

Preparation of nano porous alumina ceramic from amorphous alumina by hydrothermal synthesis

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Precursor spherical bodies of a porous alumina ceramic were prepared by forming, hydrating and calcining a powder mixed amorphous alumina, obtained by flash calcination of $\text{Al}(\text{OH})_3$, with a pore generating agent. To prepare the porous alumina ceramic from precursor bodies, they were immersed in an aqueous solution of a mixture of dilute nitric and acetic acids, and then they were hydrothermally treated and calcined. Acicular platelet crystals were transformed into acicular crystals of boehmite through the hydrothermal process. In this change, it was found that a reversible phase transformation due to the hydrothermal reaction took place between boehmite and γ -alumina. In comparison to the precursor before the hydrothermal treatment, the N_2 adsorption capacity was increased from 450 ml/g to 670 ml/g, and the pore volume which a diameter between 100 Å and 1,000 Å was increased from 0.15 ml/g to 0.77 ml/g, and the mechanical strength was increased from 1.4 MPa to 2.2 MPa after the hydrothermal treatment. Also, the product showed a remarkable thermal resistance which sustained the θ -alumina crystal structure and pores between 100 Å and 1,000 Å even though the porous alumina ceramic was heated for 24 h at 1,000°C in 40 vol% steam.

Key words: Amorphous alumina, Boehmite, Porous alumina, Nano pore, Catalyst.

Introduction

Nano porous alumina ceramics whose chemical composition is $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($0 < n < 0.6$) include very many pores in the range 30-1,000 Å and sufficient specific surface area between 100 and 400 m^2/g according to the manufacturing method. Also, if the total pore volume is about 0.3-1.1 ml/g, the surface chemical activity is very superior. Therefore, nano porous alumina ceramics are widely used as adsorbents and catalytic support [1, 3, 9-15]. A precursor for nano porous alumina ceramics may easily be obtained by calcination of pseudo-boehmite at 300-600°C [10, 15], and among the manufacturing routes for pseudo-boehmite, the most economical manufacturing method is to hydrate amorphous alumina with water [4, 5].

Generally, nano porous alumina ceramic precursor bodies of a spherical shape are prepared by a liquid phase granulation method or a rotating pan granulation method. The liquid phase granulation is a method where droplets of alumina sol are dropped in an oil bath. However, it is difficult to apply this method because amorphous alumina is so unstable thermodynamically. Generally, when amorphous alumina is forming with a spherical shape, the rotating pan granulation method which is a simple process is utilized. A amorphous

alumina can be obtained by flash calcination of gibbsite ($\text{Al}(\text{OH})_3$) within 3 s at 360-800°C, with a chemical composition of $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($0.2 < n < 1.0$). In this process, most of the gibbsite is decomposed into amorphous ρ -alumina, which includes small amount of χ -alumina, γ -alumina, and boehmite [4-6, 8, 11]. Flash calcined amorphous alumina powder has a particle size distribution between 60-120 μm . However, if the amorphous alumina powders are directly formed and hydrated, it is difficult to obtain nano porous alumina ceramic precursor bodies of a spherical shape with the superior physical properties because the formation of pseudo-boehmite is suppressed [2]. Thus, it is required that the amorphous alumina powders are ground to a particle size of 3 μm so that γ -alumina with a very high phase composition can be prepared. In the hydrothermal synthesis, precursor green bodies may be broken by the increase of volume which can happen due to crystal growth. To prevent this problem, it is desirable to mix appropriately a pore generating agent and the amorphous alumina powders in the forming process. The pore generation agent used must be a material that can be oxidized in the calcination process after hydration. When precursor green bodies are hydrated in a water chamber at 40-120°C, the reaction proceeds in the order of amorphous alumina + water and hydrated gel ($[\text{Al}(\text{H}_2\text{O})\text{OH}]^{2+}$) and pseudo-boehmite [11]. The nano porous alumina ceramic precursor bodies of a spherical shape are obtained after these green body pellets are hydrated, dried, and calcined. These precursor bodies

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can be used themselves as an adsorbent or catalytic support but have the disadvantages that the mechanical strength and thermal resistance are low and the pore volume is small.

In this study, to transform the precursor bodies with low physical properties into high-capacity nano porous alumina ceramics, they were hydrothermally treated under an acid gas atmosphere at high temperature and pressure [7]. To strengthen the bonding force, nitric acid was used, and to increase the pore volume of the precursor bodies, acetic acid as an anion donor which can combine with Al^{3+} ion was used. The immersion in the acid solution was achieved after putting the precursor bodies in a mixed solution of deionized water and acids and then immersing them under a vacuum atmosphere. At this time, the bodies were distilled under vacuum conditions until the weight of the acid solution was the same as that of the precursor bodies or a little higher than that of the precursor bodies. The precursor bodies that were immersed in the acid solution were then put in a pressure reactor. After the hydrothermal treatment at $200^{\circ}C$ for 3 h, drying, and calcination, we investigated various properties of the nano porous alumina ceramics; such as change of phase and formation, pore characteristics, mechanical strength, and thermal resistance.

Experimental Methods

Preparation of amorphous alumina powders

A stainless steel pipe of inside diameter 25 mm, length 940 mm in scale a furnace of 2.7 kW capacity with a fixed screen mesh inside the pipe and stainless steel balls 5.5 mm diameter to act as a solid heat carrier were packed to a height of 150 mm. The temperature of the packed bed was maintained continuously at $600^{\circ}C$ after heating to $600^{\circ}C$ at a rate of 10 K minute^{-1} . A 60 Hz vibrator was used to prevent the powders from stagnating on the pipe walls or between the balls, gibbsite powder was put in the stainless steel pipe at a rate of $10.56\text{ g minute}^{-1}$. The time the powder took to pass through the pipe was an average 2.86 s as a result of measuring 20 times with a microchronometer. If the powder fell freely according to Stokes Law, the powder passing through the pipe would obtain a falling rate of 3.04 ms^{-1} and it would take 0.456 s to pass through the 150 mm of stainless steel balls. However, the temperature of the packed bed was kept constantly at $580^{\circ}C$ from the bottom of bed to 80 mm, and the top of bed was approximately at $450^{\circ}C$ because the temperature became lower with increasing height of the bed. Therefore, it took 0.24 s for the powder to pass the point where was constantly kept at $580^{\circ}C$. The specific surface area of the amorphous alumina prepared by flash calcination was $280\text{ m}^2/\text{g}$, and the loss of weight was 11.70 wt % in heating the amorphous alumina at $800^{\circ}C$ for 2 h. Also, it was confirmed that gibbsite was

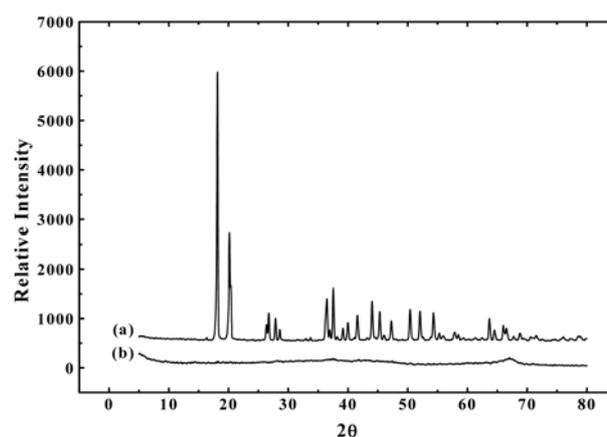


Fig. 1. XRD patterns of (a) gibbsite and (b) flash calcined alumina at $580^{\circ}C$.

decomposed to amorphous alumina by XRD patterns of Fig. 1.

Preparation of precursor bodies of a spherical shape

Powder with an average particle size of $3\text{ }\mu\text{m}$ was prepared by dispersing the amorphous alumina powder obtained by the flash calcination in an ethyl alcohol solution and wet pulverization the powder for 9 h. 10 wt% of activated carbon was added into the pulverized amorphous alumina powder and mixed with it. Spherical precursor green bodies of an average diameter 2 mm were manufactured by liquid phase cross-linking using

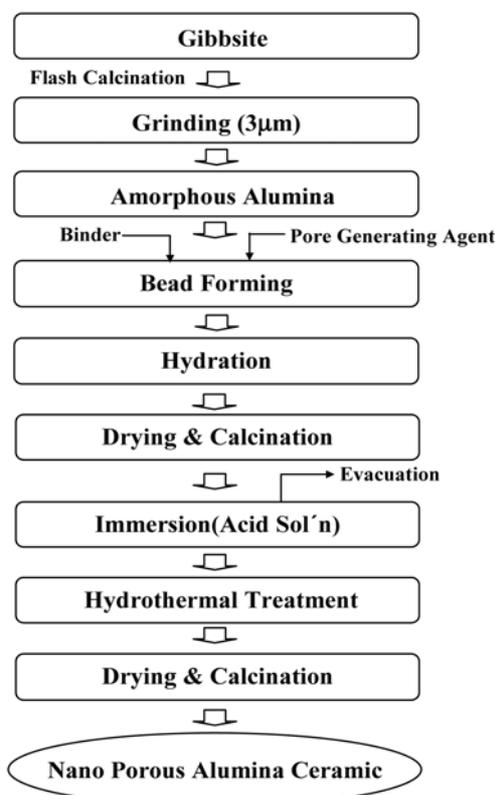


Fig. 2. Process diagram for the experimental procedure.

Table 1. Comparison of Physical Properties of the Alumina Bodies before and after the Hydrothermal Treatment

Analysis items	Before Hydro. Treat	After Hydro. Treat
Phase	γ	γ
BET surface area (m ² /g)	294	192
Pore volume (ml/g)	>10,000 Å	0.38
	5,000~10,000 Å	0.06
	1,000~5,000 Å	0.05
	100~1,000 Å	0.15
	<100 Å	0.40
Total	1.04	1.06
Crushing strength (MPa)	1.40	2.20
Thermal resistance 30~1,000 Å (ml/g) (1000 °C/24h, 40 vol% steam)	0.14	0.68
Phase	α	$\theta+\alpha$

deionized water as the binder in a rotating disc assembly reactor with a diameter of 400 mm. These green bodies were continuously ripened in moisture chamber at 120 °C for 1 h and then were hydrated in water at 90 °C for 5 h. Next, by drying them for 1 h at 150 °C and by calcining them at 650 °C for 2 h, precursor bodies used for the sample were manufactured (Fig. 2). The physical properties of the precursor bodies prepared by hydration of the amorphous alumina were given in Table 1.

Hydrothermal treatment

The mixed solution of 21.87% nitric acid and 28.57% acetic acid was prepared by mixing nitric acid and acetic acid with deionized water. This mixed solution and the precursor bodies were put in a rotary evaporator. The precursor bodies were immersed at room temperature for 3 h in a vacuum condition which removed the air from them completely. The rotary evaporator was heated to 60 °C maintaining the vacuum conditions. The mixed solution containing the precursor bodies was distilled until the weight ratio of acid solution to Al₂O₃ became 1.05. The sample was put in a glass bottle and sealed. After this the glass bottle was put in a high pressure reactor with water, the sample was hydrothermally treated at 200 °C for 3 h and condensed to 90 °C. We analyzed the change of the sample's properties by drying at 150 °C for 3 h and calcining at 650 °C for 2 h. All of the experimental procedures are given in Fig. 2. Table 1 lists the physical properties of hydrothermal treated the alumina ceramic bodies at 200 °C in acid/water vapor.

Analysis and observation

The particle size and particle size distribution of amorphous alumina powder was measured by a laser particle analyzer (Malvern Instruments SB). The change of crystal phase according to raw material and each

reaction condition was analyzed by X-ray diffraction (XRD: D/MAX-III B, Rigaku, Japan). To observe the change of crystal phase in the heating process, differential thermal analysis (DTA: TGA-2950, TA Instrument) was performed. The external form of particles and transition of crystals were investigated using scanning electron microscopy (SEM: JSM-840A, JEOL) and the fracture surfaces of alumina bodies were used to observe the morphology of particles and crystals. The specific surface area of the powder and alumina bodies were examined by the BET method (ASAP 2000, Micromeritics Instrument) and the pore size and the pore volume were measured by mercury infiltration (porosimeter, Autopore IV 9500 Micromeritics Instrument). The measurement of mechanical strength was performed by a grain crushing test (Geomechanic). After measured the breaking strengths of 20 units per sample, the mechanical strength was determined by averaging the all the value except for the maximum and minimum values among the measured values. The thermal resistance was investigated through the change of crystal and pore characteristics, for samples prepared before and after the hydrothermal treatment and measured at high temperature 1,000 °C for 24 h, in a gas mixture composed of 60 volume% N₂ gas and 40 volume% water vapor.

Results and Discussion

Changes of crystal type

As shown in Fig. 3(a), when spherical green bodies

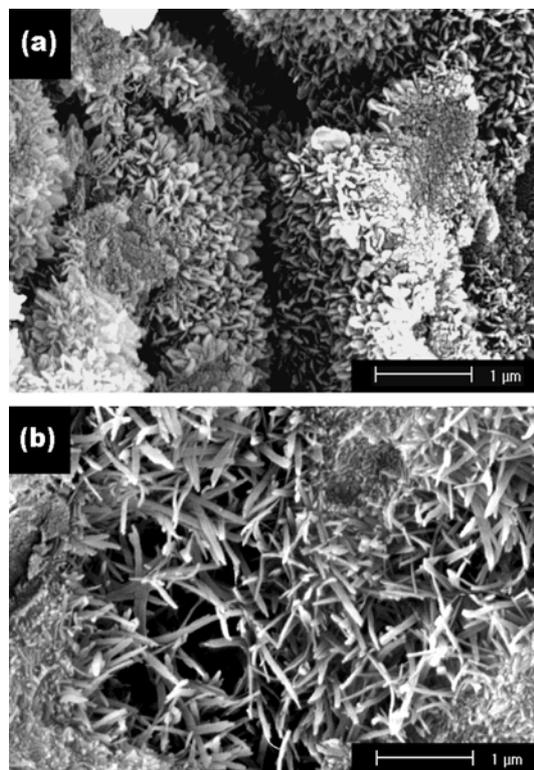


Fig. 3. SEM micrographs for a fragment of (a) an hydrated alumina body and (b) an hydrothermally treated alumina body.

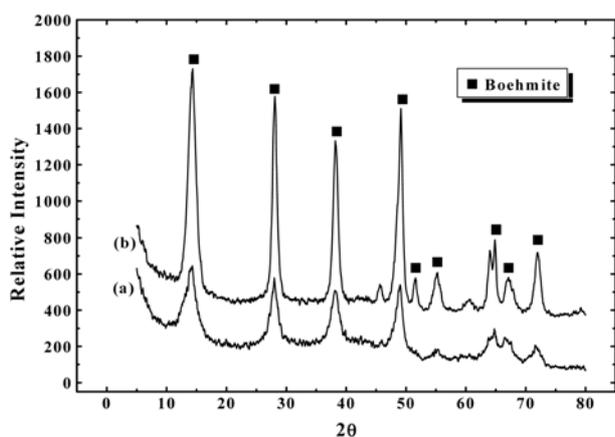


Fig. 4. XRD patterns of (a) an hydrated alumina body and (b) an hydrothermally treated alumina body.

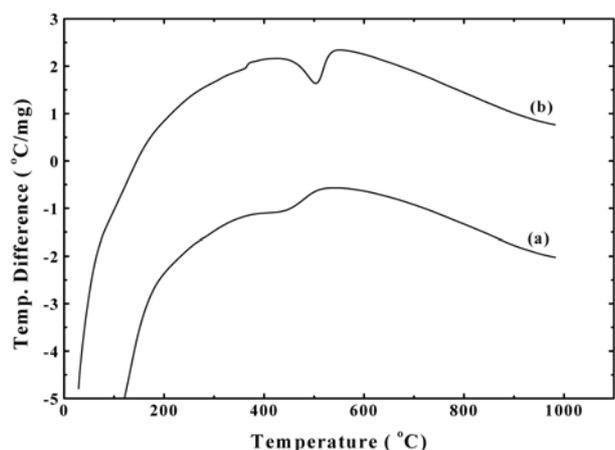


Fig. 5. DTA curves of (a) an hydrated alumina body and (b) an hydrothermally treated alumina body.

of 2 mm in diameter prepared by forming amorphous alumina were hydrated, acicular platelet crystals of pseudo-boehmite of about 0.1-0.3 μm are created around particles. Also, from the XRD patterns of Fig. 4(a) and DTA curves of Fig. 5(a), it can be found that bayerite did not transform into η -alumina at 293 $^{\circ}\text{C}$ and boehmite transformed into γ -alumina around 430 $^{\circ}\text{C}$. Figure 6(a) shows XRD patterns for the precursor body completely oxidized using activated carbon as the pore generating agent by calcining the hydrated sample at 650 $^{\circ}\text{C}$ for 2 h. This indicates that pseudo-boehmite is transformed into γ -alumina with a low diffraction intensity from this figure. The precursor bodies prepared by this method were hydrothermally treated at 200 $^{\circ}\text{C}$ in the acid solution.

Figure 3(b) shows that acicular platelet crystals of 0.1-0.3 μm were transformed into acicular boehmite crystals of 1-2 μm with a narrow width and long length. Also, the X-ray diffraction intensity of boehmite crystals increased due to crystal growth as shown in Fig. 4(b). The acetic acid used as an anion donor is dissociated and releases CH_3COO^- ions in the aqueous solution of the mixture of deionized water and acid.

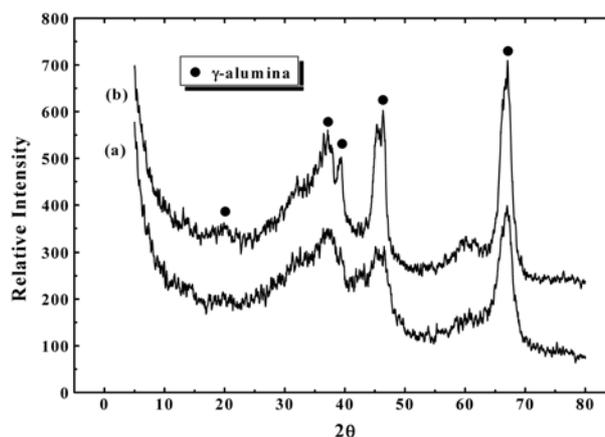


Fig. 6. Comparison of XRD patterns for the alumina bodies (a) before and (b) after the hydrothermal treatment.

When the precursor bodies were immersed in this solution and hydrothermally treated, aluminum basic salts were formed by combination of Al^{3+} cations with CH_3COO^- anions [7]. Aluminum basic salts were thermodynamically formed from the unstable amorphous hydrated gel by the action of water at an early stage of the hydrothermal synthesis. As the density increased by hydration under the control of temperature and time, the hydrated gel recrystallized gradually to stable acicular boehmite crystals. At this stage, it is necessary that the weight ratio of the acid solution to Al_2O_3 must be adjusted below 1.05 because the shape of hydrothermally treated alumina bodies collapses and adheres to each other when the weight ratio is over 1.05.

When the alumina bodies obtained by hydrothermal treatment of precursor bodies, γ -alumina, were calcined, as shown in Fig. 6(b), boehmite was transformed into γ -alumina increasing the X-ray diffraction intensity. From DTA curves of Fig. 5(b), these indicate that the strength of the endothermic reaction increases and the temperature of the phase transformation is increased to about 450 $^{\circ}\text{C}$. The changes of crystal type which occurred in the overall experimental procedure is summarized below.

Amorphous alumina \rightarrow pseudo-boehmite \rightarrow γ -alumina
 \rightarrow boehmite \rightarrow γ -alumina

As a result, we found that the hydrothermal reaction accompanies a reversible phase transformation between boehmite and γ -alumina.

Changes of pore volume

The alumina bodies prepared by the hydrothermal treatment of precursor bodies are expanded and the pore volume of them are enhanced because long acicular boehmite crystals are recrystallized and formed on the surface of particles in the hydrothermal treatment process. The diameter of bodies was measured by a micrometer after choosing samples of 30 units for each of the alumina bodies before and after the hydrothermal treatment. The diameter of the alumina bodies after the

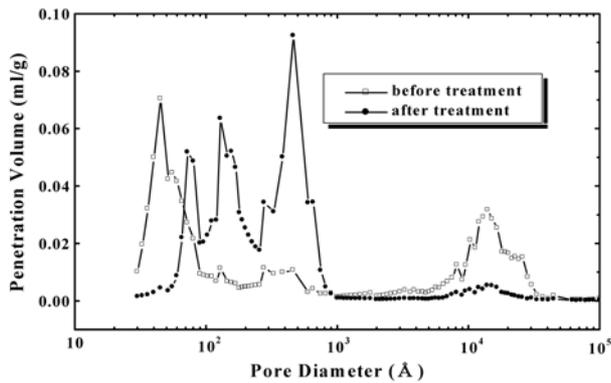


Fig. 7. Comparison of pore size distributions for the alumina bodies before and after the hydrothermal treatment.

hydrothermal treatment increased by as much as 5.33%, as a result of averaging samples of 20 units leaving out samples of 5 units from the highest and the lowest measurement values. When the precursor bodies obtained by the hydrothermal treatment were calcined again at 650 °C, the diameter of bodies shrunk by as much as 2.6%. Therefore the diameter of the alumina bodies were increased totally by as much as 2.73%. In this calcination process, the pores above 1,000 Å which arose from the oxidization of the pore generating agent are reduced by the crystal growth. Hence, the pores below 100 Å resulting from acicular platelet crystals of a small size disappeared by recrystallizing to long acicular boehmite crystals and most of the pores developed to be above 100 Å. Thus, the pore volumes between 100 Å and 1,000 Å were enhanced greatly with this increase of the volume of bodies as shown in Fig. 7.

Characteristics of N₂ adsorption

Figure 8 shows N₂ adsorption/desorption isotherms for the alumina bodies before and after the hydrothermal treatment. As shown in Fig. 7, the precursor bodies before the hydrothermal treatment have many fine pores below 100 Å, it is for the precursor bodies before the hydrothermal treatment that the specific surface area is high but the absorption capacity is low.

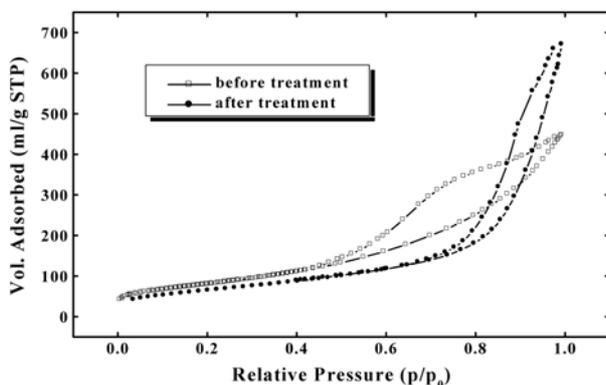


Fig. 8. Comparison of N₂ adsorption/desorption isotherms for the alumina bodies before and after the hydrothermal treatment.

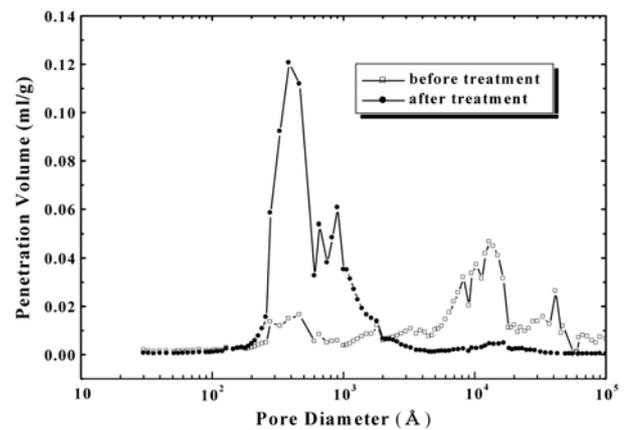


Fig. 9. Comparison of pore size distributions for the alumina bodies before and after the hydrothermal treatment, which were then thermally treated for 24 hours at 1,000 °C in 40 vol% steam.

Additionally, because a capillary condensation phenomenon occurs in the external fine pores, the hysteresis curves in which N₂ absorption/desorption isotherms do not correspond leads to extensive gaps in the hysteresis curves. In the case of the alumina bodies after the hydrothermal treatment, the specific surface area is decreased but the absorption capacity increased largely due to developing the pores between 100 Å and 1,000 Å. Because fine pores below 100 Å are few, N₂ absorption/desorption for the alumina bodies after the hydrothermal treatment performed well and the gap in the hysteresis curve is decreased.

Thermal resistance

Figure 9 shows the pore size distributions for the alumina bodies before and after being hydrothermally maintained in a moist atmosphere at high temperature. To investigate the thermal resistance, the alumina bodies before and after the hydrothermal treatment were placed in the quartz tube of a tube furnace simultaneously. The quartz tube was heated at a rate of 3 K minute⁻¹ up to 1,000 °C and was maintained at 1,000 °C for 24 h and supplied with a mixed gas of 60% volume N₂ and 40% volume steam. In this process, we found that most of the pores virtually disappeared for the alumina bodies before the hydrothermal treatment except for the pores that were formed by the pore generating agent. However, when the alumina precursor bodies were hydrothermally treated, the pores between 100 Å and 1,000 Å still existed. Also, Fig. 10 shows XRD pattern for the alumina bodies before and after the hydrothermal treatment of 24 h at 1,000 °C in 40 volume% steam. This indicates that the precursor bodies before the hydrothermal treatment were completely transformed into α -alumina. In the case of the alumina bodies after the hydrothermal treatment, part of the bodies was transformed into α -alumina but most of the alumina bodies sustained the crystal structure of θ -alumina. It is presumed that the long acicular boehmite crystals which

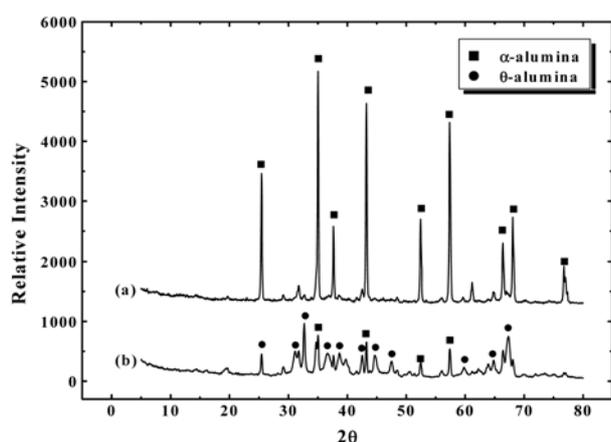


Fig. 10. Comparison of XRD patterns for the alumina bodies before and after hydrothermal treatment, which were then thermally treated for 24 hours at 1,000 °C in 40 vol% steam.

were recrystallized and formed in the hydrothermal synthesis were thermally more stable in crystal structure than acicular platelet crystals of a small size obtained by the hydration of amorphous alumina.

Mechanical strength

Nitric acid dissolves partially the surface of alumina particles and makes a colloid in the hydrothermal treatment process using high temperature and pressure. It is considered that this colloid works as a bonding agent combining alumina particles strongly and increases its abrasive resistance. Also, long acicular boehmite crystals are entangled with each other and form a strong solid bridge during growth, which greatly enhances the crushing strength of alumina ceramic bodies [1, 2]. In this process, if the alumina bodies as a precursor did not have sufficient pores, the space for crystals to grow would be lacking and the bodies would fracture from the excessive stress by volume expansion. Thus, it is important that sufficient pores are formed in alumina precursor bodies by using a pore generating agent.

Conclusions

Amorphous alumina powder obtained by flash calcination of gibbsite was mixed with 10 wt% activated carbon and formed into alumina precursor spherical green bodies and these bodies were hydrated, pseudo-boehmite with acicular platelet crystals of 0.1-0.3 μm were generated. The precursor bodies prepared by calcination of the precursor green bodies at 650 °C had a bimodal pore distribution coexisting below 100 and

above 1,000 Å. These precursor bodies were immersed in an aqueous solution of a mixture of nitric and acetic acids and were hydrothermally treated at 200 °C. Acicular platelet crystals of 0.1-0.3 μm were recrystallized to acicular boehmite crystals of 1-2 μm. Besides, the pore volume between 100 and 1,000 Å was enhanced by as much as 0.62 ml/g, and the N₂ adsorption capacity increased by as much as 220 ml/g. Even if the hydrothermal treated and calcined alumina ceramic bodies were kept for 24 h at 1,000 °C in a gas mixture containing 40 volume% steam, the pore volume between 100 and 1,000 Å decreased by as much as 11.6% from 0.77 ml/g to 0.68 ml/g since the corruption of pores was suppressed by the pore expansion. Also, part of the alumina ceramic bodies was transformed into α-alumina, but most of them preserved the crystal structure of θ-alumina indicating a high thermal resistance. The crushing strength was increased greatly to 2.2 MPa while the alumina precursor bodies before the hydrothermal treatment had a crushing strength of 1.4 MPa.

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