

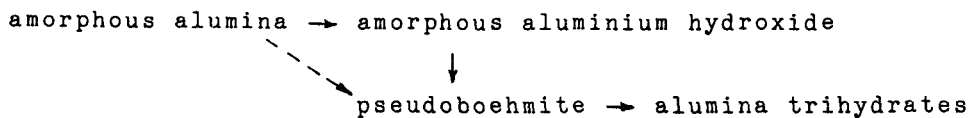
## HYDRATION OF ALUMINAS

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## ABSTRACT

The hydration of amorphous and crystalline aluminas has been investigated by keeping them in water at the temperatures from 30 at 95°C. In the hydration of amorphous alumina at low temperatures, amorphous aluminium hydroxide or pseudoboehmite is formed initially and followed by alumina trihydrates such as bayerite, and hydrargillite and/or nordstrandite. The trihydrates appear after about ten days and the amounts formed increase gradually according to the period of keeping in water. By raising the temperature, the rate of hydration is promoted, and pseudoboehmite is formed at first and then bayerite and subsequently nordstrandite. Accordingly the hydration of amorphous alumina proceeds in the following sequence:



Negligible hydration of crystalline aluminas occurs when they are kept in contact with water at 30°C, but  $\eta$ - and  $\gamma$ - aluminas are hy-

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drated to alumina trihydrates and pseudoboehmite, respectively, by raising the temperature of keeping in water.

## INTRODUCTION

Oxidation films are formed on the surface of aluminium metal under different conditions: e.g., when aluminium is heated at 400 °C in air, a very thin film which consists of amorphous alumina is formed on the surface of aluminium [1]; when aluminium foil is burnt for a short time in oxygen, amorphous alumina is formed [2]. As those oxidized films always contact with wetted air, the change in their composition on standing affects the property of aluminium metal. Thus the study of the hydration phenomena of aluminium oxides is an important subject in relation to the application of functional films of aluminium formed by electrolysis, etc. However, since the hydration phenomena of aluminium have relations with the ageing phenomena of aluminium hydroxide, a number of researchers have investigated those problems. The present author has studied the ageing of aluminium hydroxide in water and alkaline solution [3-6]. In addition, as alumina has many applications as an absorbent and as a catalyst by means of its superior absorptive ability, it is necessary to elucidate the hydration phenomena of aluminas from this aspect. Accordingly some researches have been made on the hydration of alumina [7-10], but they do not always obtain systematic results. Therefore the present paper reports the results for the investigation on the hydration of amorphous and crystalline aluminas.

## EXPERIMENTAL

### Preparation of samples

Some amorphous and crystalline aluminas prepared under various conditions were used as samples.

#### 1) Amorphous alumina

Five specimens of amorphous aluminium hydroxide (designated as A) were prepared as indicated in Table 1. The aqueous solution of sodium hydroxide in  $3 \text{ mol dm}^{-3}$  was added slowly at the rate of  $5 \text{ cm}^3 \text{ min}^{-1}$  to an aqueous solution of aluminium chloride,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , in  $1 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ ; specimens  $A_1$ ,  $A_2$  and  $A_3$  were prepared by varying the amount of alkali added to precipitate the aluminium in aqueous solution of pH values of 4.5, 6.0 and 8.0, respectively; the resulting precipitates were aged for 24 h at  $25^\circ\text{C}$  [4]. By a similar procedure, specimen  $A_4$  was formed from an aqueous solution of aluminium nitrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , at pH 6.0 [4]. Specimen  $A_5$  was obtained from a mixed aqueous solution of  $0.1 \text{ mol dm}^{-3}$  aluminium chloride and  $0.9 \text{ mol dm}^{-3}$  urea on heating for 5 h at  $95^\circ\text{C}$  [11]. All resulting precipitates were centrifuged and washed with distilled water as free as possible from alkali and anions, and then dried with acetone.

The samples of amorphous alumina (designated as  $\text{Am}_1$ ,  $\text{Am}_2$ ,  $\text{Am}_3$ ,  $\text{Am}_4$  and  $\text{Am}_5$ ) were prepared by heating the specimens of amorphous hydroxide at  $400^\circ\text{C}$  for 2 h after heating to this temperature at a rate of  $5^\circ\text{C min}^{-1}$  under atmospheric pressure [12]. Similarly the samples were also prepared by heating at  $600^\circ\text{C}$ . In these cases, the amount of the sample of amorphous alumina obtained according to the procedures mentioned above is about 30 g for each experimental treatment.

Table 1 The specimens of amorphous aluminium hydroxide used as starting material for amorphous alumina\*

Specimen No.	Conditions of precipitation					Ageing	
	Aluminium salt	Alkali	Rate of addition of alkali, $\text{cm}^3 \text{min}^{-1}$	Temp., $^{\circ}\text{C}$	pH	Temp., $^{\circ}\text{C}$	Period, h
A <sub>1</sub>	1 mol dm <sup>-3</sup> AlCl <sub>3</sub>	3 mol dm <sup>-3</sup> NaOH	5	25	4.5	25	24
A <sub>2</sub>	"	⚡	⚡	⚡	6.0	⚡	⚡
A <sub>3</sub>	"	⚡	⚡	⚡	8.0	⚡	⚡
A <sub>4</sub>	1 mol dm <sup>-3</sup> Al(NO <sub>3</sub> ) <sub>3</sub>	⚡	⚡	⚡	6.0	⚡	⚡
A <sub>5</sub>	0.1 mol dm <sup>-3</sup> AlCl <sub>3</sub>	0.9 mol dm <sup>-3</sup> urea	—	95	—	95	3

\* Amorphous aluminas Am<sub>1</sub>, Am<sub>2</sub>, Am<sub>3</sub>, Am<sub>4</sub> and Am<sub>5</sub> are prepared by heating of these specimens A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub> and A<sub>5</sub>, respectively.

## 2) Crystalline alumina

Two kinds of aluminas ( $\gamma$  and  $\eta$ ) were used as the samples of crystalline aluminas. The preparation of  $\gamma$ -alumina was carried out by heating the specimen  $A_1$  of amorphous aluminium hydroxide at 800°C for 2 h [12-15]. The sample of  $\eta$ -alumina was prepared by heating a specimen of bayerite-II [15-18], precipitated from aqueous sodium aluminate solutions by reaction with  $\text{CO}_2$  gas, for 2 h at 600°C. The amount of the sample of crystalline aluminas prepared according to these procedures was about 10 g for each experimental treatment.

### Procedure of hydration

After sample (0.5 g) and deionised and distilled water (50  $\text{cm}^3$ ) in 50  $\text{cm}^3$  stoppered conical flask were shaken to disperse sufficiently, the flask was settled in a thermostatted water bath for a selected time at 30, 50, 70 and 95°C. The sample kept in water for a selected time was filtered and dried in air, and the pH value and the amount of aluminium dissolved were checked for the filtrate. The concentration of aluminium was determined by titration with EDTA using xylenol orange (OX) as indicator [19].

The resulting materials were examined by thermogravimetry and differential thermal analysis (TG and DTA), X-ray diffraction study and infrared (IR) spectrophotometry [20]. The TG and DTA were carried out under atmospheric pressure at a heating rate of  $5^\circ\text{C min}^{-1}$  on an automatic recording thermobalance and DTA apparatus, made by the Agne Research Centre, using platinum-platinum/rhodium thermocouples. For the measurement of differential thermal electromotive force,  $\alpha$ -alumina was used as a reference material. X-ray powder

diffraction diagrams were obtained on a Geigerflex recording X-ray diffractometer with filtered copper radiation. IR spectra were recorded on Japan Spectroscopic Co., Ltd. models IRA-1 (4000-650  $\text{cm}^{-1}$ ) and IR-F (700-200  $\text{cm}^{-1}$ ) grating spectrophotometers.

## RESULTS AND DISCUSSION

### Hydration of amorphous alumina in the vicinity of room temperature

The samples of  $\text{Am}_1$  -  $\text{Am}_5$  of amorphous alumina were little changed after storage for six months under a water-saturated atmosphere at room temperature  $\sim 25^\circ\text{C}$ .

When the samples were kept in water at  $30^\circ\text{C}$ , it was found that the hydration of amorphous alumina occurs in a relatively short period. The changes in the composition of amorphous alumina by keeping in water are illustrated in Table 2, and some representative X-ray diffraction diagrams are shown in Fig.1. This shows that after a day amorphous alumina transforms to partly amorphous aluminium hydroxide and/or pseudoboehmite. Although the formation of amorphous aluminium hydroxide is anticipated from the X-ray diffraction diagrams, it is evident from the TG result that not all of the amorphous alumina is hydrated to amorphous aluminium hydroxide. The weight-losses at  $700^\circ\text{C}$  for the products derived from the keeping in water for a day reveal about 45 % (maximum) for the specimen of  $\text{Am}_5$  and 20 - 30 % for the other samples, while that for amorphous aluminium hydroxide is between 50 - 55 %. All of the samples (except  $\text{Am}_1$ ) form pseudoboehmite after keeping in water for five days, and the amount formed increases initially, but subsequently decreases or becomes constant when the keeping period is extended beyond five days. The formation of alumina trihydrate is observed after immer-

Table 2 Change in the composition of amorphous alumina by dipping in water at different temperatures

Specimen No.	Temp. °C	Dipping period, day							
		1	2	3	5	10	20	50	100
Am <sub>1</sub>	30	Am, A	Am, A	Am, A	Am, A	A, T	A, T	H <sup>2+</sup> , A	H <sup>2+</sup> , N <sup>±</sup>
	50	A, Bo <sup>±</sup>	A, Bo <sup>±</sup>	A, Bo <sup>±</sup>	A, Bo <sup>±</sup>	Bo <sup>+</sup> , A	Bo <sup>+</sup> , H <sup>+</sup> , N <sup>±</sup>	Bo <sup>+</sup> , N <sup>2+</sup> , H <sup>+</sup>	N <sup>2+</sup> , H <sup>+</sup> , Bo <sup>+</sup>
	70	Bo <sup>+</sup>	Bo <sup>+</sup>	Bo <sup>2+</sup> , T	Bo <sup>2+</sup> , T	Bo <sup>2+</sup> , T	Bo <sup>2+</sup> , N <sup>+</sup>	Bo <sup>2+</sup> , N <sup>+</sup>	Bo <sup>2+</sup> , N <sup>2+</sup>
Am <sub>2</sub>	30	Am, A	A, Am	A, Bo <sup>±</sup> , Am	A, Bo <sup>+</sup> , T	Bo <sup>+</sup> , T	Bo <sup>+</sup> , H <sup>+</sup> , B <sup>±</sup>	H <sup>+</sup> , B <sup>±</sup> , Bo <sup>+</sup>	H <sup>+</sup> , B <sup>±</sup> , N <sup>±</sup> , Bo <sup>+</sup>
	50	Bo <sup>+</sup> , A, Am	Bo <sup>+</sup> , A	Bo <sup>+</sup> , A	Bo <sup>+</sup> , T	Bo <sup>+</sup> , T	Bo <sup>+</sup> , T	Bo <sup>+</sup> , N <sup>2+</sup> , B <sup>+</sup>	Bo <sup>+</sup> , N <sup>2+</sup> , B <sup>+</sup>
	70	Bo <sup>+</sup>	Bo <sup>+</sup>	Bo <sup>+</sup>	B <sup>2+</sup> , T	Bo <sup>2+</sup> , T	Bo <sup>2+</sup> , N <sup>+</sup> , B <sup>±</sup>	Bo <sup>2+</sup> , N <sup>+</sup> , B <sup>±</sup>	Bo <sup>2+</sup> , N <sup>2+</sup> , B <sup>±</sup>
Am <sub>3</sub>	30	A, Am, Bo <sup>+</sup>	Bo <sup>+</sup> , A, T	Bo <sup>+</sup> , A, T	Bo <sup>+</sup> , T	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>
	50	Bo <sup>+</sup> , A	Bo <sup>+</sup> , T	Bo <sup>+</sup> , T	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup> , N <sup>±</sup>	Bo <sup>+</sup> , B <sup>2+</sup> , N <sup>±</sup>	Bo <sup>+</sup> , B <sup>2+</sup> , N <sup>±</sup>
	70	Bo <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup> , N <sup>±</sup>	Bo <sup>2+</sup> , B <sup>2+</sup> , N <sup>±</sup>	Bo <sup>2+</sup> , B <sup>2+</sup> , N <sup>±</sup>	Bo <sup>2+</sup> , B <sup>2+</sup> , N <sup>±</sup>
Am <sub>4</sub>	30	A, Am	A, Bo <sup>±</sup> , T	A, Bo <sup>±</sup> , T	A, Bo <sup>+</sup> , B <sup>+</sup> , H <sup>±</sup>	Bo <sup>+</sup> , A, B <sup>+</sup> , H <sup>±</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>
	50	Bo <sup>+</sup> , A	Bo <sup>+</sup>	Bo <sup>+</sup>	Bo <sup>+</sup> , T	Bo <sup>+</sup> , B <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , N <sup>±</sup>
	70	Bo <sup>+</sup>	Bo <sup>2+</sup> , T	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup> , N <sup>±</sup>	Bo <sup>2+</sup> , B <sup>+</sup> , N <sup>±</sup>	Bo <sup>2+</sup> , B <sup>+</sup> , N <sup>±</sup>
Am <sub>5</sub>	30	A, Bo <sup>±</sup>	Bo <sup>+</sup> , T	Bo <sup>+</sup> , T	Bo <sup>+</sup> , B <sup>±</sup> , H <sup>±</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , H <sup>+</sup>	B <sup>+</sup> , H <sup>+</sup> , Bo <sup>+</sup>
	50	Bo <sup>+</sup>	Bo <sup>+</sup>	Bo <sup>+</sup>	Bo <sup>+</sup>	Bo <sup>+</sup> , T	Bo <sup>+</sup> , B <sup>+</sup>	Bo <sup>2+</sup> , B <sup>+</sup>	Bo <sup>+</sup> , B <sup>+</sup> , N <sup>+</sup>
	70	Bo <sup>+</sup>	Bo <sup>2+</sup>	Bo <sup>2+</sup>	Bo <sup>2+</sup>	Bo <sup>2+</sup>	Bo <sup>2+</sup>	Bo <sup>2+</sup> , T	Bo <sup>2+</sup> , N <sup>±</sup>

\* Am = amorphous alumina, A = amorphous aluminum hydroxide, Bo = pseudoboehmite, B = bayerit, N = nordstrandite, H = hydrargillite, T = alumina trihydrate ( B or N or H ) ; The amount of aluminum hydroxide increases in the order of superscripts ±, +, 2+, and 3+.

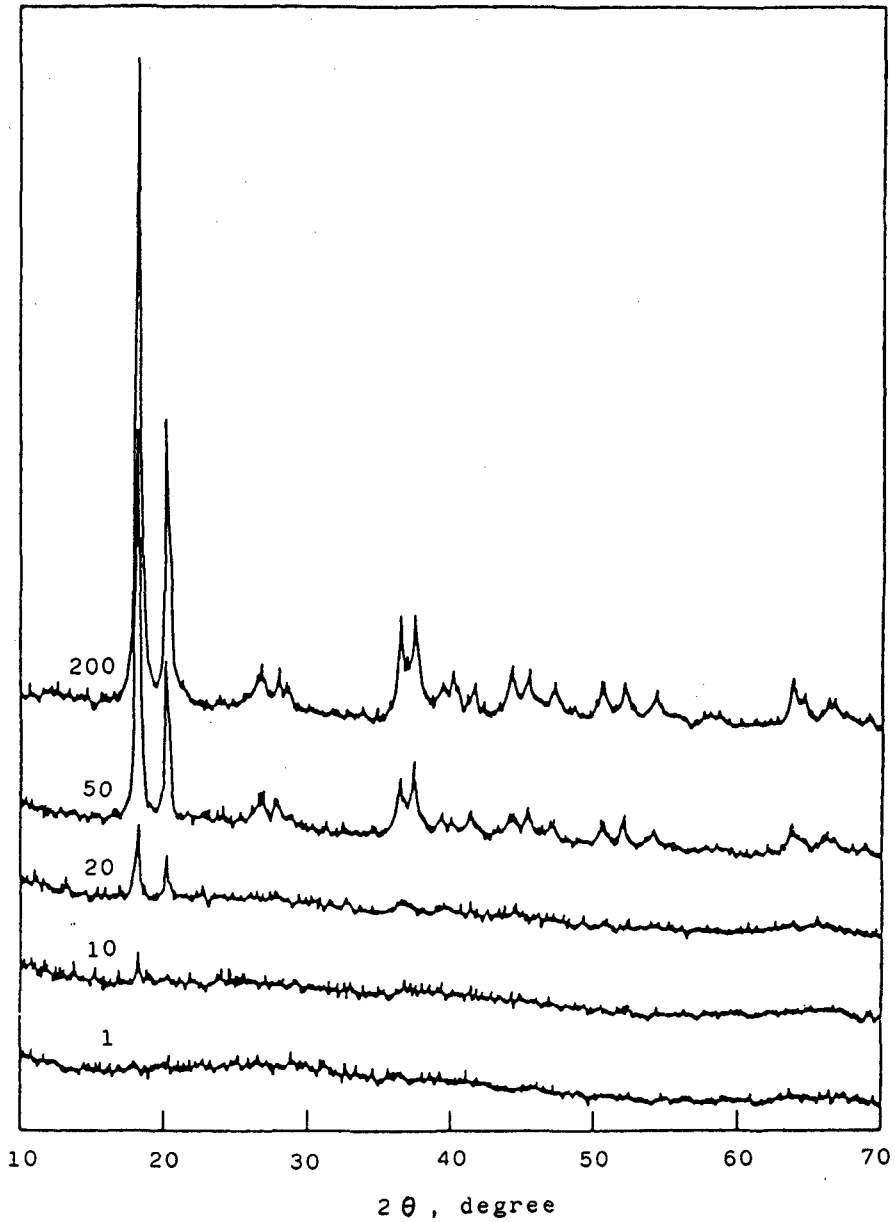


Fig. 1 X-ray diffraction diagrams for amorphous alumina dipped in water at 30°C (Specimen Am<sub>1</sub>, numerals on curves are dipping periods, day).



sion for ten days, and the amount formed increases with longer periods of keeping. The composition of alumina trihydrate consists of bayerite, hydrargillite and nordstrandite [21] and their formation occurs in this order, although most of the samples form a mixture of bayerite and hydrargillite. In the sample of Am<sub>1</sub> which only forms hydrargillite, the amount of alumina trihydrate contained in the product derived from the keeping in water for 200 days attains a value of 52 %, as indicated by the weight-loss at 250 - 300°C where the change in the TG curve is evident. Also the amount of pseudoboehmite contained in the product can be estimated from the weight-loss at 300 - 450°C where the change in the TG curve is evident. From the total content ratio of alumina trihydrate and pseudoboehmite, therefore, it is found that the samples of Am<sub>2</sub> - Am<sub>5</sub> form alumina trihydrate and pseudoboehmite of at least 70 %. Some representative results for the thermal analysis of the products derived from the sample of Am<sub>1</sub> in water at 30°C are given in Fig.2. In the DTA curve, the broad endothermic reaction at ~130°C is due to the release of adhesive water and the sharp endothermic peak at 275 or 295°C arises from the dehydration of alumina trihydrate to alumina [13, 15, 16]. The products derived from the sample of Am<sub>1</sub> in water for over 10 days form amorphous aluminium hydroxide and exhibit the endotherm at ~100°C resulting from the release of adhesive water. The composition of alumina trihydrate contained in the product derived from the sample of Am<sub>1</sub> in water is regarded to consist of hydrargillite only according to the X-ray diffraction diagram (Fig.1), but the endothermic reaction of nordstrandite at 270°C is accompanied by that of hydrargillite at 295°C.

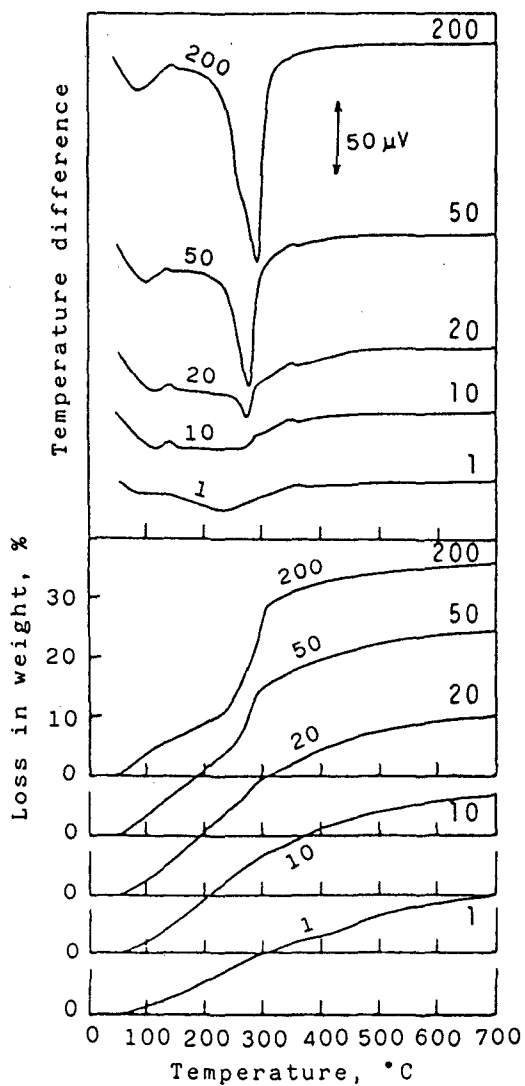


Fig. 2 TGA and DTA curves for amorphous alumina dipped in water at 30°C (Specimen  $Am_1$ , numerals on curves are dipping periods, day).

Hydration of amorphous alumina with increasing temperature

The hydration of all samples is promoted by raising the temperature of their keeping in water. Some representative X-ray diffraction diagrams of the products derived from the sample of Am<sub>1</sub> in water at 70°C are indicated in Fig.3. At 70°C most of the samples form mainly pseudoboehmite after a day in water (Table 2). In this case, it is deduced from the difference of the weight-loss of TG curve between 110 and 700°C that the reaction of hydration is completed in a day (Fig.4). By raising the temperature of keeping in water, the amount of pseudoboehmite formed increases, and in addition the alumina trihydrate formed consists largely of bayerite and nordstrandite. The formation of hydrargillite is observed in the products derived from hydration at 30°C, but is not found in the products at 70°C with exception of sample Am<sub>1</sub>. This is supposed to be related to the transformation from bayerite to hydrargillite in water or alkaline solutions [3]. Also the formation of nordstrandite occurs with increase in temperature from 50 to 70°C. This is elucidated from the thermal analysis results for the products derived from the sample of Am<sub>1</sub> by the keeping in water at 70°C (Fig.4).

In most of the samples, the amount of pseudoboehmite formed in water increases for a period of 20 days at 50°C and of 10 days at 70°C and then becomes constant. Additionally it is considered that the crystalline state of pseudoboehmite formed in water at 70°C is more complete than that precipitated by the reaction between aluminium salt and alkali at room temperature [9].

The amount of alumina trihydrate formed increases according

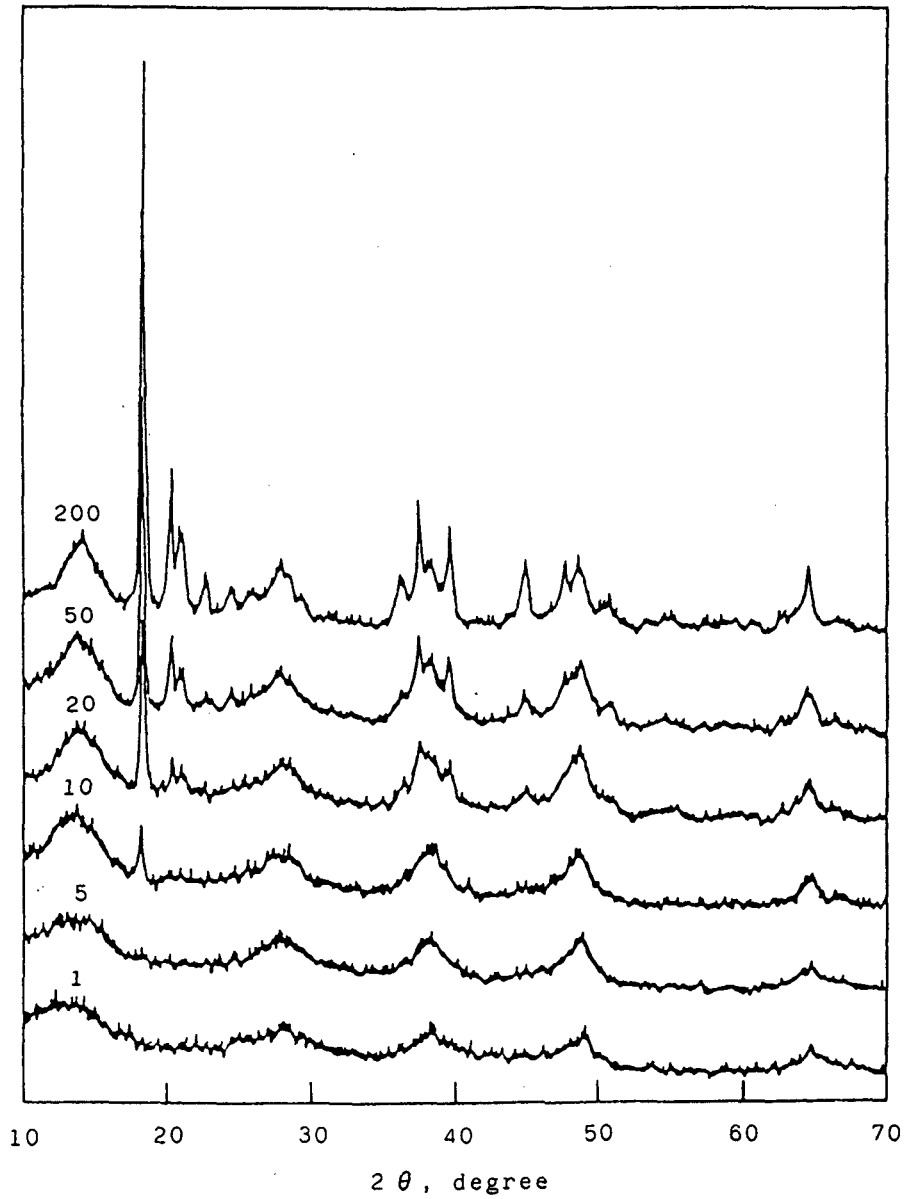


Fig. 3 X-ray diffraction diagrams for amorphous alumina dipped in water at 70°C (Specimen Am<sub>1</sub>, numerals on curves are dipping periods, day).

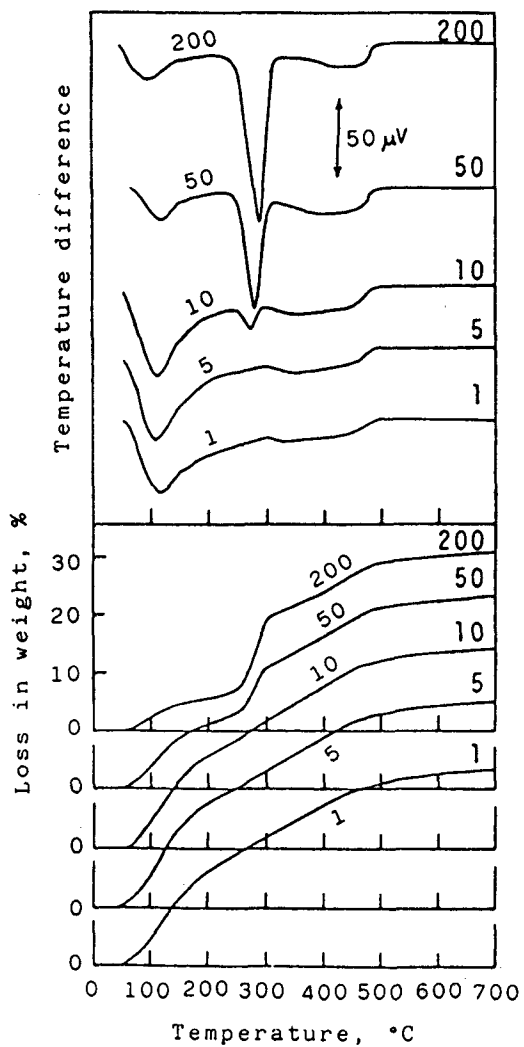


Fig. 4 TGA and DTA curves for amorphous alumina dipped in water at 70°C (Specimen  $A_{m1}$ , numerals on curves are dipping periods, day).

to the decrease in the amount of pseudoboehmite formed. As the total ratio of pseudoboehmite and alumina trihydrate contained in the product derived from hydration in water attains a nearly constant value of 60 - 70 % at the time in which alumina trihydrate appears, it is inferred that the pseudoboehmite transforms to alumina trihydrate. The X-ray diffraction data of the product derived from the sample of Am<sub>1</sub> after 200 days in water at 70°C is presented, in Table 3, and the IR spectra of the products derived from the sample of Am<sub>2</sub> in water at 50°C are given in Fig.5. The latter shows the OH stretching band at 3700 - 3300 cm<sup>-1</sup> and the OH bending band at 1100 - 880 cm<sup>-1</sup>, which are the characteristic absorptions for nordstrandite [21].

#### Hydration behaviour of amorphous alumina

Since the weight-loss of TG curves of the products derived from the samples (except Am<sub>5</sub>) by the keeping in water at 30°C increases with time until a constant value ~30 % is attained (32% after a day in the case of Am<sub>5</sub>), it is seen that the reaction of hydration proceeds gradually. In comparison with the results in Table 2, it is evident that the samples of amorphous alumina except Am<sub>1</sub> hydrate relatively shortly to amorphous aluminium hydroxide and then form pseudoboehmite and alumina trihydrate. When the samples are kept in water at the temperatures greater than 30°C, the difference of the weight-loss between 110 and 700°C increases in the products kept for 20 days in water at 50°C and attains to a constant value of 29 - 30 % (except Am<sub>5</sub> as well as the case at 30°C). At 70°C, however, after a day the weight-loss attains a value of 26 - 28 % and then decreases gradually with time. As the total ratio of

Table 3 X-ray diffraction data for the interplanar spacings and relative line intensities of alumina trihydrates and the product derived from the sample of Am<sub>1</sub> by the dipping for 200 days in water at 70°C

Hydrargillite		Bayerite		Nordstrandite <sup>2)</sup>		This work	
d(A)	I <sup>1)</sup>	d(A)	I <sup>1)</sup>	d(A)	I	d(A)	I
4.22	100	4.72	100	4.790	100	4.81	100
4.34	40	4.36	70	4.330	25	4.37	19
4.30	20			4.220	25	4.22	6
				4.162	20		
				3.896	15	3.91	3
				3.604	8	3.62	1
3.35	10			3.446	8	3.40	1
3.31	6					3.32	2
3.17	8	3.19	25			3.20	2
3.08	4	3.08	1	3.022	13	3.07	1
		2.69	3	2.867	5	2.86	1
				2.481	15		
2.44	15	2.45	3	2.454	10	2.46	6
2.42	4						
2.37	20	2.34	6	2.393	35	2.39	12
2.28	4	2.28	3	2.265	35	2.27	7
2.23	6	2.21	67			2.24	2
2.15	8	2.14	3			2.16	2
2.03	12	2.06	2			2.05	3
1.98	10	1.97	3	2.015	30	2.00	5
1.95	2	1.91	1	1.904	20	1.907	4
1.90	7	1.83	1	1.781	15	1.794	3
1.79	10	1.76	1			1.749	2
1.74	9	1.71	26				
1.67	9	1.68	2			1.685	2
1.65	3	1.64	1			1.657	1
1.63	1						
1.58	3	1.59	4	1.595	8	1.58	1
1.57	1	1.56	2				
1.55	2	1.55	4				
		1.52	1	1.513	10	1.51	—
		1.48	1				
		1.47	1	1.478	10	1.474	1
		1.45	7			1.455	2
				1.440	18	1.443	4
				1.431	6	1.433	2
				1.403	8	1.405	1
				1.388	8	1.358	—

1) These values are obtained from the height of diffraction peaks.

2) H.Saalfeld and B.B.Mehrotra, Naturwissenschaften, 53, 128 (1966).

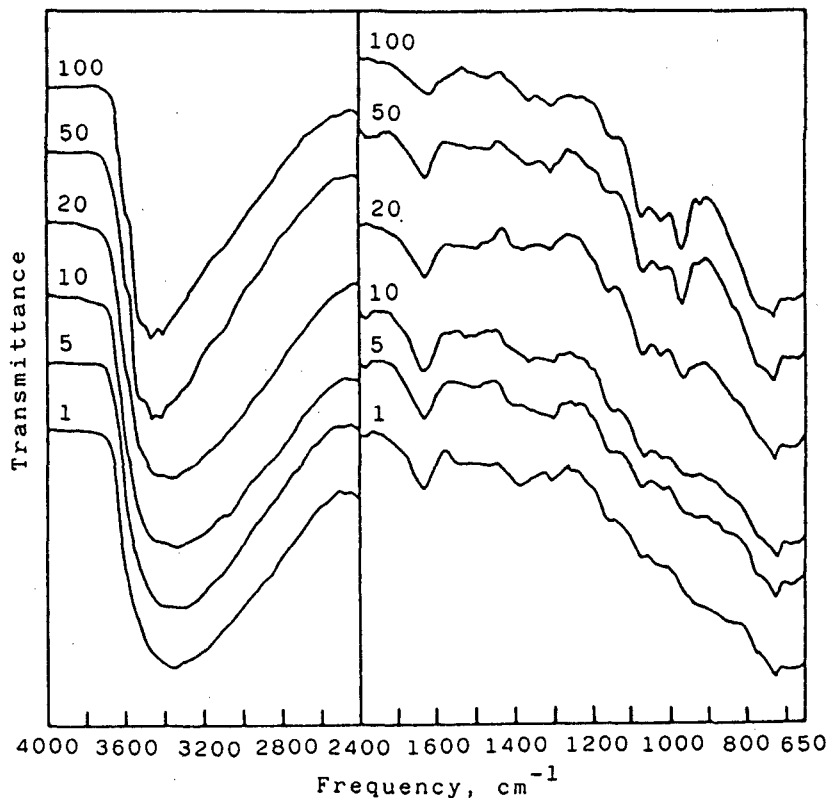
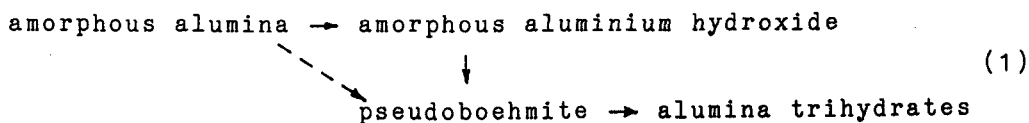


Fig. 5 Infrared spectra for amorphous alumina dipped in water at 50°C (Specimen Am<sub>2</sub>, numerals on curves are dipping periods, day).

pseudoboehmite and alumina trihydrate contained in the products derived from the keeping in water, in which the difference of the weight-loss between 110 and 700°C becomes nearly constant, is estimated to be 60 - 70 %, it is expected that pseudoboehmite is quantitatively crystallized to alumina trihydrate. Hence it is presumed that the hydration of amorphous alumina proceeds in the following sequence:





Here it is supposed that the transformation from amorphous alumina to aluminium hydroxide in water is due to the direct hydration of amorphous alumina in solid phase. Because the concentrations of aluminium dissolved during the keeping in water of the samples, Am<sub>1</sub> - Am<sub>5</sub>, are  $10^{-4}$  -  $10^{-3}$  mol dm<sup>-3</sup> and their solutions are in the weak acidic regions at pH 3 - 5, it is assumed that the transformation from amorphous alumina to aluminium hydroxide is not attributed to the recrystallization of aluminium ion dissolved in water during the keeping. By raising the temperature of keeping in water to 70°C, it is apparent that pseudoboehmite is formed directly from amorphous alumina. In this case, however, it is interpreted that the formation of pseudoboehmite is promoted by raising temperature, and accordingly the formation of amorphous aluminium hydroxide is not observed.

As mentioned above, the hydration of amorphous alumina proceeds in a process leading ultimately to a mixture of pseudoboehmite and alumina trihydrate via the formation of aluminium hydroxide and pseudoboehmite. This hydration phenomenon is analogous to the ageing process of alumina gel [3 - 6, 22]. The hydration process of amorphous alumina is affected by the crystalline state of the samples, treatment temperature and the change in pH of aqueous solution, resulting in the formation of various aluminium hydroxides shown in Table 2.

A similar examination was carried out for the samples of amorphous alumina prepared by heating the specimens of amorphous aluminium hydroxide at 600°C for 2 h. As a result, it was found that although the hydration of the samples prepared at 600°C is slightly more difficult than that of the samples prepared at 400°C, the hy-

dration process is fundamentally the same when the time of contact with water is extended. However, the ratio of pseudoboehmite to alumina trihydrate contained in the hydration product derived from amorphous alumina prepared at 600°C is relatively higher than that prepared at 400°C, and this tendency is enhanced by raising the temperature of the keeping in water. For example, when the samples of amorphous alumina prepared by heating the specimen A<sub>2</sub> at 400 and 600°C were kept in water for 100 days at 30 and 70°C, the ratios of pseudoboehmite to alumina trihydrate contained in the products were 1.35 and 1.48 at 30°C and 1.79 and 1.97 at 70°C, respectively.

#### Hydration of crystalline alumina

Negligible hydration of crystalline aluminas occurred when they were kept in water for a long time at room temperature, but their hydration was promoted by raising the temperature. Some representative X-ray diffraction diagrams for  $\eta$ - and  $\gamma$ -aluminas kept in water at 95°C are indicated in Fig.6, in comparison with those for amorphous alumina prepared by heating the specimen A<sub>1</sub> at 600°C. In the keeping at 95°C,  $\eta$ -alumina forms a small amount of alumina trihydrate for 5 h, and its amount increases and simultaneously a little of pseudoboehmite is also formed after 10 h;  $\gamma$ -alumina is transformed partly to pseudoboehmite after 5 h, although amorphous alumina hydrates to pseudoboehmite for 5 h. Even at lower temperatures <95°C, however, the hydration reaction will proceed if the period of contact with water is prolonged enough. In the case of  $\eta$ -alumina in water at 50°C, the presence of bayerite is observed after 20 days, and nordstrandite is also formed in coexistence with small amounts of pseudobehmite after 50 days. In addition, the X-ray dif-

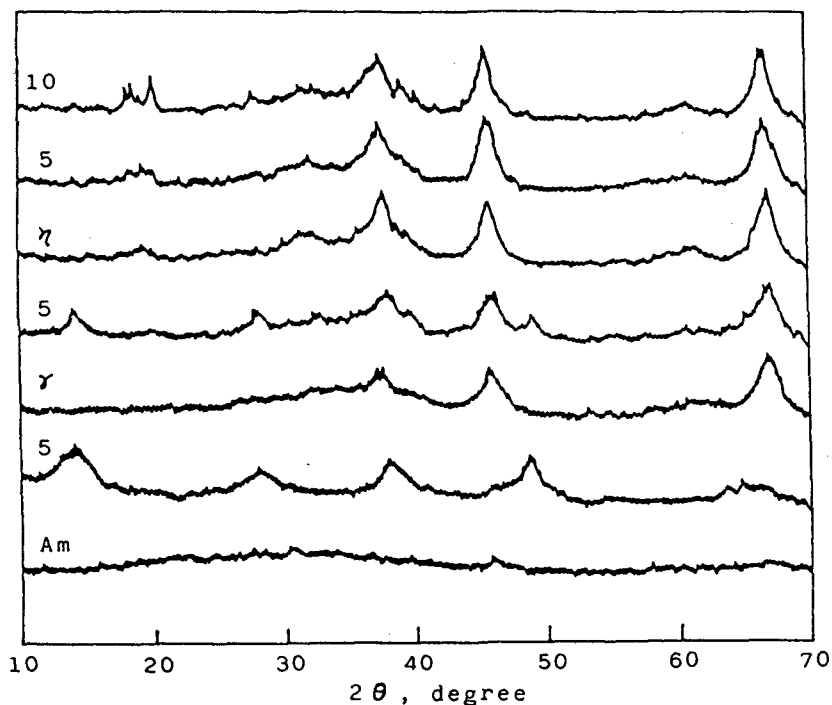


Fig. 6 X-ray diffraction diagrams for aluminas dipped in water at 95°C (numerals on curves are dipping periods, h; Am is prepared by heating of  $A_1$  at 600°C).

fraction diagrams for  $\eta$ -alumina after the keeping in water for 100 days at different temperatures of 30, 50 and 70°C are presented in Fig.7. The composition of products derived from the keeping in water at 30, 50 and 70°C consist primarily of bayerite [ $(\eta, B^+)$ ,  $(B^{3+}, N^+, \eta)$  and  $(B^{3+}, H^{2+}, N^+, \eta)$ , respectively], and also small amounts of pseudoboehmite coexist in the products at 50 and 70°C. From this it is evident that as the temperature of keeping in water is increased, the amount of  $\eta$ -alumina decreases and the formation of alumina trihydrates increases.

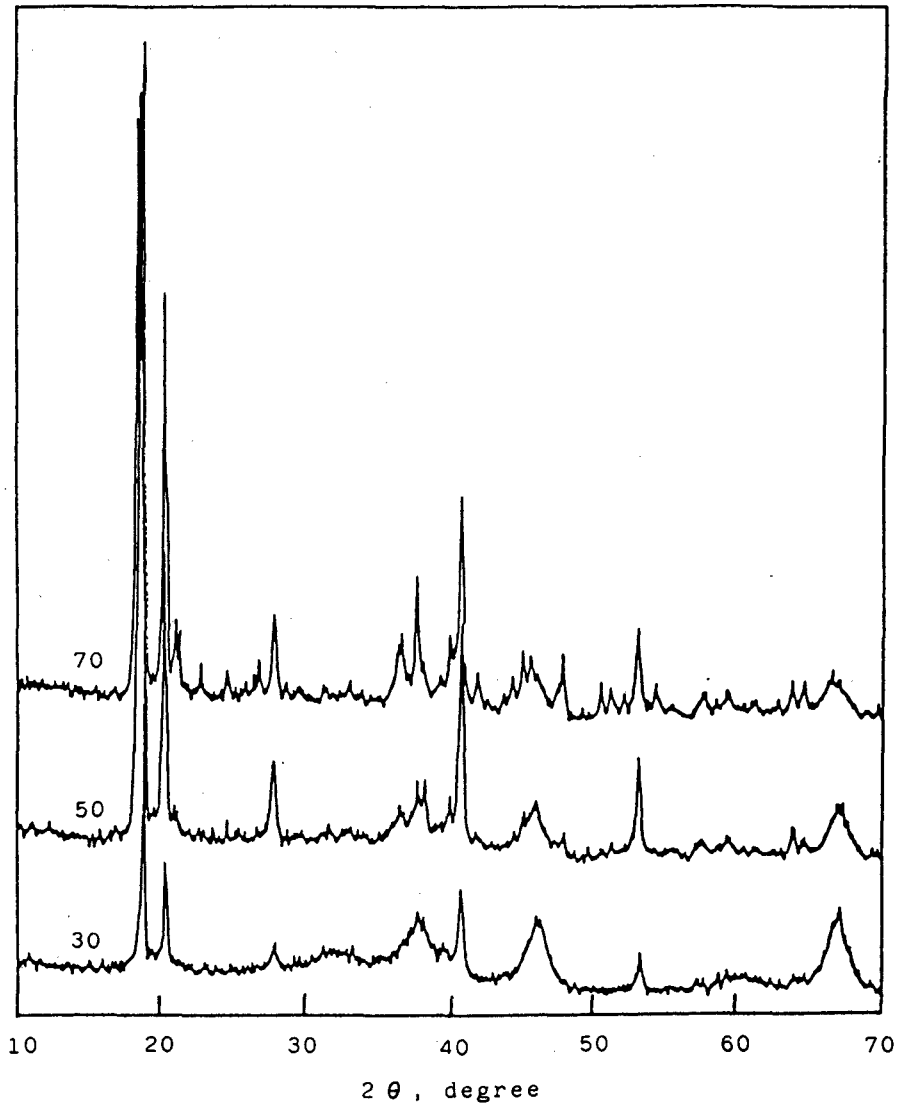


Fig. 7 X-ray diffraction diagrams for  $\eta$ -alumina dipped in water for 100 days at different temperatures (numerals on curves are dipping temperatures,  $^\circ\text{C}$ ).

## CONCLUSION

From the results mentined above, it is concluded that amorphous and crystalline ( $\gamma$  and  $\eta$ ) aluminas are essentially hydrated to aluminium hydroxide when they are kept in water. In the hydration of amorphous alumina at low temperatures, amorphous aluminium hydroxide appears in the beginning of process, and then the mixture of pseudoboehmite and alumina trihydrates such as bayerite, hydrargillite and/or nordstrandite are formed and their formed amounts increase with increasing the period of contact with water. By raising the temperature  $>30^{\circ}\text{C}$ , the rate of hydration is promoted, and the amount of pseudoboehmite formed increases and then bayerite and nordstrandite are formed. Afterwards the amount of nordstrandite increases when the period of keeping in water is extended beyond 50 days. Therefore the hydration of amorphous alumina is expressed in the schematic process (1). Although the hydration of crystalline aluminas does not hydrate appreciably in water at room temperature, when the temperature is raised,  $\eta$ - and  $\gamma$ -aluminas are hydrated to alumina trihydrates and pseudoboehmite, respectively.

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