow[d, "200^\circ\text{C}"] & \chi\text{-}Al_2O_3 \arrow[r, "800^\circ\text{C}"] & \kappa\text{-}Al_2O_3 \arrow[r, "1000^\circ\text{C}"] & \alpha\text{-}Al_2O_3 \\
\text{boehmite} \arrow[r, "500^\circ\text{C}"] & \gamma\text{-}Al_2O_3 \arrow[r, "800^\circ\text{C}"] & \delta\text{-}Al_2O_3 \arrow[r, "900^\circ\text{C}"] & \theta\text{-}Al_2O_3 \arrow[u, "1000^\circ\text{C}"']
\end{tikzcd}$$

Day *et al* (ref.23) came to an almost simialr conclusion relating to the origin of the two series of anhyrous products. However, they postulated that the boehmite framed in the dehydration of hydrargillite is produced by a second reaction between the original dehydration product, considered as χ-alumina which is highly adsorbent, and the water which is released during the reaction. Later, Ginsberg *et al* (ref.24) obtained a result which is similar to the transformation series presented by Brown *et al* (ref.22). Also Sealfeld (ref.25) concluded that relatively large crystals of hydrargillite follow the sequence boehmite → γ- → θ- → α-alumina under hydrothermal conditions, and additionally the χ- → κ- → α-alumina series during atmospheric heating.

Further the work of De Boer *et al* (ref.26), of Tertian *et al* (ref.27) and of the other workers showed that the thermal reactions of hydrargillite are dependent on many variables, in particular on the crystal size of the hydrargillite. Thibon *et al* (ref.2) found that hydrargillite in the form of fine particles does not dehydrate to boehmite on heating. According to Tertian *et al* (ref.27), the thermal transformation of hydrargillite at normal pressure is as follows: fine hydrargillite dehydrates slowly to α-alumina via the χ- and κ-transformation forms, while coarse hydrargillite dehydrates slowly to α-alumina by two simultaneous routes, via the χ- and κ-forms, and via boehmite and γ-, δ- and θ-alumina. Brindly (ref.28), who used hydrargillite crystals smaller than about 1μ stated that several κ-type structures exist, and that, according to the circumstances, one or other of these may be dominant, but not always the same structure. Goswami *et al* (ref.29) also suggested that the thermal decomposition of hydrargillite proceeds in the sequence boehmite + χ- and κ- + γ-alumina for the well crystalline sample, although the formation of boehmite is not observed for the poor crystalline one. In addition Drobot *et al* (ref.30) suggested the similar heating processes as hydrargillite → γ-alumina → θ- + κ-alumina → α-alumina.
↘ boehmite ↗

On the one hand, the thermal transformation of bayerite to α-alumina has been also studied by a number of workers. Stumpf *et al* (ref.15) reported that the thermal transformation of bayerite proceeds through the stages boehmite, η-. δ-, θ- and α-alumina. Thibon *et al* (ref.16) and Imelik *et al* (ref.31) came to a similar conclusion. Brown *et al* (ref.22) postulated that the η-alumina derived from the thermal decomposition of bayerite should be regarded as an extremely poorly crystalline γ-alumina. Day *et al* (ref.23) suggested that bayerite on calcination yields γ-alumina, from which boehmite is formed only on hydration, and which on further calcination passes through the δ- and θ-forms before finally yielding α-alumina. Trokhimets *et al* (ref.32) also reported the similar result that the formation of boehmite during dehydration arises from the dehydration of amorphous alumina formed at first. Alexanian (ref.18) proposed that the course of the thermal transformation of bayerite goes via γ-, δ-, θ- and α-alumina. According to Tertian *et al* (ref.33), the calcination of bayerite produces successively η-, θ- and α-alumina. Glemser *et al* (ref.19), on the other hand, indicated that the sequence is boehmite-A, η-, θ- and α-alumina.

In this study, however, the author suggests that the dehydration reactions of hydrargillite and bayerite are influenced by the particle size of the samples used, and that hydrargillite-I (coarse) dehydrates to a mixture of boehmite and λ-alumina which goes to α-alumina via κ- and θ-alumina, while

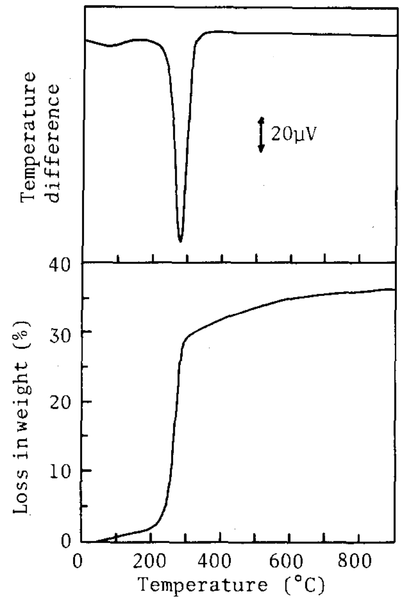

Fig.3. TG and DTA curves of nordstrandite (N)

hydrargillite-II (fine) dehydrates to λ-alumina; bayerite-I (coarse) dehydrates to a mixture of boehmite and η-alumina which proceeds to θ- and α-alumina, while bayerite-II (fine) dehydrates to η-alumina.

For nordstrandite, on the other hand, the curves of TG and DTA, (Fig.3) show an endothermic reaction at 280 °C and the weight-loss of 36.2 % at 1000 °C, respectively. These results resemble that for the type II of bayerite and/or hydrargillite. In contrast, the infrared spectrum reveals the characteristic absorptions due to the OH stretching bands at 3700-3300 (3490, 3410 and 3360) cm^{-1} and the OH bending bands at 1070 and 980 cm^{-1}, which disappear during dehydroxylation. The x-ray diffraction results (Table 2) for the products derived from the specimen on heating at various temperatures give the thermal transformation of nordstrandite to α-alumina via η- and θ-alumina, in agreement with Hauschild's process (ref.12). In addition the DTA curve of the material derived from the preheated specimen reveals an exothermic reaction ascribed to the transformation of θ-alumina to α-alumina at 1260 °C.

It is thus presumed that alumina trihydrates transform thermally to α-alumina as follows:

hydrargillite-I → λ-alumina → κ-alumina → θ-alumina → α-alumina,
↘ boehmite′ ↗
hydrargillite-II → λ-alumina → κ-alumina → θ-alumina → α-alumina,
bayerite-I → η-alumina → θ-alumina → α-alumina,
↘ boehmite″ ↗
bayerite-II → η-alumina → θ-alumina → α-alumina

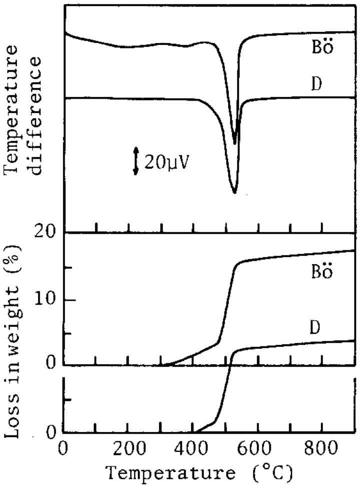

Fig.4. TG and DTA curves of boehmite (Bö) and diaspore (D).

and nordstrandite → η-alumina → θ-alumina → α-alumina.

Thermal decomposition of alumina monohydrates. The curves of TG and DTA of boehmite and diaspore are given in Fig.4. The x-ray results for the thermal decomposition products of the specimens are presented in Table 2. The infrared spectra indicate the following characteristic absorptions: for boehmite, the OH stretching bands at 3260 and 3070 cm^{-1} and the OH bending bands at 1150 and 1060 cm^{-1}; for diaspore, the broad band around 2910 cm^{-1} due to the OH stretching vibration and the OH bending modes at 1065 and 965 cm^{-1}. These bands disappear during dehydroxylation of the specimens (ref.2).

The DTA curve of boehmite exhibits the very weak endothermic reaction at 380 °C and the strong endothermic peak at 520 °C (Fig.4(b)). The losses in weight at 470 and 1000 °C give the values of 2.77 and 17.8 %, respectively. It is thought that the observed weight-loss agrees with the theoretical value of 15 %, if the weight-loss at the first step is regarded as the release of the excess water molecules existing in the hydrogen-bonding layer. The product derived from the endothermic reaction at 520 °C suggests the formation of γ-alumina. The DTA curve of diaspore reveals an endothermic peak at 515 °C, occuring at the point near the change of the shape in the TG curve (Fig.4(b)). The formation of α-alumina is evidently observed in the product derived from the endothermic reaction, indicating that diaspore dehydrates directly to α-alumina.

Moreover the x-ray diffraction results (Table 2) for the products derived from boehmite, heated at various temperatures, suggest that the thermal transformation of anhydrous alumina to α-alumina proceeds in the sequence γ → δ → θ → α. The DTA curve (Fig.2) of the material derived from the preheated specimen exhibits an exothermic reaction attributed to the transformation of θ-alumina to α-alumina at 1265 °C. The similar exothermic reaction, however, is not observed in the DTA curve of diaspore which thermally decomposes directly to α-alumina.

The thermal transformation of boehmite to α-alumina has been studied by many researchers. Stumpf *et al* (ref.15) reported that the thermal transformation of boehmite proceeds in the sequence γ-, δ-, θ- and α-alumina. Later, Day *et al* (ref.23) and Tertin *et al* (ref.33) supported Stumpf's opinion. In contrast, Thibon *et al* (ref.16) suggested that the calcination of boehmite at successively higher temperatures yields η-, θ- and α-alumina. Thereupon Brown *et al* (ref.22) postulated that boehmite decomposes to γ- or η-alumina, depending on the crystallinity of boehmite, and that the η-form may be regarded as an extremely poorly crystalline γ-alumina. Prettere *et al* (refs.17,34), however, proposed that the course of the thermal decomposition of boehmite goes to η-, θ′- (formed in well crystallized boehmite only), θ- and α-alumina. Further Glemser *et al* (ref.19) suggested that the thermal transformation of boehmite occurs in the sequence η-, δ- and α-alumina. According to Stolarek *et al* (ref.35), the formation of δ-alumina derived from boehmite depends on the preparation condition of sample.

For the thermal transformation of diaspore, Stumpf *et al* (ref.15) indicated that diaspore thermally decomposes to α-alumina. Accordingly the results for the thermal decomposition of boehmite and diaspore obtained by Stumpf *et al* fundamentally consist with those by the present author: boehmite dehydrates to γ-alumina proceeding in the sequence δ-, θ- and α-alumina, while diaspore dehydrates directly to α-alumina.

Hence it is concluded that alumina monohydrates transform thermally to α-alumina as follows:

boehmite → γ-alumina → δ-alumina → θ-alumina → α-alumina
and diaspore → α-alumina.

Thermal decomposition of gelatinous aluminium hydroxides

Dehydration of gelatinous aluminium hydroxides. For the specimens of the gelatinous precipitates, the values of the molar ratio $[H_2O]/[Al_2O_3]$, determined by the loss in weight on heating at 110 and 1000 °C, respectively, for 1 hr, and the temperatures at the endothermic and exothermic reactions in the DTA curve are shown in Table 3. The TG and DTA curves of amorphous aluminium hydroxide are illustrated in Fig.5. Table 4 gives the x-ray diffraction results for the thermally decomposed products of samples. The infrared spectra of samples show the following absorption bands: for amorphous aluminium hydroxide, the OH stretching band at about 3500 cm^{-1} and the OH bending band at 1635 cm^{-1}, attributed to the presence of adhesive water, and the broad bands centered around 950 and 650 cm^{-1}; for pseudoboehmite, the intense absorption due to the OH bending band at 1060 cm^{-1} and the broad band centered around 720 cm^{-1}; for intermediate boehmite, the characteristic OH stretching bands of boehmite at 3280 and 3080

TABLE 3
Temperatures of reactions in DTA curves and losses in weight in heating for gelatinous precipitates

Specimen No.	Temp. of reaction in DTA curves a) (°C)				Loss in weight b) (%)		Molar ratio, c) $[H_2O]/[Al_2O_3]$	
	Endo.		Exo.					
	I	II	I	II	110°C	1000°C	110°C	1000°C
G1	130	260	770	1100	20.0	55.3	2.54	7.00
G2	125	260	775	1100	20.2	34.5	2.50	6.67
G3	125	250	775	1130	21.6	52.3	2.57	6.20
G4	125	250	785	1110	21.8	55.9	2.79	7.17
G5	120	175 315	790 855	1090	22.5	60.9	3.26	8.81
G6	120	250	800	1125	27.6	54.3	3.42	6.72
G7	135	175 305	800	1105	27.0	52.5	3.22	6.25
G8	125	440	—	1140	16.0	35.3	1.40	3.09
G9	125	440	—	1140	14.7	35.9	1.29	3.17
G10	140	400	—	1135	16.2	34.0	1.39	2.92
G11	115 d)	450	—	1120	6.5	26.3	0.56	2.02

a) Endo. and Exo. represent the endothermic and exothermic reactions, respectively. b) The values are losses in weight on heating at 110 and 1000 °C, respectively, for 1 hr. c) The value are determined by the weight-losses. d) The values in DTA are amended from those in ref.5.

cm^{-1}, although those bands of pseudoboehmite are covered by the stretching vibration of an adhesive water molecule. These absorption bands disappear completely during dehydration.

The DTA curves of amorphous aluminium hydroxide (Fig.5(b)) exhibit a large endothermic peak at ~130 °C, due to the release of adhesive water, and the very broad endothermic reaction centered around 250-300 °C, resulting from the thermal decomposition of aluminium hydroxide to amorphous alumina, and yet the TG curve shows the gradual weight-loss on heating. From Table 3 it is also seen that the differences of the losses in weight for the specimens of amorphous aluminium hydroxide between 100 and 1000 °C are roughly proportional to the intensities of the endothermic reaction centered around 250-300 °C in the DTA curves (Fig.5(b)). In the DTA curves of pseudoboehmite (Fig.6(b)), an endothermic reaction at ~130 °C, due to the release of adhesive water, and the broad endothermic one at ~450 °C, ascribed to the dehydration of aluminium hydroxide to γ-alumina. For the DTA curve of intermediate boehmite (Fig.6(b)), it seems the relative intensity of two endothermic reactions at 115 and 450 °C, attributed to the presence of adhesive water and dehydration of intermediate boehmite to γ-alumina, respectively, becomes contrary. Those reactions occur at the points near the change of the shape in the TG curve. The interpretation of them is supported

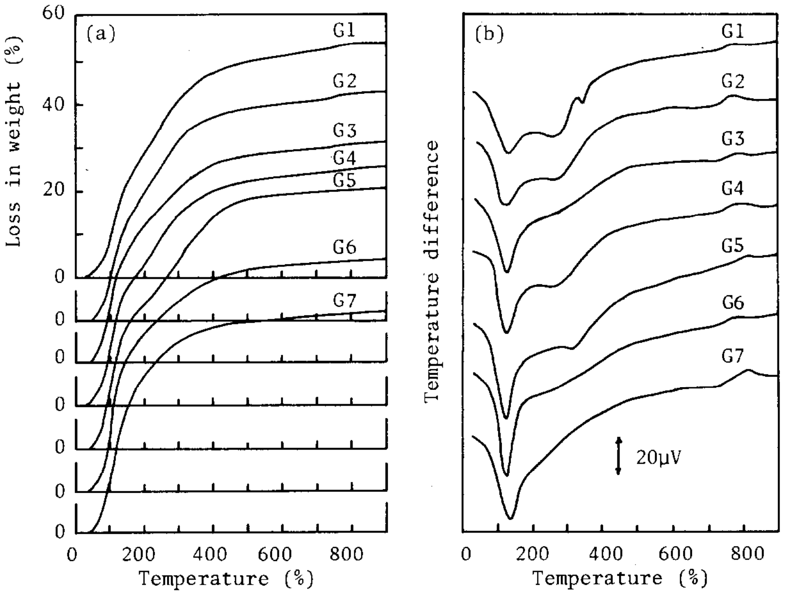

Fig.5. TG and DTA curves of amorphous aluminium hydroxide (figures on curves represent specimen no. in Table 1). (a) TG curve, (b) DTA curve

by the variation in the infrared absorption band of hydroxyl group and in x-ray diffraction pattern caused by the thermal decomposition. In addition, however, when the values of the molar ratio $[H_2O]/[Al_2O_3]$ for the specimens of pseudoboehmite and intermediate boehmite at 110 °C are subtracted from those at 1000 °C, Table 3 suggests that their specimens contain about a half molecule of water more than boehmite (refs.2,3,5,11). Accordingly it is inferred that the release of the excess water molecules existing in the hydrogen-bonding layer occurs in the wide range of temperature between low endothermic reaction and higher one.

Thermal transformation of anhydrous alumina to α-alumina. X-ray diffraction results (Table 4) for anhydrous alumina derived from gelatinous aluminium hydroxides, heated at various temperature, indicate that the thermal transformation of anhydrous alumina to α-alumina proceeds as follows: for anhydrous aluminium hydroxide, amorphous → γ (and/or κ) → θ → α; for pseudoboehmite, γ → (δ) → α; for intermediate boehmite, γ → δ → θ → α. In contrast, the DTA curves (Fig.7) of the materials derived from the preheated specimens exhibit the exothermic reactions due to the transformation of θ-alumina to α-alumina at ~1100 °C for amorphous aluminium hydroxide, and at 1140 °C for pseudoboehmite and at 1120 °C for intermediate boehmite. The temperature of reaction rises in the order of amorphous aluminium hydroxide, pseudoboehmite and intermediate boehmite. In addition the exothermic reactions at 770-800 °C corresponding to the transformation of amorphous alumina to γ-alumina appear in the DTA curves for amorphous aluminium hydroxide, although the low exothermic reactions are not distictly

TABLE 4
X-ray diffraction results for the products derived from gelatinous aluminium hydroxides at various temperatures

Temp. (°C)	Phase detected[a]										
	G1[b]	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11
200	A	A	A	A	A	A	A	Bo	Bo	Bo	Bó
300	Am	Am	Am	Am	Am	Am	Am	Bo	Bo	Bo	Bó
400	Am	Am	Am	Am	Am	Am	Am	γ	γ	γ	γ+Bó
500	Am	Am	Am	Am	Am	Am	Am	γ	γ	γ	γ
600	Am	Am	Am	Am	Am	Am	Am	γ	γ	γ	γ
700	κ+γ	Am	Am+(γ)[c]	Am	Am	Am+(γ)	Am	γ	γ	γ	γ+(δ)
800	κ+γ	γ +(κ)	γ	γ	γ	γ	γ	γ+(δ)	γ	γ	γ+δ
900	κ+(γ)	γ+κ	γ+(κ)	γ	γ	γ	γ	γ+(δ)	γ+δ	γ+δ	δ+(γ)
950	κ+(γ)	γ+κ	γ+(κ)	γ+(κ)	γ	γ	γ	δ	δ+(θ)	δ	δ+(θ)
1000	κ+α+θ	κ+θ+α	γ+κ+θ	θ+θ+α	γ+α+(θ)	γ+(θ)	γ+α+(θ)	δ+(θ)	δ+(θ)	δ+(θ)	δ+θ
1050	α+(θ)	α	θ+κ+α	α	α+(θ)	θ+α	α+(θ)	θ+δ+α	δ+θ+α	δ+θ+α	θ+α
1100	α	α	α	α	α	α	α	α	α+(θ)	α	θ
1200	α	α	α	α	α	α	α	α	α	α	α+θ
1300	α	α	α	α	α	α	α	α	α	α	α

a) A, Bo, Bó and Am represent amorphous aluminium hydroxide, pseudoboehmite, intermediate boehmite and amorphous alumina, respectively.
b) Specimen no. in Table 1.
c) Parenthesis indicates a small amount.

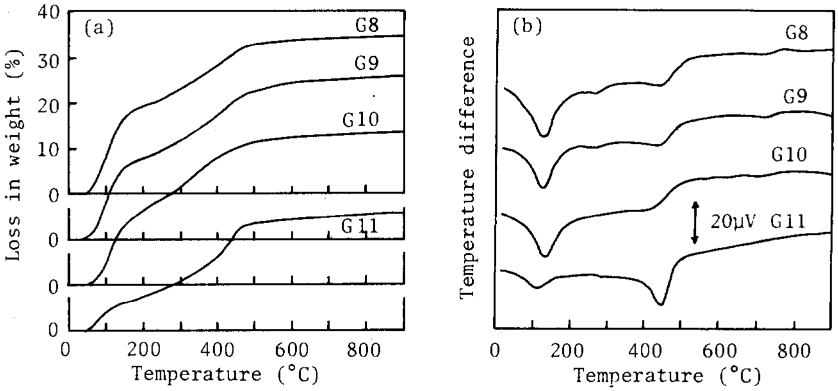

Fig.6. TG and DTA curves of pseudoboehmite and intermediate boehmite (figures on curves represent specimen no. in Table 1). (a) TG curve, (b) DTA curve

observed in the DTA curves of pseudoboehmite and intermediate boehmite. In these processes, it is inferred that the exothermic reactions ascribed to the transformation from γ-alumina to θ-alumina will be masked by that from θ-alumina to α-alumina. For the cases of pseudoboehmite and intermediate boehmite, however, the exothermic reactions due to the transformation from γ-alumina to δ- and θ-alumina are observed as the broad shoulders at 1050 and 1000 °C, respectively.

In previous papers (refs.5,6), it has been reported that the transformations to α-alumina of anhydrous alumina by the thermal decomposition of amorphous aluminium hydroxide and pseudoboehmite proceed in the sequences of amorphous → γ → θ → α and γ → θ → α, respectively. In this study, however, if we extend the condition of the preparation of gelatinous aluminium hydroxide, it is found that there are the following phenomena under certain circumstances: amorphous aluminium hydroxide decomposes thermally via κ-alumina to α-alumina; γ-alumina derived from pseudoboehmite proceeds to θ- and α-alumina via δ-alumina. From this it is deduced that gelatinous aluminium hydroxides transform thermally to α-alumina as follows:

Amorphous aluminium hydroxide → amorphous alumina → γ-alumina
(and/or κ-alumina) → θ-alumina → α-alumina,
pseudoboehmite → γ-alumina → (δ-alumina) → θ-alumina → α-alumina
and intermediate boehmite → γ-alumina → δ-alumina → θ-alumina → α-alumina.

It is thought that the presence of κ-alumina in the decomposition process of amorphous aluminium hydroxide which goes to hydrargillite by ageing in mother liquor might be in relation to the thermal transformation of hydrargillite (refs. 4,5). Futher it seems that the transformation process to α-alumina of pseudoboehmite via γ- and θ-alumina approaches to that of boehmite via γ-, δ- and θ-alumina (refs.2,5).

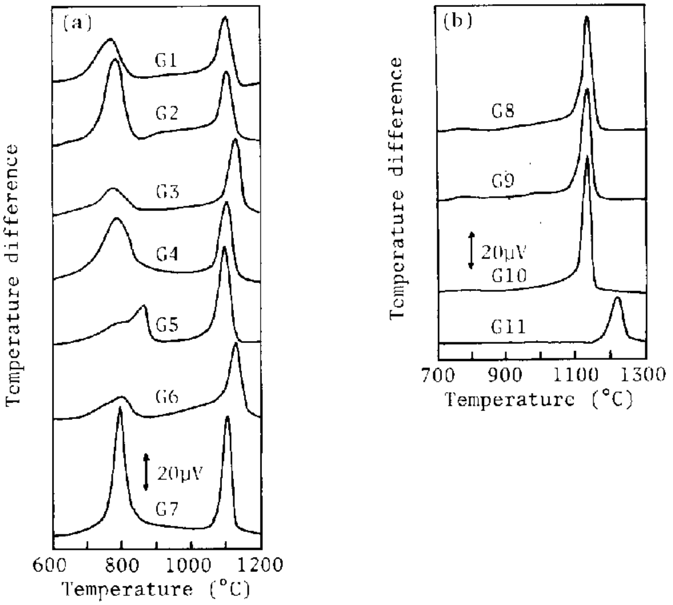

Fig.7. DTA curves of the materials derived from amorphous aluminium hydroxide, pseudoboehmite and intermediate boehmite (figures on curves represent specimen no. in Table 1). (a) Amorphous aluminium (b) pseudoboehmite and intermediate boehmite

Formation of anhydrous alumina by thermal decomposition of aluminium salts

The formation of anhydrous alumina by the thermal decomposition of aluminium salts such as hydrates of chloride, nitrate and sulphate of aluminium, lactate, citrate and tartrate of aluminium and formate and acetate of basic aluminium (refs.14,36,37) was examined in comparison with the thermal transformation processes of aluminium hydroxides to α-alumina. As a result, it was found that amorphous alumina which goes to γ-, δ-, θ- and α-alumina is at first formed by the thermal decomposition of all aluminium satls. In addition the following exothermic reactions due to the transformation of amorphous alumina to γ-alumina and of θ-alumina to α-alumina are observed in the DTA curves of the materials derived from the preheated specimens of those salts: at 800 and 1140 °C for chloride, 820 and 1060 °C for nitrate, 1245 °C for sulphate, 1230 °C for alum, 830 and 1050 °C for lactate, 940 and 1180 °C for citrate, 900 and 1080 °C for tartrate, 820 and 1080 °C for formate, and 830 and 1280 °C for acetate, although the transformation of amorphous alumina to γ-alumina is indistinct for sulphate and alum. As these transformation behaviours resemble the cases of gelatinous aluminium hydroxide, it is expected that the compositions of anhydrous aluminas formed by the thermal decomposition of aluminium salts are little different from those derived from gelatinous aluminium hydroxides.

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