

DTA and TG Studies on Aging of Hydrous Alumina Gels and Amorphous Alumina in Water*

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Hydrous alumina gels and amorphous alumina were aged in water at 70°C for a long period, and the gels in part were hydrothermally treated at temperatures from 100° to 180°C for 5 h. The gels were prepared by adding ammonia water to an aqueous solution of aluminium chloride. Amorphous alumina was obtained by calcining aluminium chloride at 600°C for 10 h. The water-to-sample ratio and stirring were adopted as principal variables in aging experiments at 70°C. Aged products were examined by X-ray diffraction, differential thermal analysis (DTA) and thermogravimetry (TG). Pseudo-boehmite was formed rapidly at very early stages of aging, which was followed by the formation of alumina trihydrate sensitively detected by DTA for the dehydration. The development of DTA peaks for the dehydration of aged products corresponded to the degree of crystallinity and the amount of alumina hydrates detected by X-ray diffraction. The thermal dehydration of trihydrates as aging products at 70°C proceeded directly to alumina without the intermediate formation of crystalline boehmite or pseudo-boehmite. Thermal analysis techniques, especially DTA, were found to be powerful to studying the formation and crystallization of alumina hydrates from hydrous alumina gels and amorphous alumina in water.

1. INTRODUCTION

Hydrous alumina gels are prepared by the addition of a base to a solution of aluminium salt, and by the hydrolysis of aluminium alkoxide, aluminium amalgam or sodium aluminate. Although freshly precipitated gels are amorphous, crystallization takes place to form alumina hydrate or

aluminium hydroxide[†] if aged in the mother liquor or in water. A considerable number of studies have been made on aging of hydrous alumina gels in aqueous media. It has long been known that the aging process basically proceeds with the sequence of freshly precipitated amorphous gels, pseudo-boehmite (poorly crystalline boehmite) and bayerite¹⁻⁶⁾, and then bayerite transforms into gibbsite (hydrargillite)⁷⁻⁹⁾. Shimizu and Funaki^{10,11)} have disagreed with this scheme, especially the transformation from bayerite to gibbsite, and have proposed that the gels convert into pseudo-boehmite, bayerite and gibbsite individually. Thus the aging process and the products have not been established yet. The reason may be

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† Aluminium oxide is combined with water in definite stoichiometric ratios to form hydrated oxides or hydroxides²⁾, such as $Al_2O_3 \cdot H_2O$ or $AlOOH$, and $Al_2O_3 \cdot 3H_2O$ or $Al(OH)_3$. In the present study, such compounds are generally called alumina hydrates neglecting the structural complexity.

that these are affected by numerous factors such as pH, temperature, concentration, additives, impurities, stirring condition and so forth when precipitated and aged.

On the other hand, a few studies have been carried out on the hydration of amorphous alumina in aqueous media. Imelik¹²⁾ found that η -alumina converted into gibbsite or boehmite by changing temperature in water vapor or water. Papée and Tertian¹³⁾ reported that nearly amorphous alumina in admixture with boehmite was obtained by the thermal decomposition of gibbsite and bayerite, and that the rehydration of the alumina gave bayerite in water at 25°C. Papée¹⁴⁾ also obtained 65% bayerite by the immersion of nearly amorphous ρ -alumina in water for 1 week, which was prepared by the calcination of alumina trihydrate. Funaki and Shimizu¹⁵⁾ studied the hydration of amorphous alumina in water at room temperature prepared by the thermal decomposition of various aluminum salts. The hydration yielded bayerite or gibbsite. They¹⁶⁾ also obtained amorphous alumina from nitrate and chloride, and examined the hydration of the alumina at room temperature and 40°C as a function of aging temperature, pH, stirring and refreshment of water.

Besides the aging of hydrous alumina gels and amorphous oxide in aqueous media, the formation of crystalline hydrates or hydroxides on aluminium has been studied in nearly pure water at temperatures below 100°C from a standpoint of the use of aluminium in water, especially the use for a water-cooled nuclear reactor. It has been reported that the growth of hydrated oxide films on aluminium in water critically depends on the water temperature used. Hart¹⁷⁾ found that the film growth proceeded in three stages of the formation: amorphous oxide, boehmite and bayerite. Hence the final film consisted of the three layers below a critical temperature between 60 and 70°C. Above the critical temperature only the boehmite film was formed on the top of the amorphous film initially existed. Altenpohl and Post¹⁸⁾ recognized relatively thin layers composing of bayerite and other undefined aluminium hydroxides at temperatures below about 75°C, and detected the presence of boehmite above 75°C from X-ray or electron diffraction photographs. Kondo and Nomura¹⁹⁾ concluded that the corrosion of high-

purity aluminium in pure static water progressed with the successive formation of pseudo-boehmite, boehmite and bayerite at temperatures from 50 to 80°C. Thus the formation and crystallization of hydrated oxide or hydroxide on aluminium in water have not completely confirmed yet at temperatures around 70°C.

The crystallization and hydration of amorphous alumina species and alumina hydrates have generally been examined through the techniques of X-ray diffraction, electron diffraction, electron microscopy, infra-red absorption spectroscopy and thermal analysis. Mackenzie et al.^{3,20,21)} have showed that the aging process can be followed very conveniently by differential thermal analysis (DTA) from their intensive studies on thermal behaviors of alumina gels and the aged products. Altenpohl and Post¹⁸⁾ have proved DTA and infra-red spectral analysis to be powerful tools in the investigation of hydrated aluminium oxides formed on aluminium in water or water vapor.

The main purpose of the present study is to obtain informations concerning (1) the possibility for the identification and characterization of alumina hydrates as products during the aging of alumina gels and amorphous alumina in water, (2) the correlation between the degree of crystallinity and the DTA peak for the dehydration of pseudo-boehmite, and (3) aging behaviors and mechanisms of alumina gels and amorphous alumina in water at 70°C. These studies have been performed by means of X-ray diffraction, DTA and TG on aged products.

2. EXPERIMENTAL

2.1 Preparation of Samples

Two kinds of samples were prepared from reagents of guaranteed grade, and used for aging experiments as starting materials.

Hydrous alumina gel samples, referred to as Gel, were prepared by the rapid addition of 13g of 4N NH₄OH solution to 20g of 10% AlCl₃ solution with vigorous stirring to maintain the pH of the solution at about 8.3 when precipitated. Changes in pH accompanying the addition of the NH₄OH solution to the AlCl₃ solution are important for determining an optimum condition of precipitation. These changes can be followed by the

experimental determination of the pH values during the precipitation process. Therefore, prior to the preparation of Gel samples, the titration curve was obtained for the addition of 4N NH_4OH solution to 20g of 10% AlCl_3 solution as shown in Fig. 1. When the NH_4OH solution added to the AlCl_3 solution, white precipitates started to form in part and then dissolved into the solution around pH 3. After the precipitates repeated forming and dissolving, the bulk solution suddenly became semitransparent and gelatinous, and it showed slight resistance to stirring at about pH 5. Further additions of the NH_4OH solution led to a marked increase in the pH value to 8–9, resulting in the formation of white precipitates and the extinction of stirring resistance. Based on the titration curve shown in Fig. 1, hydrous alumina gels were precipitated by the foregoing procedure. After the completion of the precipitation, the gels were centrifuged and washed several times by water to

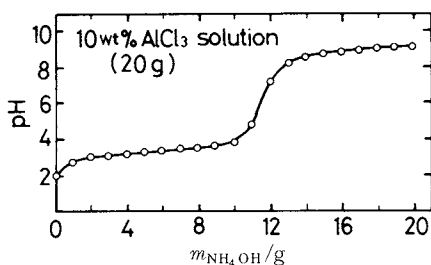


Fig. 1. Changes in pH accompanying the titration of 10wt% AlCl_3 solution with 4N- NH_4OH solution.

a point of the neutralization. The water content of the Gel samples thus obtained was approximately 95%.

Amorphous alumina samples, referred to as Am, were obtained by the thermal decomposition of aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) in air at 600°C for 10 h, and by passing through a screen of 60–100 mesh.

Both starting materials, Am and Gel, were amorphous to X-ray, and allowed to age in water.

2.2 Procedure and Apparatus

The weighed samples were immersed in deionized water having a specific resistance more than $5 \text{ M}\Omega\text{-cm}$ contained in glass tubes. The tubes were placed in a thermostatted water-bath controlled at 70°C for a chosen period up to 100 days. The experimental conditions of aging are listed in Table 1. The water-to-sample ratio and stirring were adopted as principal variables in the present study. Most of the aging experiments were carried out under the static condition, and each one experiment in Am and Gel under the stirred condition by air-bubbling. One of Am samples was exposed to the atmosphere of saturated water vapor at 70°C using a glass vessel as shown in Fig. 2. Amorphous alumina powder was pasted with ethyl alcohol, pressed in the form of thin layer on a flat glass holder for X-ray diffraction samples, and then placed in the test vessel thermostatted at 70°C .

In addition to the aging at 70°C , some of Gel samples were hydrothermally treated in water at temperatures from 100 to 180°C for 5 h using

Table 1. Experimental Conditions of Aging in Water of 70°C .

Run No.	Weight of Sample (m/g)	Volume of Water (V/cm^3)	Condition
Gel-1	10	90	Static
Gel-2	10	60	Static
Gel-3	10	30	Static
Gel-4	10	—	Static
Gel-5	10	90	Stirred
Am-1	2	90	Static
Am-2	2	60	Static
Am-3	2	30	Static
Am-4	4	90	Static
Am-5	4	90	Stirred

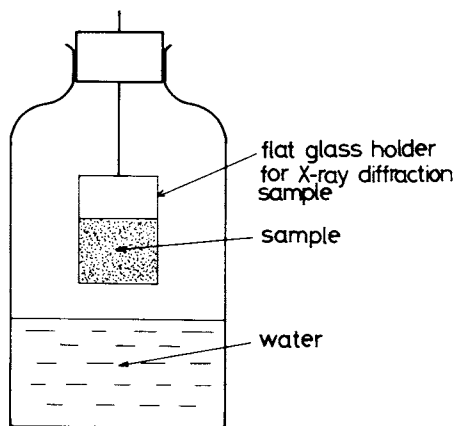


Fig. 2. Test vessel for the exposure of Am samples to the atmosphere of saturated water vapor at 70°C.

an autoclave.

A small portion of the samples immersed in water for various periods was examined by X-ray diffraction, DTA and TG after removing bulk water by drying in Am samples and by the centrifuge in Gel samples. X-ray diffraction patterns were obtained with a diffractometer using Ni-filtered CuK α radiation. A scanning rate in 2θ of 2°/min between 10 and 70°C was used for the identification of aged products. The interlayer spacing of pseudo-boehmite was evaluated from (020) reflections at a scanning rate in 2θ of 1/4°/min.

DTA and TG curves were simultaneously obtained in air at a heating rate of 10°C/min with Rigaku Thermoflex using about 25mg of sample and α -Al₂O₃ as a reference for DTA.

3. RESULTS AND DISCUSSION

3.1 Crystallization of Hydrated Alumina Gels

Fig. 3 shows some examples of changes in typical X-ray diffraction peaks of Gel samples aged in water at 70°C for various periods. Pseudo-boehmite was observed after 12 h at the latest in all the samples. The formation of trihydrate was detected after 24 h in Gel-1, Gel-2 and Gel-5, 2 days in Gel-3, and 4 days in Gel-4. The diffraction peaks for the trihydrate grew at the expense of peaks for pseudo-boehmite with increasing the aging period except in Gel-4 and Gel-5. The peaks

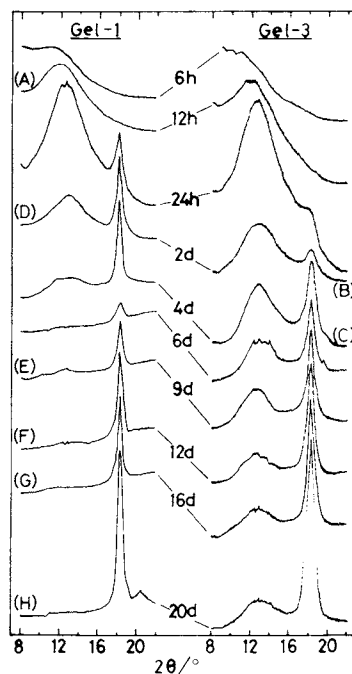


Fig. 3. Changes in X-ray diffraction patterns of Gel-1 and Gel-3 samples aged in water for various periods from 6 h to 20 days at 70°C.

for pseudo-boehmite completely disappeared after 6 days in Gel-1 and 9 days in Gel-2. In Gel-5 aged with stirring, although the growth of the trihydrate was more rapid than in other samples, the diffraction peaks for pseudo-boehmite remained fairly strong even after 20 days.

Typical DTA and TG curves for the dehydration of Gel samples aged in water at 70°C are shown in Fig. 4 with X-ray diffraction patterns of corresponding samples. DTA curves of aged products at early stages gave two fairly large and broad endothermic peaks around 80–90°C and 350–360°C. Considering X-ray diffraction patterns, these peaks were probably due to the desorption of loosely bound water, and to the dehydration of pseudo-boehmite, respectively. With the progress of aging, one more endothermic peak appeared and grew around 250–280°C, corresponding to the development of X-ray diffraction peaks of the trihydrate. The DTA peaks for the dehydration of pseudo-boehmite slightly shifted to higher temperatures, suggesting an increase in the degree of crystallinity of pseudo-boehmite, in the same way as in Am samples shown afterwards. Since most of

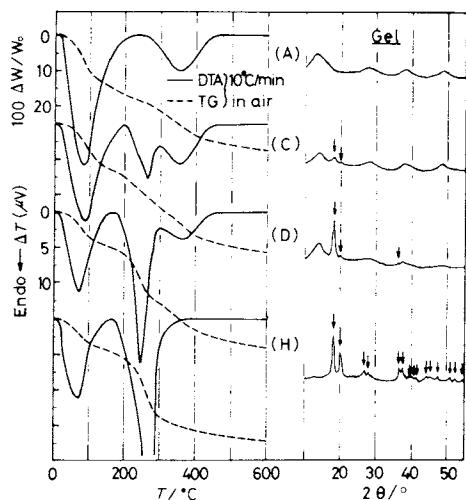


Fig. 4. Typical DTA and TG curves for the dehydration of Gel samples aged in water at 70°C corresponding to the X-ray diffraction patterns. Arrows on the X-ray diffraction patterns indicate the peaks for the trihydrate. Parentheses (A) ~ (H) correspond to those for typical X-ray diffraction patterns shown in Fig. 3.

the aged samples consisted of mixtures of two or three materials; gels, pseudo-boehmite and trihydrate, no definite plateaus were observed on TG curves. However, some breaks and plateau-like slopes suggested the formation of new hydrates.

Mackenzie et al.^{3, 20, 21)} followed the aging process of alumina gels by DTA for the dehydra-

tion of pseudo-boehmite and trihydrate. In the present study, the amount of aged products was estimated from the peaks of X-ray diffraction and DTA, on the assumption of the proportionality of the peak strength to the amount of products. The results in Gel samples are presented in Table 2. Little effect of water-to-sample ratio and stirring was observed in the formation of pseudo-boehmite at early stages, suggesting the direct hydration process was predominant. Pseudo-boehmite disappeared earlier with increasing water-to-sample ratio, except in Gel-5 with stirring. As the water-to-sample ratio became larger, the trihydrate formed and grew more rapidly. The dissolution of pseudo-boehmite is reduced at lower values of water-to-sample ratio since the aging solution reaches saturation more readily. Consequently it is assumed that the formation and growth of the trihydrate takes place by the dissolution of pseudo-boehmite in water and the reprecipitation of the trihydrate.

As described by Aldcroft and Bye⁵⁾, the crystallization of precipitated aluminium hydroxide gels in water was relatively rapid, namely, pseudo-boehmite was formed in the first 3 to 4 h and subsequently bayerite was formed. McHardy and Thomson⁶⁾ reported that pseudo-boehmite initially formed in aging of aluminium hydroxide gels in water was only a transitory phase and altered rapidly to bayerite with some gibbsite. In the study of the corrosion of aluminium in water at temperatures between 50 and 80°C, Kawasaki

Table 2. Products Formed by Aging Gel Samples in Water at 70°C.

Run No.	Aging Period (t/day)								
	0.5	1	2	4	6	9	12	16	20
Gel-1	Bm ³⁺ (A)**	Bm ²⁺ , T ⁺ (B)	Bm ²⁺ , T ²⁺ (D)	Bm [±] , T ²⁺ (E)	T [±] (F)	T ⁺	T ²⁺ (G)	T ²⁺	T ³⁺ (H)
Gel-2	Bm ⁺ (A)	Bm ²⁺ , T [±] (B)	Bm ²⁺ , T ⁺ (C)	Bm ²⁺ , T ²⁺ (D)	Bm [±] , T ⁺ (E)	T ⁺	T ²⁺ (G)	T ³⁺	T ³⁺ (H)
Gel-3	Bm ⁺ (A)	Bm ²⁺	Bm ²⁺ , T [±] (B)	Bm ³⁺ , T ⁺ (C)	Bm ⁺ , T ²⁺	Bm ²⁺ , T ²⁺ (D)	Bm ⁺ , T ²⁺	Bm ⁺ , T ²⁺	Bm ⁺ , T ³⁺ (E)
Gel-4	Bm ⁺ (A)	Bm ²⁺	Bm ²⁺	Bm ³⁺ , T [±] (B)	Bm ³⁺ , T [±]	Bm ³⁺ , T [±]	Bm ²⁺ , T ⁺ (C)	Bm ²⁺ , T ⁺	Bm ²⁺ , T ⁺
Gel-5	Bm ⁺ (A)	Bm ²⁺ , T [±] (B)	Bm ³⁺ , T ⁺ (C)	Bm ³⁺ , T ²⁺ (D)	Bm ³⁺ , T ³⁺	Bm ³⁺ , T ³⁺	Bm ³⁺ , T ³⁺	Bm ³⁺ , T ²⁺	Bm ³⁺ , T ²⁺

Bm = pseudo-boehmite, T = trihydrate

* Superscripts 3+, 2+, + and ± indicate amounts of products estimated to be large, medium, small and trace, respectively.

** Parentheses (A) ~ (H) indicate typical X-ray diffraction patterns obtained with aged Gel samples as shown in Fig. 3.

*et al.*²²⁾ favored the dissolution-precipitation process rather than the hydration process for the crystallization of bayerite on the surface of boehmite formed on aluminium. This was because the solubility of boehmite in water was ten times larger than that of bayerite, and bayerite was thought to be more stable than boehmite in this temperature range.

Shimizu, Miyashige and Funaki¹⁰⁾ observed that trihydrate was formed directly from alumina gels without the formation of pseudo-boehmite at 18°C. The conversion of pseudo-boehmite into trihydrate did not occur at 40°C although the successive formation of pseudo-boehmite and trihydrate was apparently observed. Therefore, Shimizu, Ishijima and Funaki¹¹⁾ disagreed the aging process of alumina gels in aqueous media expressed by the sequence: alumina gels → pseudo-boehmite → bayerite → gibbsite from X-ray diffraction examinations. Pseudo-boehmite, when once formed, was stable and never converted to trihydrate. Bayerite immersed in various aging solutions at room temperature even for 1 year was not transformed to gibbsite. Thus they have reached the following conclusions: (1) alumina gels dissolve in aging solutions, from which the crystalline alumina hydrates are directly precipitated corresponding to several conditions, and (2) crystalline alumina hydrates once precipitated are stable in aging solutions, and the solid-state transformation of the crystalline alumina hydrate is not recognized after fairly long aging. Shimizu and Funaki^{11,16)} estimated that the solubility of crystalline hydrates in water was smaller than that of alumina gels.

It is not very easy to distinguish three hydrates; bayerite, gibbsite and nordstrandite because of the similarity in X-ray diffraction patterns. However,

the trihydrate in Gel samples of the present study was considered to be mainly gibbsite. Shimizu, Miyashige and Funaki¹⁰⁾ observed the formation of gibbsite in the aging of alumina gels at 18°C in water of pH 7.5. As the pH value increased, gibbsite was replaced by bayerite and then nordstrandite. In some Gel samples of the present study, a shoulder was observed at lower temperature side on the DTA peak for the dehydration of trihydrate. Mackenzie^{20,21)} and Sato²³⁾ indicated that the DTA peak temperature for the dehydration of bayerite was approximately 10°–20°C lower than that for gibbsite in spite of the similarity of DTA curves. Sato also suggested an effect of the particle size of samples on the type of the dehydration. Hence the observed shoulder may be resulted from the dehydration of bayerite or the difference in the particle size.

In addition to the aging at 70°C, some of Gel samples were hydrothermally treated in water at temperatures from 100 to 180°C for 5 h in an autoclave. Gel samples converted into pseudo-boehmite with various values of the interlayer spacing calculated from the X-ray diffraction peak for (020) reflections. Table 3 shows the values of the interlayer spacing and DTA peak temperature for the dehydration of pseudo-boehmite hydrothermally prepared at various temperatures. The initial peak temperature at which the dehydration started decreased markedly with lowering temperature of the treatment, giving broader peaks at lower temperatures. The maximum peak temperature increased approximately from 370 to 460°C with an increase in the temperature of the treatment from 100 to 180°C. These results correspond to a decrease in interlayer spacing and an increase in the degree of crystallinity of pseudo-boehmite.

Table 3. Interlayer Spacing and DTA Peak Temperatures for the Dehydration of Pseudo-boehmite Prepared Hydrothermally at Various Temperatures.

Hydrothermal Treatment	Interlayer Spacing ($d/\text{Å}$)	DTA* Peak Temperature ($T/^\circ\text{C}$)		
		Initial	Maximum	Final
100°C, 5h	6.70	227	371	439
120°C, 5h	6.58	238	390	490
140°C, 5h	6.46	235	395	485
160°C, 5h	6.40	361	448	486
180°C, 5h	6.25	361	462	487

* 10°C/min in air.

It has been reported that trihydrate decomposes to intermediate anhydrous alumina directly or through the formation of boehmite on heating, which finally transforms to α - Al_2O_3 . Brown, Clark and Elliott²⁴⁾ concluded that the thermal decomposition of gibbsite to anhydrous alumina proceeded directly or through the formation of well-crystallized boehmite, and that bayerite decomposed to anhydrous alumina through the formation of poorly-crystallized boehmite. Sato²³⁾ and Shimizu and Funaki²⁵⁾ indicated that the thermal decomposition of trihydrates followed two independent routes as described above, and that the decomposition was affected by the particle size of trihydrates. As obvious in Table 3, the product hydrothermally prepared from Gel samples at 180°C for 5 h has the interlayer spacing fairly close to that of true crystalline boehmite (6.11Å), and shows the DTA peak for the dehydration at about 460°C. On the other hand, no endothermic peak is observed at temperatures around 460°C on the DTA curves for the dehydration of Gel samples aged at 70°C as shown in Fig. 4. Besides, the DTA peak for the dehydration of pseudo-boehmite remains almost constant or slightly diminishes in spite of the marked development of trihydrates. Therefore, it is concluded that trihydrates formed from Gel samples decompose directly to alumina neither through the formation of crystalline boehmite nor through that of pseudo-boehmite.

3.2 Hydration of Amorphous Alumina

Figs. 5 and 6 show some examples of DTA and TG curves for the dehydration of Am samples aged in water at 70°C for various periods with X-ray diffraction patterns of corresponding samples. The DTA curves exhibited two endothermic peaks at the early stage of aging, and an additional endothermic peak was observed with the prolonged aging. The first peak centered at 80°C, which was particularly large at the early stage of aging, began to appear on heating from room temperature. This peak was observed in all the samples and attributed to the desorption of loosely bound water in amorphous alumina. The other endothermic peak observed near 340–360°C in all the samples was due to the dehydration of pseudo-boehmite formed by aging in water, which was confirmed by X-ray diffraction of samples obtained before and after

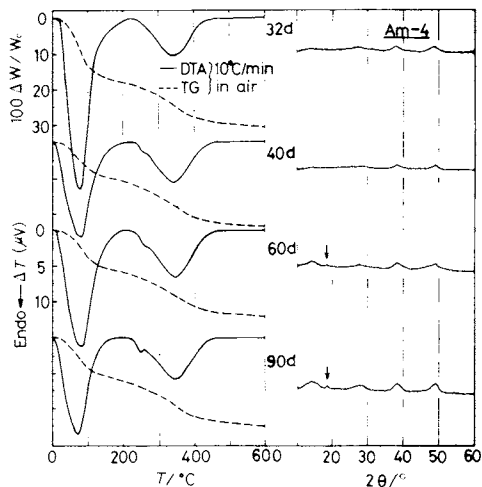


Fig. 5. DTA and TG curves for the dehydration of Am-4 samples aged in water for various periods at 70°C and X-ray diffraction patterns of corresponding samples. Arrows on the X-ray diffraction patterns indicate the peaks for the trihydrate. (d: day)

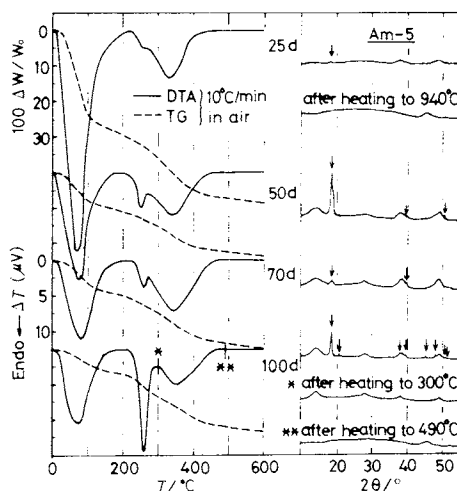


Fig. 6. DTA and TG curves for the dehydration of Am-5 samples aged in water for various periods at 70°C and X-ray diffraction patterns of corresponding samples. Arrows on the X-ray diffraction patterns indicate the peaks for the trihydrate. (d: day)

the DTA peak on heating. This peak slightly shifted to higher temperatures, and grew larger with increasing the aging period until about 40 days. These results indicate the progressing of the crystallization and an increase in the amount of pseudo-boehmite, respectively. Little change was

recognized after a lapse of 40 days in the formation of pseudo-boehmite.

The formation of trihydrate was detected by X-ray diffraction after 21 days in Am-5, and 50 days in other Am samples. At these stages, one more endothermic peak appeared around 260°C on DTA curves. This peak, which was not observed at the early stage of aging, was considered to be due to the dehydration of the trihydrate. The growth of this DTA peak corresponded to an increase in peak strength of X-ray diffraction.

In the Am-4 sample after 40 days, the formation of the trihydrate was detected on DTA curves as a shoulder around 260°C in spite of the absence of the X-ray evidence. As already described, the formation of the trihydrate was detected after 21 days by X-ray diffraction in Am-5. It is seen from Fig. 6 that only pseudo-boehmite was identified by X-ray diffraction after heating the samples containing the trihydrate to 300°C, and γ -Al₂O₃ after heating to temperatures above 490°C. Just the same as in Gel samples, the thermal dehydration of the trihydrate proceeded directly to anhydrous alumina. Since most of the aged samples consisted of mixtures of two or three materials, no definite plateaus were observed on TG curves.

Table 4 shows the amounts of aged products estimated from peaks of X-ray diffraction and DTA in the same way as in Gel samples described previously. The aged Am samples showed the formation of pseudo-boehmite after 25 h at the latest, independent of water-to-sample ratio and stirring. For the purpose of detailed examinations on the formation of pseudo-boehmite in early stages, the short-term aging of Am samples was made under the same condition as Am-4. The

formation of pseudo-boehmite was detected in the first 20 min by X-ray diffraction. In addition, one of Am samples was exposed to the atmosphere of saturated water vapor at 70°C as shown in Fig. 2. Pseudo-boehmite was observed by X-ray diffraction after 24 h even without immersing directly in water. From these two results, it is concluded that the conversion of amorphous alumina into pseudo-boehmite is apparently rapid, that is, almost instantaneous, and is probably caused not by the dissolution-precipitation process but by the direct hydration process.

On the contrary, Vedder and Vermilyea²⁶⁾ concluded that the essential steps in the aluminium + water reaction were the formation of amorphous oxide, the dissolution of the amorphous oxide, and the precipitation of aluminium hydroxide. The hydrous layer appeared to be identical to pseudo-boehmite above room temperature and more crystalline at higher reaction temperatures. They also found that the fairly fast conversion of amorphous material into pseudo-boehmite was followed by the slow conversion into a mixture of bayerite at 60°C.

As obvious from Table 4, the formation and growth of the trihydrate were promoted by stirring. The trihydrate gradually grew in larger water-to-sample ratio, whereas little growth was observed in the smaller ratio. The formation of the trihydrate started after the growth of pseudo-boehmite attained the almost stationary state in all the samples. Consequently the dissolution-precipitation process was assumed to be more predominant for the formation of the trihydrate rather than the solid-state hydration process.

Shimizu, Mitsui and Funaki¹⁶⁾ prepared amor-

Table 4. Products Formed by Aging Am Samples in Water at 70°C.

Run No.	Aging Period (t/day)						
	1	4	8	21	50	70	100
Am-1	Bm ^{±*}	Bm ⁺	Bm ²⁺	Bm ²⁺	Bm ³⁺ , T [±]	Bm ³⁺ , T ⁺	Bm ³⁺ , T ⁺
Am-2	Bm [±]	Bm ⁺	Bm ²⁺	Bm ²⁺	Bm ³⁺ , T [±]	Bm ³⁺ , T ⁺	Bm ³⁺ , T ⁺
Am-3	Bm [±]	Bm ⁺	Bm ²⁺	Bm ²⁺	Bm ³⁺ , T [±]	Bm ³⁺ , T [±]	Bm ³⁺ , T [±]
Am-4	Bm [±]	Bm ⁺	Bm ²⁺	Bm ²⁺	Bm ³⁺ , T [±]	Bm ³⁺ , T ⁺	Bm ³⁺ , T ⁺
Am-5	Bm [±]	Bm ⁺	Bm ²⁺	Bm ²⁺ , T [±]	Bm ³⁺ , T ³⁺	Bm ³⁺ , T ²⁺	Bm ³⁺ , T ³⁺

Bm = pseudo-boehmite, T = trihydrate

* Superscripts 3+, 2+, + and ± indicate amounts of products estimated to be large, medium, small and trace, respectively.

phous alumina by the thermal decomposition of hydrated aluminium nitrate or chloride at 600°C for 30 h, and immersed the alumina in water at a pH of 3–11 at room temperature and 40°C for 50 days. A similarity was recognized between aging behaviors of amorphous alumina and alumina gels in water. Since the refreshment of water prevented the formation of trihydrates, they proposed the dissolution-precipitation process for the conversion of amorphous alumina into crystalline alumina hydrates without adopting the direct absorption-hydration process, taking into consideration of estimated values of solubility for aluminas, alumina gels and alumina hydrates in water. This result confirms the proposed process in the present study.

Although the identification by X-ray diffraction was not so easy as described in Gel samples, the trihydrate formed in Am samples was considered to be nordstrandite. In the aging experiments of amorphous alumina by Shimizu, Mitsui and Funaki¹⁶⁾, only gibbsite was observed around pH 7 and bayerite above pH 9 at 20°C, and only bayerite at 40°C. Shimizu, Miyashige and Funaki¹⁰⁾ obtained pure nordstrandite from alumina gels aged in ammonia solutions of pH 11.1–11.6 and higher concentrations. Aldcroft and Bye⁵⁾ indicated that the formation of nordstrandite from amorphous aluminium hydroxide was promoted by the presence of ethylene glycol in the aqueous mother liquor, whereas it was not detected in water. A slight difference of aging conditions may lead to a change in types of products since the aging process and the products are affected by numerous factors including pH, concentration, temperature, additives of aging solutions.

4. CONCLUSION

The aging process and the products of hydrous alumina gels and amorphous alumina in water were studied by X-ray diffraction, DTA and TG. The aging in water at 70°C proceeded with a rapid formation of pseudo-boehmite and the subsequent formation of trihydrates. The development of DTA peaks for the dehydration of aged products corresponded to the degree of crystallinity and the amount of alumina hydrates detected by X-ray diffraction. Trihydrates as aged products at 70°C

decomposed directly to alumina without the intermediate formation of crystalline boehmite or pseudo-boehmite. Thermal analysis techniques, especially DTA, proved to be useful tools for studying the formation and crystallization of alumina hydrates during the aging of amorphous alumina species in water.

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