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Synthesis of AlN powder from $Al(OH)_3$ by reduction–nitridation in a mixture of NH_3–C_3H_8 gas

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Abstract

Aluminum nitride (AlN) powders were synthesized by gas-reduction–nitridation of aluminum hydroxide ($Al(OH)_3$) powders using a mixture of NH_3 and C_3H_8 gases. A high conversion to AlN (over 70% of naitridation ratio) and single-phase AlN were achieved over 1200 °C. The specific surface area of the products decreased with increasing of reaction temperature and soaking time, and products obtained contain much lesser oxygen than those of the previous researches. The reason why such nanosized AlN powders were easily obtained from $Al(OH)_3$ was considered to be the higher surface areas of transition alumina formed by dehydration of $Al(OH)_3$ during firing.

Keywords: Powders-solid state reaction; $Al(OH)_3$; Al_2O_3; Nitrides; ALN

1. Introduction

Aluminum nitride (AlN) has excellent properties for using as an electronic packing due to its high electrical insulation, high intrinsic thermal conductivity (~320 Wm^{-1} K^{-1}), and low thermal expansion coefficient, which is close to that of Si. It is important to establish a low-cost process for the production of AlN powder with high-purity and high sinterability.[1,2] Several researchers have been investigating the preparation of high-purity AlN powders from various precursors such as aluminum citrate,[3] $(NH_4)_3AlF_6$,[4] aluminum polynuclear complexes[5] and aluminum sulfide[6] and have reported that reactivity strongly depends on the starting materials. However, referred to above, such as aluminum oxide precursors is often prepared from specialized apparatus and process in many cases.

On the other hand, aluminum hydroxide ($Al(OH)_3$) is commonly produced through the Bayer process and is widely utilized in industrial field, e.g. flame retardants, pigments and pharmaceuticals.[7] Generally, It is possible to get $Al(OH)_3$ powders at much lower prices than other typical aluminum sources such as γ-Al_2O_3 and α-Al_2O_3 of the similar grade since they are mostly produced from $Al(OH)_3$. It is therefore, desirable, to develop a process for the synthesis of AlN from $Al(OH)_3$ which has a economic advantage.

$Al(OH)_3$ has demonstrated the high reactivity as a starting material in the previous study. Carbothermal reduction–nitridation (CRN) of $Al(OH)_3$ used as a starting material has received considerable attention, which concluded that the nitridation reaction rate from $Al(OH)_3$ was higher than that from conventional α-Al_2O_3[8–11] and the resultant AlN had low oxygen content.[11] $Al(OH)_3$ fabricated by CRN was systematically investigated, however, the problem of the previous studies is that it needs high temperature (above 1500 °C) and long time firing for the synthesis of AlN.

More recently, Kroke et al.[12] used several kinds of aluminum oxide precursors including $Al(OH)_3$ as starting materials, and reported that the aluminum oxide precursors reacted with NH_3 atmospheres at 1000–1400 °C to form single-phase AlN with crystallites of 5–60 nm. Suehiro et al. also synthesized AlN nano particles[13] and fibers[14] from commercialized transition alumina using NH_3 and C_3H_8. Up to 95% of Al_2O_3 was converted to AlN at 1300 °C. They claimed that not only nitridation at the low temperatures was progressed but also the morphology of the starting material maintained after the

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reaction. It seems that reaction of $Al(OH)_3$ with ammonia should be better technique for the preparation of AlN powder at low temperature and short time. In order to produce the AlN ceramics with dense sintered body and high thermal conductivity, it needs to prepare AlN particles with low oxygen content and to complete the nitridation before the promotion of grain growth.

In this paper, AlN powders were prepared from $Al(OH)_3$ by reduction–nitridation in NH_3 and C_3H_8 gas mixture, and to clarify the changes in the morphology and the phase present during the nitridation process.

2. Experimental

$Al(OH)_3$ powder (C-301, Sumitomo Chem. Co., Tokyo) composed of gibbsite (γ-$Al(OH)_3$) was used as a starting material. The average particle size and specific surface area of powder respectively were about 1 μm and 6 $m^2\ g^{-1}$. The main characteristic of the raw powder is summarized in Table 1.

The raw powder was weighted, placed in a high-purity alumina boat. Then, the boat was set in a tube furnace, followed by letting Ar gas (99.999% purity) flow in order to eliminate oxygen in the system. When the temperature was reached at 700 °C, the flowing gas was switched to the gas mixture of NH_3 (99.999% purity) and 0.5 vol.% C_3H_8 (99.99%) with a predetermined proportion at the flow rate of 4 L/min.

The sample was continuously heated to the reaction temperature of the 1000–1400 °C at the 8 °C/min for 0–120 min. Then, it was cooled down in NH_3 atmosphere. Phases present in the products were indentified by X-ray diffractometry system (XRD; RINT2500, Rigaku, Tokyo Japan) using Cu Kα radiation. Morphologies were observed by scanning electron microscopy (SEM; JSM-5200, JEOL, Tokyo Japan). Specific surface areas of the powders were measured by the single-point of Brunauer–Ematt–Teller (BET; Quantasorb, Quantachrome, Boynton Beach, FL, USA) method. Furthermore, the extent of nitridation was calculated from weight change by oxidation of the resultant powder in air with thermogravimetry[15] (TGA; TG-8120, Rigaku, Tokyo, Japan).

Oxygen contents were measured by oxygen/nitrogen analyzer based on infrared absorbance technique (EGMA-650, HORIBA) after correcting calibration curve of standard samples. Short-term contact of products with ambient air was performed to avoid the oxygen by vacuum-encapsulate of sample case.

Table 1
Characteristics of the raw $Al(OH)_3$ powder

Characteristic	Powder
Purity (%)	>99.6
Crystalline phase	γ-$Al(OH)_3$
Specific surface area ($m^2\ g^{-1}$)	6
Mean particle size (μm)	1.0
XRD crystallite size (nm)[a]	51
Transition to α-Al_2O_3 (°C)[b]	1293

[a] Calculated from the γ-$Al(OH)_3$ (0 0 2) peak.
[b] Determined by differential thermal analysis.

3. Results and discussion

Fig. 1 shows the XRD patterns of the raw material and the products. In comparison with JCPDS cards, χ-Al_2O_3 (JCPDS 13-373) and γ-Al_2O_3 (JCPDS 10-425) were identified in the product fired at 700 °C in Ar flow. It is well known that there are two dehydration routes in γ-$Al(OH)_3$[16] during heating as shown in Fig. 2. The transformation of metastable γ-$Al(OH)_3$ to stable α-Al_2O_3, obtained though high temperature treatments, is well known. All the transition phases are stable at room temperature but the sequence of transformation was not reversible with decreasing temperature. One is that $Al(OH)_3$ was dehydrated at low temperatures to form boehmite (γ-AlOOH), which became γ-Al_2O_3. It is known that other parts of γ-$Al(OH)_3$ directly changes into χ-Al_2O_3.[16–21] Therefore, transformation of the raw $Al(OH)_3$ powder used in this study seems to be appropriate. Fig. 3 shows SEM photographs of

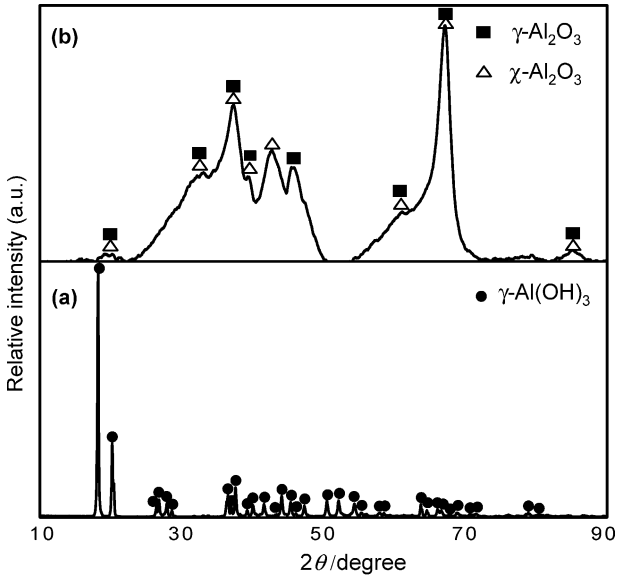

Fig. 1. XRD patterns of the (a) raw material and (b) the product fired at 700 °C in Ar.

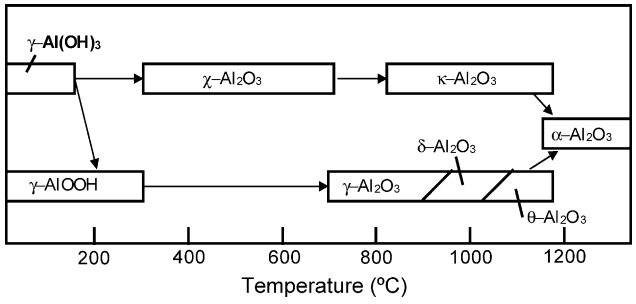

Fig. 2. Thermal dehydration routes of γ-$Al(OH)_3$ to α-Al_2O_3[16].

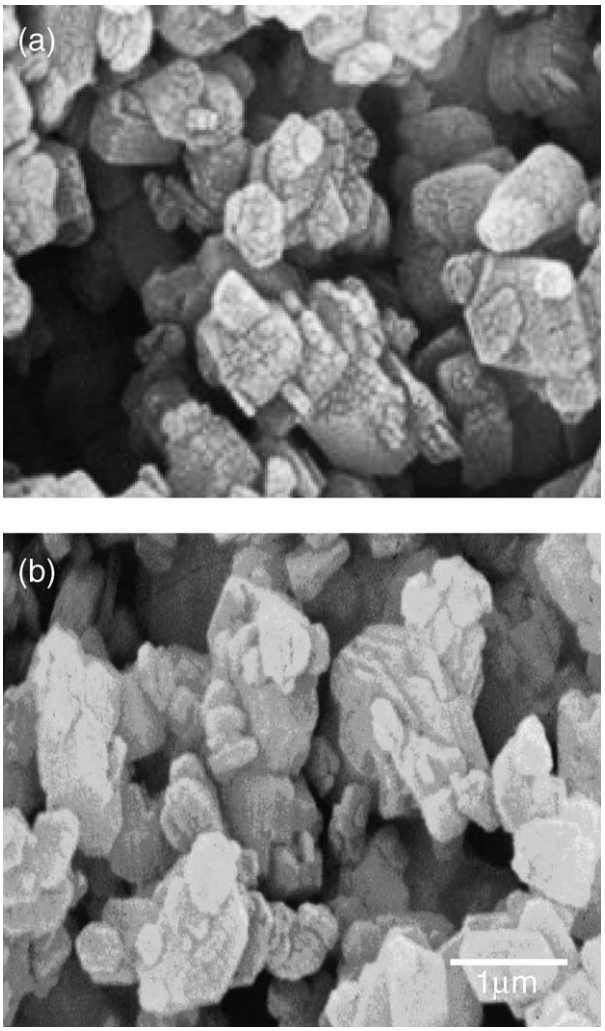

Fig. 3. SEM photographs of the (a) raw material and (b) the products fired at 700 °C in Ar.

the raw material and the products synthesized at 700 °C. Appearance of the sample did not change before and after firing. However, the specific surface area of the product was 330 $m^2\,g^{-1}$, which was much higher value than 6 $m^2\,g^{-1}$ of the raw $Al(OH)_3$. The high value seems to be attributed to the fine pores formed during dehydration.

Fig. 4 shows the XRD patterns of the resultant powders fired at the temperature in the range from 1100–1400 °C for 120 min. It was found that the products fired at 1100 °C contained a small amount of unreacted γ-Al_2O_3. Furthermore, at 1200 °C, α-Al_2O_3 was detected in the sample. AlN was the only identified phase in the products synthesized over 1300 °C in the NH_3–C_3H_8 mixed gas flow. Taking it into consideration that Al_2O_3 remains even in the product fired at 1400 °C in Al_2O_3–N_2–C system, it can be concluded that not only using $Al(OH)_3$ but also reduction–nitridation in a mixture of NH_3–C_3H_8 gases has an extremely effect on the enhancement of formation of AlN powder. XRD patterns of the products fired in NH_3–C_3H_8 at various temperatures without soaking time were shown in Fig. 5. In spite of firing at

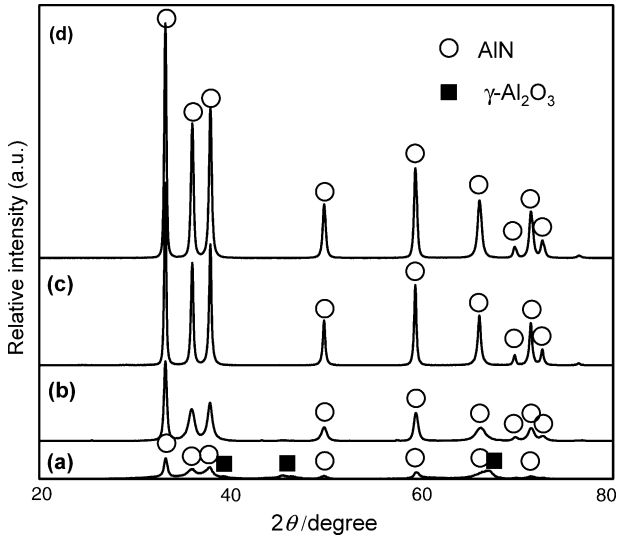

Fig. 4. XRD patterns of the products synthesized at: (a) 1100 °C; (b) 1200 °C; (c) 1300 °C; and (d) 1400 °C for 120 min.

high temperatures, little α-Al_2O_3 was formed γ and χ-Al_2O_3 remained in the products. The result suggested that AlN was generated from not α-Al_2O_3 but γ and χ-Al_2O_3.

Fig. 6 shows nitridation ratio of the products. It was found that the nitridation started at 1100 °C although AlN was not able to be confirmed from XRD pattern. This temperature is much lower than that of the previous paper.[22] In the sample of fired at high temperatures for long soaking time, nitridation ratio did not reach 100%. Such a lower nitridation ratio probably resulted from aluminum hydroxide species formed by the reaction between AlN with high surface area (shown in Fig. 8) and oxygen in air. However, the presence of such a surface oxide layer on the AlN particles could not be confirmed by XRD.[13,23]

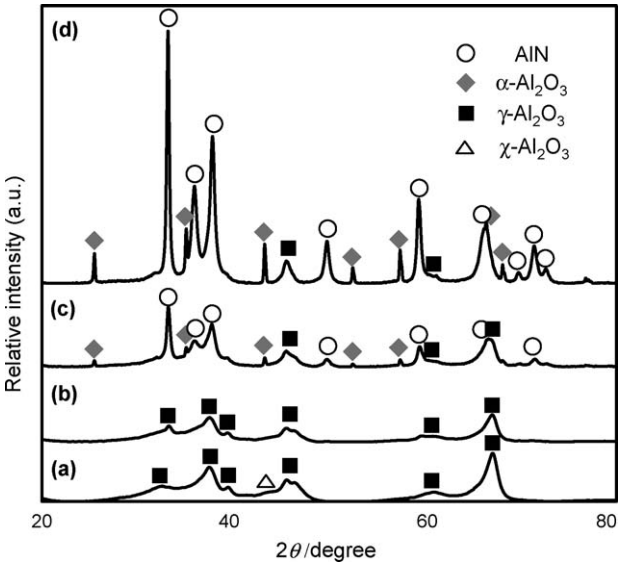

Fig. 5. XRD patterns of the products synthesized at 1000–1400 °C without soaking time: (a) 1100 °C; (b) 1200 °C; (c) 1300 °C; and (d) 1400 °C.

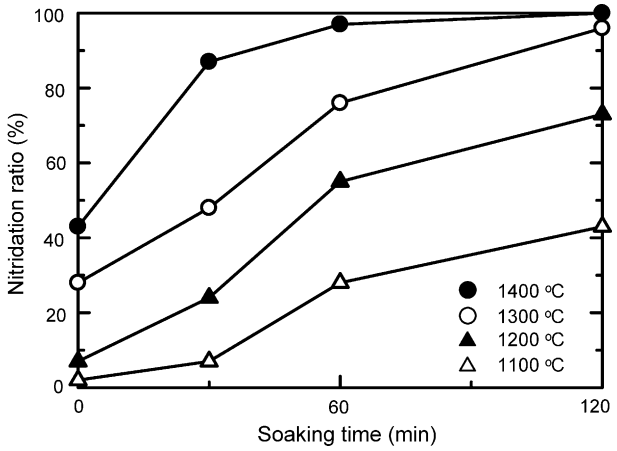

Fig. 6. Nitridation ratio of the products synthesized at 1100–1400 °C.

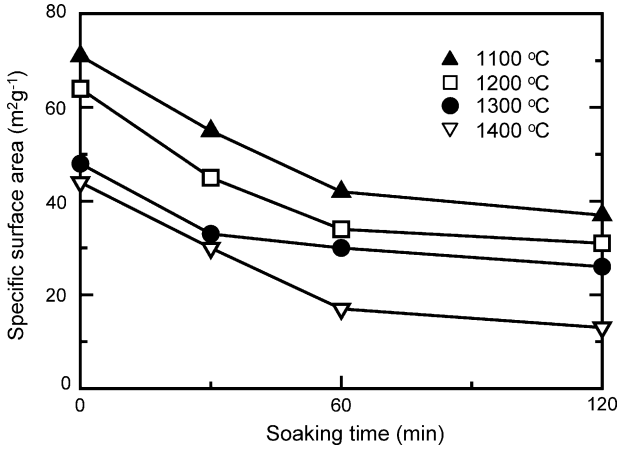

Fig. 8. The specific surface areas of the products synthesized at various temperature for 0–120 min.

Fig. 7 shows SEM photographs of the products synthesized at the temperatures in the range of 1100–1400 °C for 120 min. It was observed that the product was composed of nanosized composites particles, of which size increased with an increase in the firing temperature. Grain growth and coalescence of nano particle was observed in the sample of produced at 1400 °C (Fig. 7d).

The specific surface areas of the products measured by the single-point BET method are plotted in Fig. 8. The specific surface area decreased with increasing in the reaction temperature and soaking time. For example, the specific surface area of the products changed from 37 to 13 $m^2\ g^{-1}$ as the firing at 1100–1400 °C for 120 min. However, these values are much higher than that of commercialized AlN powders. The reason for formation of such fine grained AlN powders easily from $Al(OH)_3$ is considered to be based on high surface area of transition alumina changed from the hydroxide and high reactivity of a mixture of NH_3–C_3H_8 gases.

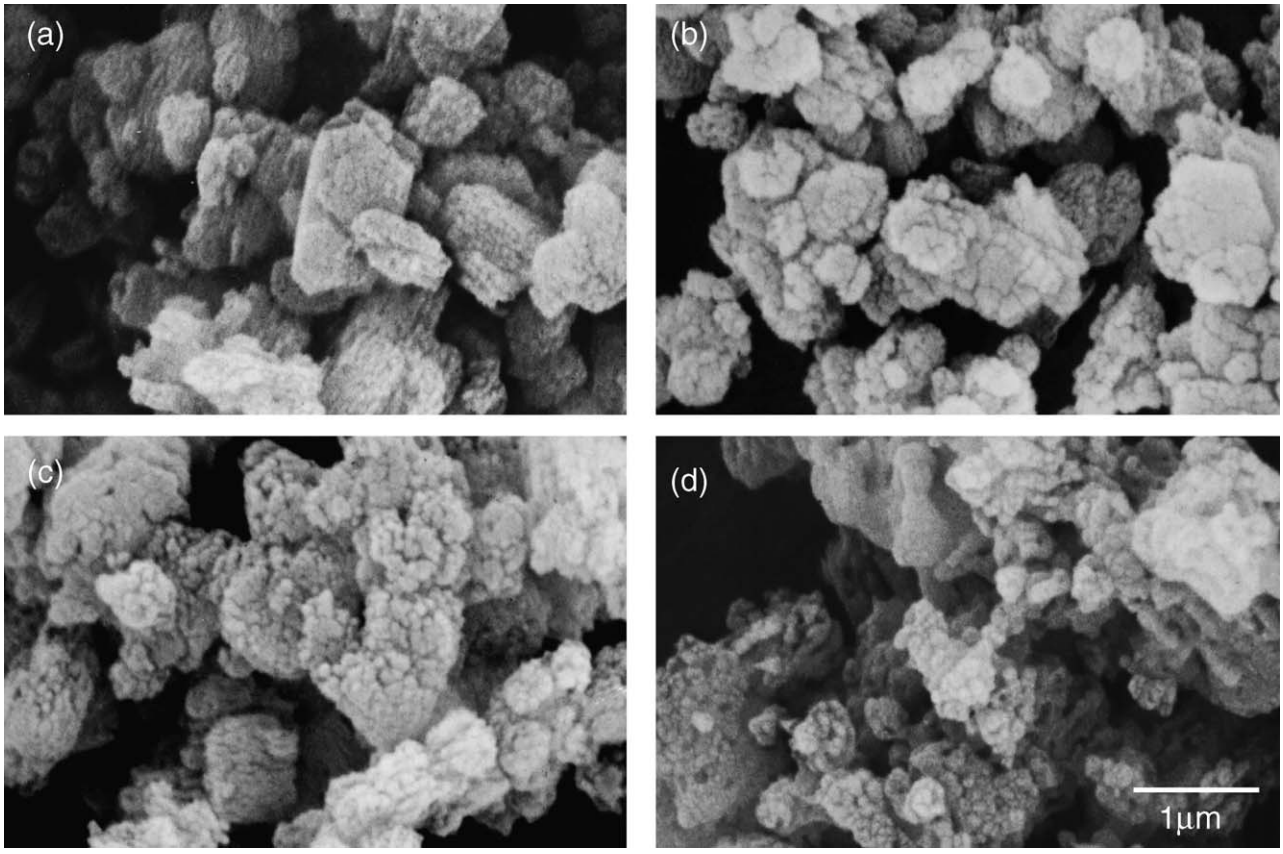

Fig. 7. SEM photographs of the products synthesized at: (a) 1100 °C; (b) 1200 °C; (c) 1300 °C; and (d) 1400 °C for 120 min.

Table 2
Comparison of A1N powders produced from $Al(OH)_3$ and Al_2O_3

Raw material	Synthesis method	Temperature (°C)	Soaking time (h)	Oxygen content (w%)	SSA (m^2/g)	Particle size (nm)	Remarks
γ-$Al(OH)_3$	NH_3—C_3H_8	1400	2	1.6	12.7	144[a]	This study
			1	1.9	17.6	104[a]	
		1300	2	3.1	25.7	71[a]	
γ-AlOOH	CRN[b]	1400	4	17.0	N/A	N/A	Mitomo et al.[10]
		1500	8	3.1	N/A	N/A	
γ-$Al(OH)_3$	CRN[b]	1500	5	1.9	N/A	N/A	Tsuge et al.[11]
γ-Al_2O_3		1550	5	1.5	N/A	N/A	
γ-$Al(OH)_3$	NH_3	1400	2	2.5	N/A	∼60[c]	Kroke et.al.[12]
γ, δ-Al_2O_3	NH_3—C_3H_8	1400	1	4.1	19.7	93[a]	Suehiro et al.[13]

[a] BET particle size.
[b] Carbothertnal reduction–nitridation.
[c] Measured by TEM observation.

Results of this study and previous studies are summarized on Table 2. It is shown that oxygen content decreased with increasing reaction temperature. Oxygen content of the powder obtained was lower than that prepared by CRN method using $Al(OH)_3$ and Al_2O_3 powders which are finer than that used in study.[10,11] Furthermore, AlN powder obtained comparatively had oxygen content lower than those prepared by the same techniques using the NH_3.[12,13] The low oxygen content of the particle is considered to be due to the high reactivity of the resultant Al_2O_3 with high surface area formed from $Al(OH)_3$. It can be concluded that $Al(OH)_3$ as a raw material is most suitable for the preparation of pure AlN particles with low oxygen content.

4. Conclusion

γ-$Al(OH)_3$ powders was heat treated at 700 °C with Ar atmosphere. As a result, it was confirmed that transition alumina with high specific surface area was obtained depending on a phase transition. AlN powders were synthesized from $Al(OH)_3$ as a starting material applying with the NH_3–C_3H_8 mixed gases. The single-phase AlN powder was obtained at 1300–1400 °C. It was found that the generated transition alumina began to nitride at 1100 °C. AlN powder with low oxygen contents and fine particle size could be synthesized by NH_3–C_3H_8 system from $Al(OH)_3$.

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