

Thermal stability of aluminas by hydrothermal treatment of an alkoxide-derived gel

T. FUKUI, M. HORI

Technical Research Center, Krosaki Corporation, 1-1 Higashihama, Yahata-nishi, Kitakyushu 806, Japan

Alumina precursors were prepared by hydrothermal treatment of alkoxide-derived alcogels. The crystalline structure of precursor boehmites and their microstructural change during heat treatment were examined and the specific surface area of the alumina precursors after heating was measured. The alumina prepared by hydrothermal treatment at 270 °C retained high specific surface areas at high temperatures; e.g. 35.0, 8.3 and 5.4 m² g⁻¹ at 1200, 1400 and 1500 °C, respectively. The thermal stability of the aluminas depended on the hydrothermal temperatures. For excellent thermal stability, the following factors are necessary: (1) grain growth of boehmite as an alumina precursor, and a grain size of more than 20 nm for the (1 2 0) plane; (2) a crystallite size for the (2 0 0) plane exceeding that for the (0 0 2) plane; (3) anisotropic growth of the boehmite crystal. In the transition alumina region (≤ 1200 °C), the thermal stability of the alumina is caused by raising the α transformation temperature, resulting from decreasing the number of grain boundaries by boehmite growth. In the α -alumina region (> 1200 °C), inhibiting the three-dimensional grain growth achieves thermal stability, resulting from preservation of the anisotropic structure introduced into the boehmite.

1. Introduction

Environmental problems are arousing growing interest, and regulations against exhaust gases are being strengthened. Recently, catalytic combustion has been proposed to inhibit the generation of thermal NO_x (nitrogen oxide) and to increase the combustion efficiency [1]. To control catalytic combustion, development of a catalyst support which can be used at temperatures above 1000 °C is necessary. Transition aluminas have been widely used as a catalyst support because of their high specific surface area and thermal stability. However, these aluminas could not be used as a support for catalytic combustion, because their specific surface area rapidly decreases due to transformation to α -alumina at temperatures above 1000 °C.

In recent developments in catalytic combustion, new materials having thermal stability at high temperatures have been applied. Yamashita and co-workers [2, 3] reported the effect of lanthanoid addition within alumina. Formation of lanthanoid- β -aluminas raised the thermal stability at high temperatures, ≥ 1000 °C. Machida *et al.* [4] reported that barium-doped alumina, prepared by a metal alkoxide method, maintained a specific surface area of > 10 m² g⁻¹ at high temperatures of ≥ 1400 °C because of the formation of low sinterable barium hexa-aluminate (BaO-6Al₂O₃) with magunetoplumbite structure. Further, silica-modified aluminas are also known to have a relatively large surface area at high temperatures [5–7].

Production of thermally stable aluminas with no additives by textural control was also attempted.

Maeda *et al.* [8] prepared aluminas with a controlled microstructure by a complex-assisted sol-gel method using polyglycol. The resultant alumina had an excellent thermal stability at ≥ 1000 °C. Mizushima and Hori [9] reported that alumina aerogels dried under the supercritical condition of ethanol (270 °C, 26.5 MPa) had an excellent thermal stability at ≥ 1000 °C; i.e. approximately 100 m² g⁻¹ at 1200 °C. However, thermal stability at ≥ 1400 °C was not achieved by the above structural controls. On the other hand, Tsutsumi *et al.* [10] prepared a porous alumina film with ordered alumina particles using cast films of synthetic bilayer membranes as a molecule template. The resultant film maintained approximately 10 m² g⁻¹ specific surface area with unchanged two-dimensional microstructure after sintering at 1500 °C, although it transformed to α -phase at ≥ 1000 °C. The most remarkable point of this report is no decrease in specific surface area with γ to α transformation. However, this method is inconvenient as a preparation method for catalytic support.

We also reported a preparation method for the alumina precursors, boehmite, by the hydrothermal treatment of alkoxide-derived alcogels [11]. The resultant alumina exhibits a thermal stability at high temperatures, i.e. approximately 10 m² g⁻¹ specific surface area at 1400 °C. Several studies of the boehmite preparation were reported by hydrothermal and analogous treatments [7, 11–13]. Adschiri *et al.* [14] indicated that the hydrothermal condition affects the morphology, crystal structure and particle size of boehmite. However, the relationship between the

thermal stability, hydrothermal conditions and boehmite structures, was not discussed. The aim of the present work was to clarify the reasons for the thermal stability of the hydrothermal alumina gels. The crystalline structure of precursor boehmites and their microstructural change during heat treatment were examined and the effect of preparation conditions on thermal stability described. The relationship between thermal stability, and the crystalline structure and microstructure has also been discussed.

2. Experimental procedure

2.1. Preparation of alumina precursors

Aluminas were prepared using reagent-grade raw materials. Ethyl acetoacetate aluminium di-iso-propylate (etacAl), 27.43 g, in ethanol, 25 ml, was hydrolysed with 1 M aqueous ammonia-ethanol (7.2 ml-50 ml; H₂O/etacAl = 4). The resultant transparent solution was aged at 60 °C for 2 days, after which a transparent alcogel was obtained. The alcogel was hydrothermally treated at a temperature between 170 and 270 °C for 6 h, and then dried in air at 100 °C. The alumina precursors obtained were labelled HT-170, HT-200, HT-240 and HT-270 (the numbers indicating the hydrothermal treatment temperature). For comparison, alumina xerogel and aerogel were prepared. An alumina xerogel was obtained by drying at 100 °C under atmospheric pressure (termed the xerogel). An alumina aerogel was obtained by heating for 6 h under the supercritical condition of ethanol (270 °C, 26.5 MPa) followed by removal of solvents with decreasing pressure (termed the aerogel). Under supercritical conditions, a compound becomes gaseous fluids with a density near to that of a liquid. Thus, the supercritical drying inhibits the stress generated by liquid-gas phase transformation, resulting in virtually no shrinkage of the alcogel after drying.

2.2. Characterization

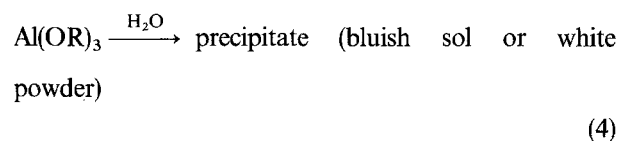
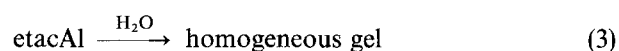
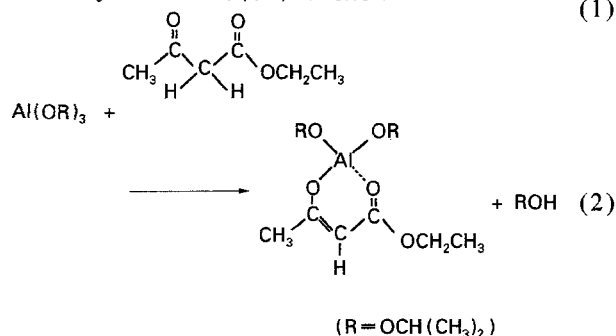
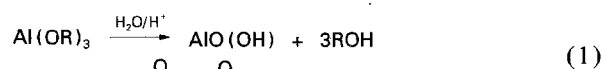
The HTs were fired in air at a heating rate of 100 °C h⁻¹ to various temperatures for 5 h. BET surface area was measured by the nitrogen adsorption method (Monosorb, Quanta Chrome). Crystalline phases were identified by the powder X-ray diffraction method (XRD; RAD-RB, Rigaku Co.) using CuK_α radiation with a graphite monochromator. The crystalline size was determined by the X-ray line broadening technique with Scherrer equation using an integral width of a diffraction peak. Microstructure was observed using a scanning electron microscope (SEM; JSM-T20, Joel). The aerogel obtained, a commercial γ -alumina (Puralox SBa-130, Condea Chemie) and a commercial boehmite (Dispal 11N7-80, Vista Chemical), were used as comparative samples.

3. Results

3.1. Preparation of alcogel

Boehmite as an intermediate was prepared by hydrolysis of aluminium alkoxide, i.e. a sol-gel method, Reaction 1. Boehmite powders with high surface area could

be obtained: e.g. Vista Chemicals, Catapal or Dispal sires, but their surface areas decrease accompanied by α transformation. The alkoxide-derived alcogel was therefore used to avoid a decrease in surface area. However, the hydrolysis rate of aluminium alkoxides is usually rapid, and thus it is difficult to prepare a homogeneous gel. As controllable hydrolysis methods, the following routes are attractive: (1) low alkoxide concentration, (2) slow supply rate of water, and (3) stabilization of alkoxide to water using a polydentate organic compound. In the present study, an alcogel was prepared by method 3, because large reactor scale and long reaction time are necessary for methods 1 and 2, respectively. Ethyl acetoacetate, which easily decomposes by heat treatment, was selected as a polydentate chelating reagent. Ethyl acetoacetate aluminium di-iso-propylate (etacAl) synthesized as in Reaction 2, was used, and a transparent alcogel was obtained, Reaction 3



The resultant alcogel was dried (1) under atmospheric pressure, (2) under atmospheric pressure after the hydrothermal treatment, and (3) by heating under the supercritical condition [9] of ethanol followed by removal of solvents with decreasing pressure.

3.2. Specific surface area and crystalline phase

Tables I and II give the specific surface area (SSA) and the crystalline phase of the aluminas after heating. After heating at 1200 °C, the SSAs of the commercial aluminas decreased to 5.3 m² g⁻¹ accompanied by α transformation, but the HT-270 maintained a high SSA of 35.0 m² g⁻¹ and did not completely transform to α -phase. When transformed to α -phase, the HT-270 maintained SSAs of 8.3 and 5.4 m² g⁻¹, which were the highest values of the present aluminas, at 1400 and 1500 °C, respectively. The aerogel, which was reported to be one of the most thermally stable [9], maintained a high SSA of 63.8 m² g⁻¹ at 1200 °C compared to that of HT-270, but its SSA decreased to 2.7 and

TABLE I Specific surface areas of different aluminas heated at various temperatures

Temperature (°C)	HT-270	Xerogel	Aerogel	γ -alumina	Beohmite
As-prepared	103.9	518.1	316.8	179.6	74.7
800	119.1	258.0	273.5	162.8	80.3
1000	81.8	49.9	136.1	120.5	64.8
1100	72.7	—	110.8	18.5	51.4
1200	35.0	0.1	63.8	5.3	5.3
1400	8.3	—	2.7	1.2	1.5
1500	5.4	—	1.5	—	—

TABLE II Crystalline phases of different aluminas heated at various temperatures

Temperature (°C)	HT-270	Xerogel	Aerogel	γ -alumina	Beohmite
As-prepared	B ^a	B ^a	B ^b	—	—
800	γ	γ	γ	γ	γ
1000	δ	$\theta > \alpha$	$\theta > \delta$	$\theta > \delta$	δ
1100	$\delta \geq \theta$	α	θ	$\alpha \geq \text{un}^c$	θ
1200	$\delta \geq \theta > \alpha$	α	θ	α	α
1400	α	α	α	α	α

^a B, beohmite.

^b B, pseudo-beohmite.

^c un, unknown peak.

1.5 m² g⁻¹ at 1400 and 1500 °C, respectively, due to α transformation. In the xerogel, α transformation was already initiated at 1000 °C, and densification was completed at 1200 °C. In the case of heating to 1200 °C, the SSA value depends on the α transformation temperature, but not above 1200 °C.

The effect of hydrothermal treatment temperature on the thermal stability was investigated. Fig. 1 shows the relationship between hydrothermal treatment temperatures and SSAs of the HTs. The effect of hydrothermal treatment temperature on the SSAs of the HTs heated at ≥ 1100 °C was different from those of the HTs heated at ≤ 1000 °C; transition aluminas transform to α -alumina at temperatures between 1100 and 1200 °C. The SSA of the HTs increased with increasing hydrothermal treatment temperature when heated at 1200 °C; i.e. 35.0 m² g⁻¹ at 270 °C (HT-270) and 4.1 m² g⁻¹ at 170 °C (HT-170), while those of the HTs slightly decreased when heated at ≤ 1000 °C.

Fig. 2 shows changes in SSAs of the HTs after heating at 1100 °C. The effect of hydrothermal treatment temperature was observed after prolonged heating [11]. After heating for 100 h the SSA of the HT-270 slightly decreased, from 72.7 m² g⁻¹ (for 5 h) to 58.4 m² g⁻¹, while those of the HT-200 and the HT-240 apparently decreased to 7.1 and 21.0 m² g⁻¹, respectively. Under the present conditions, the difference in the thermal stability depends on the hydrothermal treatment temperature. The aqueous sol derived from alkoxide was known to crystallize to beohmite on ageing at ≥ 80 °C [12]. According to the report by Adschiri et al. [14], the hydrothermal conditions of an aqueous metal salt solution, such as pressure or temperature, strongly affect the particle size, morphology and crystal structure of beohmite. In an earlier study, we reported the crystallization of the HT gels to beohmite [11]. Thus, different hydrothermal

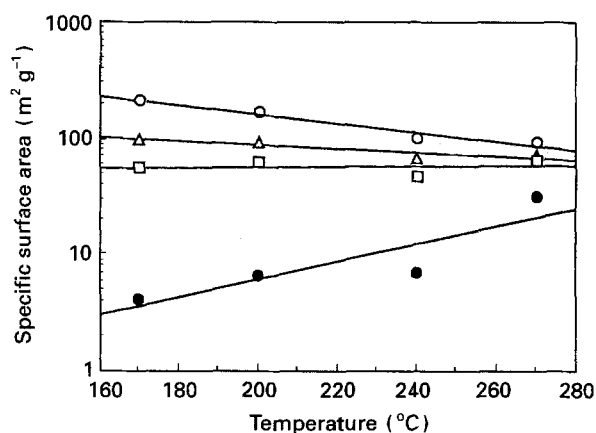


Figure 1 Relationship between hydrothermal treatment temperature and specific surface areas of the HTs after heating at various temperature for 5 h; (○) as-prepared, (△) 1000 °C, (□) 1100 °C, and (●) 1200 °C.

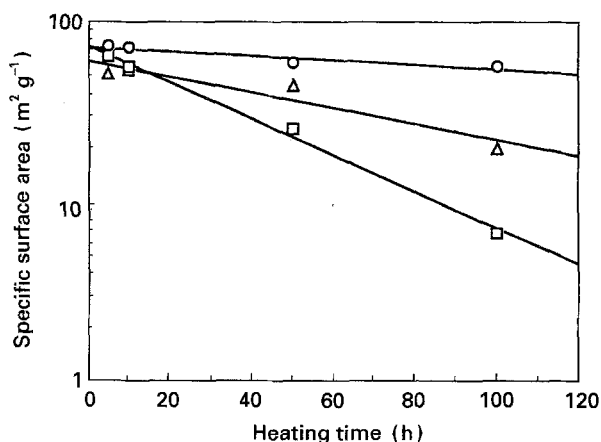


Figure 2 Changes in specific surface areas of the HTs treated under different hydrothermal conditions after heating at 1100 °C, (○) HT-270, (△) HT-240, and (□) HT-200 [11].

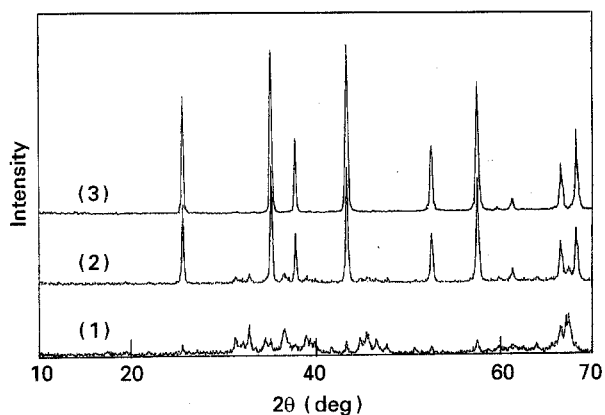


Figure 3 XRD patterns of (1) HT-270, (2) HT-240, and (3) HT-200, after heating at 1100 °C for 100 h.

conditions are predicted to give different crystallite sizes and crystal structures of boehmite.

The XRD patterns of HT-270, HT-240 and HT-200 after heating at 1100 °C for 100 h are shown in Fig. 3. For HT-270, most of the crystalline phases were transition aluminas, such as δ - and θ -phases, with traces of α -phase. HT-240 contained a few transition aluminas, and HT-200 was completely crystallized to α -phase. When hydrothermally treated at high temperatures, the transition phases are stabilized, causing high SSA to be maintained.

3.3. Crystal structure

Table III shows crystallite sizes for (0 2 0), (2 0 0), (0 0 2) and (1 2 0) planes of the HTs and the commercial boehmite. Grain sizes for all planes increased with increasing hydrothermal treatment temperature, and were almost constant at ≥ 240 °C, except for the (1 2 0) plane. HT-270 has two special features: the large crystallite size and the crystallite size for the (2 0 0) plane which is larger than that of the (0 0 2) plane. Those for the commercial boehmite were 13.5, 25.2, 30.1 and 21.2 nm, for the (0 2 0), (2 0 0), (0 0 2) and (1 2 0) planes, respectively, which were largely the same as those of HT-270; however, that for the (2 0 0) plane was smaller than that of the (0 0 2) plane. The aerogel had excellent thermal stability up to 1200 °C, but had small crystallite sizes of 3.1, 17.0, 13.6 and 5.6 nm, for the (0 2 0), (2 0 0), (0 0 2) and (1 2 0) planes, respectively, compared to those of the HT-270.

The XRD profiles due to the (0 2 0) plane of boehmite are shown in Fig. 4. Peak profiles for HT-270 and the aerogel, which were derived from the alcogel, were not symmetrical, while the commercial boehmite had a symmetrical peak profile. This peak separation was reported for the alumina precursor prepared by the polyglycol-assisted method, which was caused by intercalation of organics into the boehmite layer [15]. In the case of the present boehmite, however, no exothermic peak for combustion of residual organics was observed, and weight loss at 1300 °C was 15.9% on TG-TDA profiles; 15.02% for AlOOH transforming to γ -Al₂O₃, as calculated. Accordingly, anisotropic growth of boehmite particles is suggested.

TABLE III Hydrothermal treatment temperature versus crystallite size

Sample	Hydrothermal treating temperature (°C)	Crystallite size (nm) ^a			
		(0 2 0)	(2 0 0)	(0 0 2)	(1 2 0)
HT-170	170	2.7	10.0	15.7	5.2
HT-200	200	5.5	17.6	20.5	11.1
HT-240	240	14.4	26.3	23.8	17.1
HT-270	270	15.2	27.4	24.3	20.6
Boehmite	–	13.5	25.2	30.1	21.2
Aerogel	270 ^b	3.1	17.0	13.6	5.5

^a Determined by X-ray line broadening technique.

^b Under the supercritical condition of ethanol.

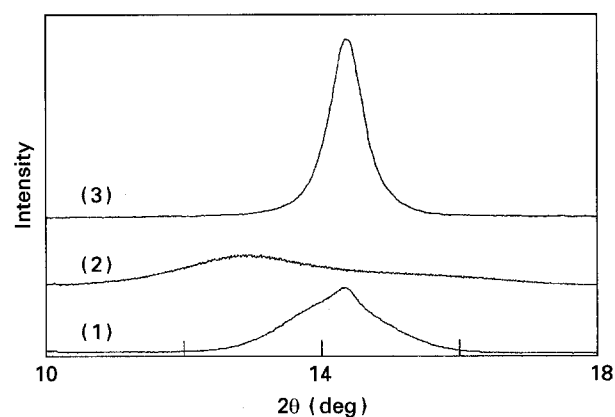


Figure 4 XRD profiles for the (0 2 0) plane of (1) HT-270, (2) the aerogel, and (3) the commercial boehmite.

3.4. Microstructure

Fig. 5 shows scanning electron micrographs of HT-270 after heating at various temperatures. HT-270 consisted of fine agglomerated particles of approximately 0.2 μ m, and grain growth was not observed at ≤ 1200 °C. After heating at 1400 °C, a unique texture with striped alignments was formed, and the grains grew slightly, approximately 0.3 μ m. The alumina grains were two-dimensionally connected and formed a layered structure. The HT-170 textures at ≤ 1000 °C were similar to those of HT-270 (Fig. 6). At 1400 °C, however, the grains grew to ≥ 1 μ m and partially sintered.

Fig. 7 shows scanning electron micrographs of the comparative samples after heating. In the case of the commercial γ -alumina and boehmite, those grains already grew and sintered at 1200 °C accompanied by α crystallization. The aerogel had a sparse texture, compared with that of the HTs, which was kept at 1200 °C. On the other hand, the grains grew to approximately 1 μ m at 1400 °C, but the formation of necking and sintering did not proceed because of the sparse texture. The thermal transition of the aerogel texture apparently differs from that of HT-270. These results suggest that the mechanism for the appearance of thermal stability at high temperatures above 1200 °C is essentially different from that of HT-270.

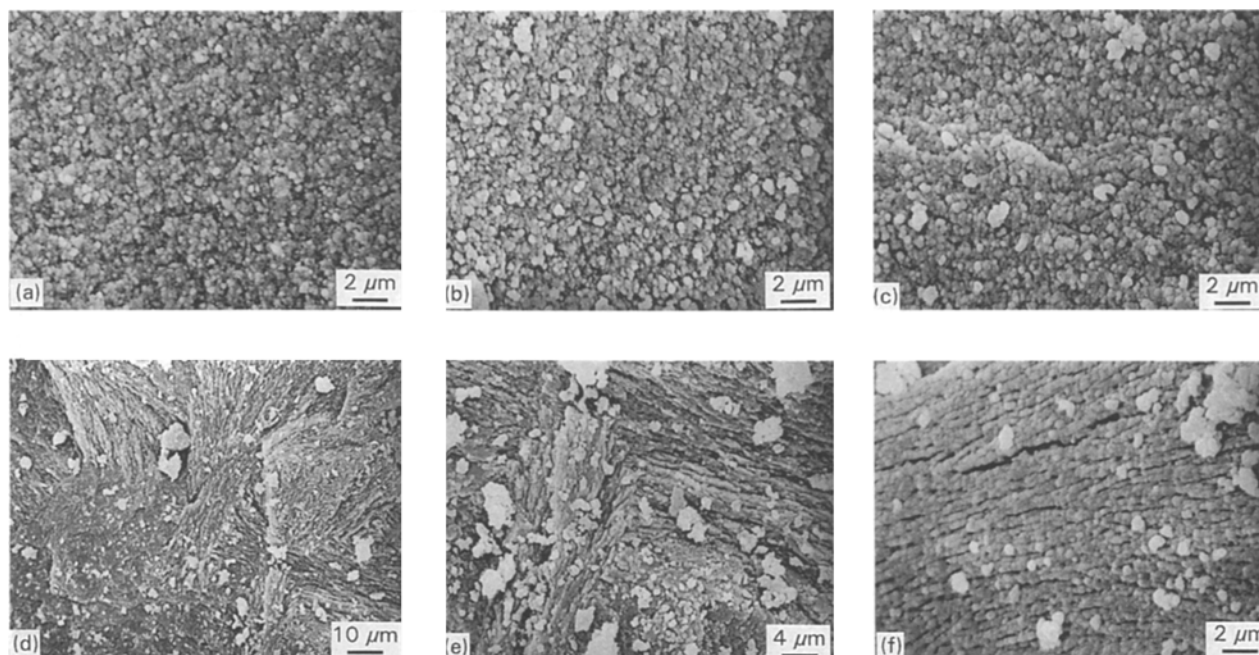


Figure 5 Scanning electron micrographs of HT-270 heated at various temperatures for 5 h. (a) As-prepared, (b) 1000 °C, (c) 1200 °C, (d–f) 1400 °C.

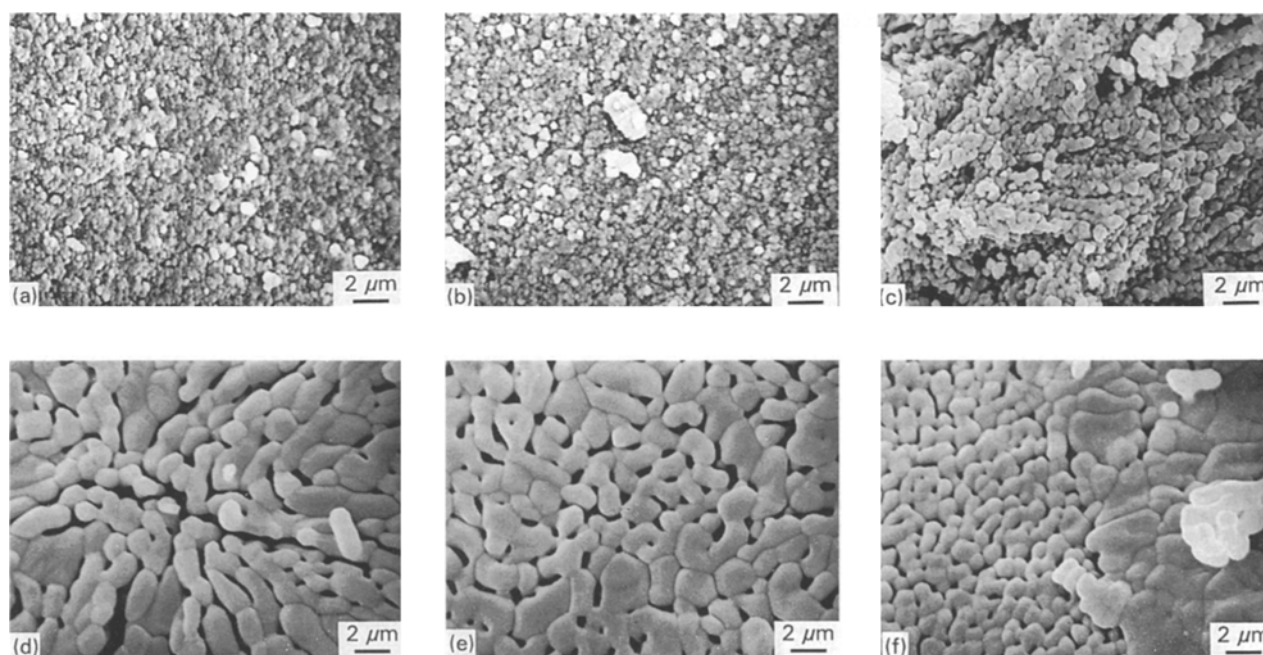


Figure 6 Scanning electron micrographs of HT-140 heated at various temperatures for 5 h. (a) As-prepared, (b) 1000 °C, (c) 1200 °C, (d–f) 1400 °C.

4. Discussion

4.1. Thermal stability in the transition alumina region

Alpha transformation of transition aluminas has been considered to accompany grain growth through an ion-diffusion process, because the rearrangement of oxygen ions to a hexagonal close-packed structure (α -phase) from a cubic close-packing structure (γ , δ and θ phases) is necessary for α formation. On the other hand, Schaper *et al.* [16] proposed that decreas-

ing SSAs of transition aluminas proceeds by self-sintering, resulting in transition aluminas transforming to α -phase. Sintering of transition aluminas proceeds by neck formation through surface diffusion at temperatures between 800 and 1100 °C. The resultant neck includes many defects and stresses, and is unstable, and can easily become a nucleation site; thus, α transformation begins by sintering of transition aluminas. Because the α transformation proceeds through nucleation and growth, a trend for the

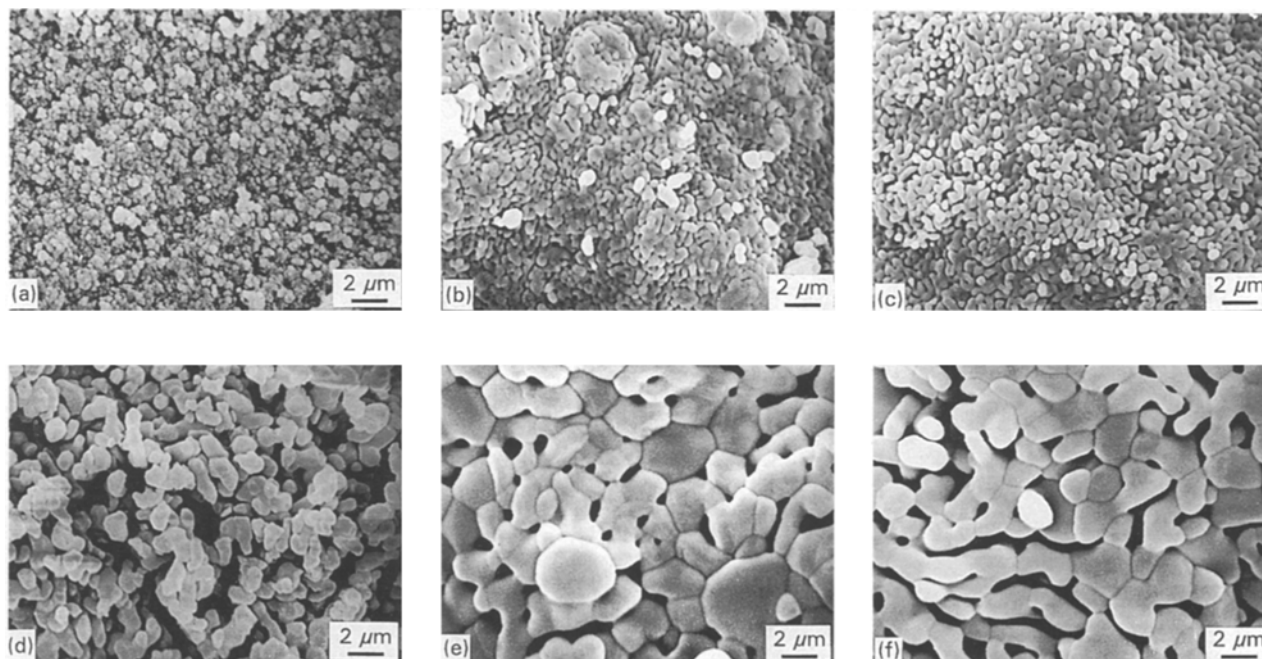


Figure 7 Scanning electron micrographs of (a, d) the aerogel, (b, e) γ -alumina and (c, f) beohmite heated at (a–c) 1200 °C and (d–f) 1400 °C for 5 h.

nucleation reflects the phase transformation temperature. Accordingly, α transformation is inhibited by the structural control with decreasing grain boundaries, and thermal stability of the alumina should be improved. For example, the alumina aerogel prepared under a supercritical condition, possessing a low density, whose α transformation temperature was elevated, had excellent thermal stability at 1200 °C (Tables I and II). The aluminas prepared by spray-pyrolysis of a fibre-like beohmite suspension [17] and by the complex-assisted sol-gel method using polyglycol [8], were also stabilized by a similar mechanism.

The present HT gels consisted of grain-grown beohmite (Tables I and III). When hydrothermally treated at high temperature, beohmite particles grow (Table III), and the number of grain boundaries decreases; i.e. HT-270 < HT-240 < HT-200 < HT-170. After heating at 1100 °C for 100 h, α transformation of the HT-270 was inhibited compared to that of HT-200 and HT-240 (Fig. 3). The trend for grain growth corresponds to that for thermal stability. Accordingly, the thermal stability of HT-270 at ≤ 1200 °C is caused by inhibiting α transformation resulting from decreasing the grain boundaries by beohmite grain growth. However, the thermal stability after α transformation, above 1200 °C, cannot be explained by “inhibiting α transformation by decreasing the grain boundaries”.

4.2. Thermal stability in the α -alumina region

The most special feature of HT-270 is the unique texture with a striped alignment formed by heating at 1400 °C (Fig. 5). This texture would cause the thermal stability at high temperatures of above 1400 °C. Tsutsumi *et al.* [10] reported a preparation method

for porous alumina film with approximately $100 \text{ m}^2 \text{ g}^{-1}$ at 1500 °C. The film exhibited anisotropy parallel to the film plane; e.g. (1 1 1) and (1 1 2) planes of θ -alumina, and a multi-layer morphology of α -alumina. In this method, raw materials were dried and sintered under a two-dimensionally fixed state, and the α -alumina film with ordered plate-like particles structure was obtained. The HT-270 has an anisotropic crystal structure as shown by the X-ray diffraction profile (Fig. 3). Anisotropy introduced in the precursor beohmite would inhibit the three-dimensional grain growth of α -alumina, resulting in the two-dimensional grain growth.

A commercial beohmite is usually prepared and grain-grown under a sol state dispersed in a solvent. The present HTs, however, were hydrothermally treated under the three-dimensionally fixed state. Therefore, while the grains of beohmite in the sol grow freely, an irregular grain growth proceeds in the gel, resulting in the formation of the anisotropic crystal structure. The anisotropy introduced by hydrothermal treatment would be maintained after the transformation to α -phase, and would be attractive for improvement of the thermal stability at high temperatures due to inhibition of the three-dimensional grain growth.

5. Conclusions

Alumina precursors were prepared by the hydrothermal treatment of alkoxide-derived alcogels. The alumina produced by hydrothermal treatment at 270 °C (HT-270) maintained high specific surface areas of 8.3 and $5.4 \text{ m}^2 \text{ g}^{-1}$ after heating at 1400 and 1500 °C, respectively. The thermal stability of the aluminas depends on the hydrothermal temperatures. For excellent thermal stability, the following factors

are required: (1) grain growth of boehmite as the alumina precursor, > 20 nm grain size for the (1 2 0) plane; (2) a crystallite size for the (2 0 0) plane exceeding that for the (0 0 2) plane; and (3) anisotropic growth of boehmite crystal. In the transition alumina region ($\leq 1200^\circ\text{C}$), the thermal stability of the alumina is caused by raising the α transformation temperature, resulting from a decrease in the number of the grain boundaries caused by the boehmite grain growth. In the α -alumina region ($> 1200^\circ\text{C}$), inhibiting the three-dimensional grain growth achieves thermal stability, resulting from preservation of the anisotropic structure introduced into the boehmite.

References

1. R. PRASAD, L. A. KENNEDY and E. RUCKENSTEIN, *Catal. Rev. Sci. Eng.* **26** (1984) 1.
2. H. YAMASHITA, A. KATO, N. WATANABE and S. MATSUDA, *Nippon-Kagaku-Kaishi* (1986) 1169.
3. S. MASTUDA and H. YAMASHITA, *Syokubai* **29** (1987) 293.
4. M. MACHIDA, K. EGUCHI and H. ARAI, *J. Catal.* **103** (1987) 385.
5. B. BEGUIN, E. GARBOWSKI and M. PRIMET, *ibid.* **127** (1991) 595.
6. T. MORI, T. HORIUCHI, T. IDA and Y. MURASE, *J. Mater. Chem.* **2** (1992) 577.
7. M. INOUE, H. OTSU, H. KOMINAMI and T. INUI, *J. Mater. Sci. Lett.* **11** (1992) 269.
8. K. MAEDA, F. MIZUKAMI, M. WATANABE, N. ARAI, S. NIWA, M. TOBA and K. SHIMIZU, *ibid.* **9** (1990) 522.
9. Y. MIZUSHIMA and M. HORI, "Eurogel '91", edited by S. Vilmint, R. Nass and H. Schmidt (Elsevier Science, Amsterdam, 1992) p. 195.
10. N. TSUSTUMI, K. SAKATA and T. KUNITAKE, *Chem. Lett.* **1992** (1992) 1465.
11. T. FUKUI and M. HORI, *J. Mater. Sci. Lett.* **13** (1994) 413.
12. B. E. YOLDAS, *Am. Ceram. Soc. Bull.* **54** (1975) 289.
13. M. INOUE, H. KOMINAMI and T. INUI, *J. Am. Ceram. Soc.* **73** (1990) 1100.
14. T. ADSCHIRI, K. KANAZAWA and K. ARAI, *ibid.* **75** (1992) 2615.
15. M. INOUE, Y. KONDO and T. IMUI, *Inorg. Chem.* **27** (1988) 215.
16. H. SCHAPER, E. B. M. DOESBURG, P. H. M. de KORTE and L. L. VAN REIJEN, *Solid State Ionics* **16** (1985) 261.
17. T. ISHIKAWA, R. OHASHI, H. NOKABAYASHI, N. KAKUTA, A. UENO and A. FURUTA, *J. Catal.* **134** (1992) 87.

Received 16 November 1993
and accepted 21 September 1994