Synthesis of Aluminum Nitride Powder from Aluminum Hydroxide by Carbothermal Reduction-Nitridation

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알루미나 수화물로부터 탄소환원질화법에 의한 질화알루미늄 분말의 합성

황진명 · 정원중 · 최상욱

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ABSTRACT

In this study, AlN powder of fine particle size and of high purity was synthesized by the carbothermal reduction-nitridation of monodisperse, spherical $Al(OH)_3$ which had been prepared by sol-gel method using $Al(O-sec-C_4H_9)_3$ as the starting material. Depending on the mixing order and kinds of reducing agents, the optimum condition for the preparation of AlN was determined as follows. AlN single-phase was produced by the carbothermal reduction-nitridation of (1) Benzene-washed $Al(OH)_3$ and the reducing agent, carbon, which was mixed in a ball mill: for 5 hours at 1400°C under NH_3 atmosphere; (2) The mixture prepared by hydrolysis of alkoxide solution into which carbon had been dispersed beforehand: for 5 hours at 1350°C; (3) $Al(OH)_3$ Poly(furfuryl alcohol) composite powder: for 2.5 hours at 1350°C, (4) The mixture of $Al(OH)_3$ and polyacrylonitrile: for 5 hours at 1400°C. Addition of CaF_2 increased the nitridation rate when carbon or polyacrylonitrile was used as the reducing agent; but it had no effect on the nitridation rate when furfuryl alcohol was used as the reducing agent.

요   약

본 연구에서는 $Al(O-sec-C_4H_9)_3$를 출발물질로 하여 졸-겔법으로 제조한 구형의 단분산 알루미나 수화물을 탄소환원질화반응시켜 미립의 고순도 질화알루미늄 분말을 합성하였다. 이때 사용한 환원제의 혼합순서 및 종류에 따라 최적의 열처리 조건이 다음과 같이 달라졌다. 즉, (1) 환원제로서 탄소를 사용하여 벤젠으로 세척한 알루미나 수화물과 볼밀로 혼합하여 암모니아 분위기하에서 1400°C에서 5시간 (2) 탄소를 미리 알콕사이드 용액에 넣은 다음 가수분해시켜 얻은 혼합물을 1350°C에서 5시간, (3) 환원제로 탄소 대신에 furfuryl alcohol을 첨가하여 얻어진 알루미나 수화물과 고분자 물질의 복합체를 1350°C에서 2.5시간 또는 polyacrylonitrile을 사용한 혼합물을 1400°C에서 5시간 동안 각각 질화반응시킴으로써 단일상의 질화알루미늄을 얻을 수 있었다. 환원제로 탄소와 polyacrylonitrile을 사용할 때 반응촉진제로서 CaF_2를 넣을 경우 모두 질화반응이 촉진되어 반응시간이 단축되었으나 furfuryl alcohol을 사용한 경우에는 영향이 없었다.

1. Introduction

Aluminum nitride (AlN) is very useful material in the field of electronics technology. It is expected to be applied for IC packages and substrates owing to its high thermal conductivity (200 W/m·k) which is 5~6 times higher than that of Al_2O_3, high electrical resistivity (R.T.>10^3 Ωcm), and low thermal expansion coefficient (4.4×10^{-6}/°C). But since the thermal conductivity of AlN decreases rapidly by the existence of even small amount of impurities, high-purity starting material is necessary. Also, to enhance the sinterability, it

is essential to use powder having a fine particle size, a narrow particle size distribution, and minimal agglomeration[1-4].

AlN powder is usually synthesized by the carbothermal reduction-nitridation of α-Al₂O₃ and this reaction needs the high temperature above 1600℃[5,6].

The Al(OH)₃ powder prepared by sol-gel method[7], on the other hand, has several desirable properties such as good reactivity due to high specific surface area, high purity, and controlled particle morphology. Therefore this powder may be caused to reduce the reaction temperature. Unfortunately, previous studies[8,9] about synthesis of AlN by this process were not performed systematically and they do not provide sufficient information on the effects of various experimental variables such as the kinds of reaction gas and/or starting material, kinds and mixing order of the reducing agents, reaction temperature, reaction time and additives.

In this work, monodisperse, spherical Al(OH)₃ prepared by sol-gel method was subjected to the carbothermal reduction-nitridation to produce AlN powder at low temperature and, at the same time, the effects of experimental variables mentioned above on nitridation reaction were investigated. Also, the effect of additive, CaF₂ to the various systems[Al(OH)₃-reducing agents-NH₃] on nitridation reaction rates was investigated.

2. Experimental procedure

2.1. Preparation of Al(OH)₃ by hydrolysis of Al(O-sec-C₄H₉)₃

Monodisperse, spherical Al(OH)₃ was prepared via sol-gel process reported previously by Oghihara *et al.*[10]. First, 0.05 mol/l Aluminum sec-butoxide* (Al(O-sec-C₄H₉)₃, ASB) was dissolved in n-octanol** (50 vol%) at 60℃ and this solution was mixed with acetonitrile** (40 vol%) and hydroxypropyl cellulose** (HPC) which was used as dispersant. Deionized water (molar ratio of H₂O/alkoxide=4) diluted in n-octanol (9 vol%)-butanol** (1 vol%) was added to the alkoxide-octanol-acetonitrile-HPC solution. In the mixed solution, the concentration of octanol, butanol, and acetonitrile were 59,

*: Alfa Co. 99%
**: Aldrich Co., Reagent

40, and 1 vol%, respectively.

Precipitation occurred quickly and the particles precipitated in the solution were aged for 5 hours in a water bath maintained at 25℃. The precipitated particles were separated from the solvent using a centrifuge and then dried at 110℃ for 24 hours.

2.2. Synthesis of AlN by the carbothermal reduction-nitridation

Al(OH)₃ thus obtained was subjected to the carbothermal reduction-nitridation as follows to produce AlN; (1) mixing Al(OH)₃ with carbon by ball mill, (2) addition of carbon before the hydrolysis of alkoxide, (3) using furfuryl alcohol and polyacrylonitrile as a reducing agent, (4) using additive, CaF₂.

2.2.1. Sample preparation

2.2.1.1. Mixing Al(OH)₃ with carbon by ball mill

As the starting materials, Al(OH)₃, benzene-washed Al(OH)₃, calcined γ-Al₂O₃ and α-Al₂O₃ were selected. Carbon black (99.93%) was used as a carbon source. The starting material and carbon were mixed in 1 : 14 molar ratio. These powders and carbon were mixed by wet ball mill using plastic pot with alumina balls. And then, powder mixture was dried at 100℃. As the reaction gas, N₂ gas, gas mixture of N₂/10%H₂, or NH₃ gas were used.

2.2.1.2. Addition of carbon before the hydrolysis of alkoxide

The ratio of carbon to alkoxide was controlled in an atomic ratio, Al/C=1 : 7. The carbon powder was uniformly dispersed in acetonitrile by applying ultrasonic vibration. This was mixed with 0.05 mol/l ASB/n-octanol solution. Deionized water (molar ratio of H₂O/alkoxide=4) diluted in n-octanol-butanol was subsequently added to alkoxide solution at the rate of 0.5 ml/min. The precipitates formed by the hydrolysis of alkoxide were aged at 25℃ and separated from the solvent using a centrifuge. And then, the as-prepared powders were dried

2.2.1.3 Using furfuryl alcohol and polyacrylonitrile as a reducing agent, and using additive, CaF₂

When furfuryl alcohol** (C₄H₃O(CH₂OH)) was used, the sol was formed by dispersing Al(OH)₃ ultrasonically in dilute nitric acid (1 ml of HNO₃ in 90 ml of H₂O). Furfuryl alcohol(molar ratio of furfuryl alcohol/Al(OH)₃ =4) was dissolved in the sol, which began to darken

because of the polymerization. The reaction vessel was placed in an oven 100℃ for 24 hours. A black, solid product was ground to powder.

When polyacrylonitrile** (PAN) was used, PAN was dissolved in dimethylformide** (DMF) and to the resultant solution was added Al(OH)₃ (PAN/Al(OH)₃=4 : 1 in weight ratio). After Al(OH)₃ powder was ultrasonically dispersed, sol was dropped into water. At this time dimethylformide dissolves into water, and powder consisting of PAN and Al(OH)₃, precipitates. The precipitates were separated by vacuum filtration.

To investigate the effect of additive, CaF₂ on nitridation reaction rate, the samples from different reducing agents and CaF₂ were mixed by wet ball milling for 24 hours. The content of CaF₂ was fixed at 3 wt%.

2 2.2 Nitridation reaction

The prepared powder mixture above was placed on an alumina boat, which was inserted into the middle of mullite tube and heated up at 1000℃ to 1400℃ in flowing reaction gas (flowing rate, 100 m*l*/min). Residual carbon in each product was burned out at 700℃ for 2 hours in air. Fig. 1 shows the flow chart of this experiment.
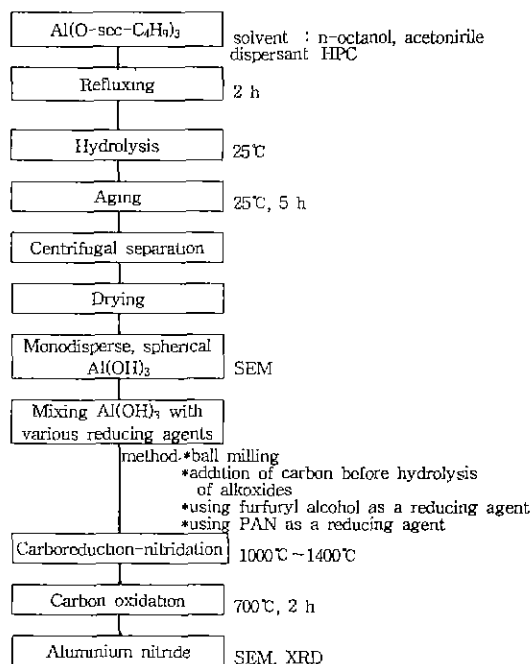
2.3. Powder characterization

The powder morphology of Al(OH)₃ and AlN were observed by the SEM and the particle size distributions of Al(OH)₃ were measured by the laser particle size analyser. Tthe degree of nitridation reaction with reaction condition was investigated by the XRD.

3. Results and Discussion

3.1. Preparation condition of Al(OH)₃ powder

For the synthesis of AlN powder having fine particle size and high purity, the optimum condition for the preparation of monodisperse. spherical Al(OH)₃ powder was determined by the variation of factors such as ASB/H₂O molar ratio, hydrolysis water adding rate, aging temperature and time.

The optimum condition found in this study are as follows; ASB/H₂O molar ratio 1 : 4; hydrolysis water adding rate, 0.5 m*l*/min; aging temperature, 25℃ ; and aging time; 5 hours. This powder having spherical shape is shown in Fig. 2. The mean particle size of 1.1 µm and a narrow particle size distribution mainly within the range of 0.3~3 µm is observed in Fig. 3.

3.2. Mixing Al(OH)₃ with carbon by ball mill

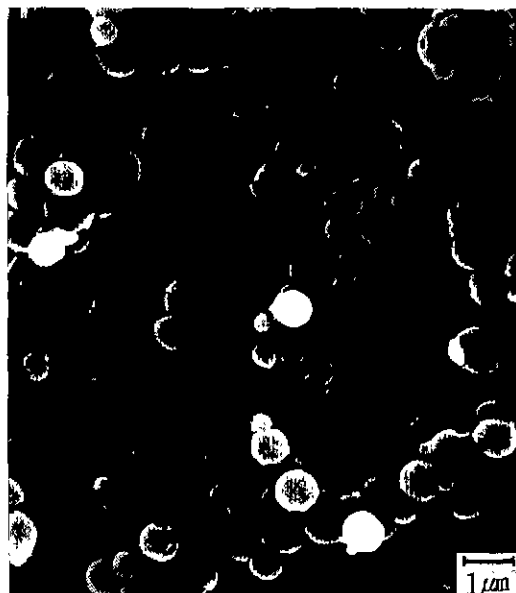**Fig. 1.** Flow chart of experimental procedure for the synthesis of AlN and its characterization.

Fig. 2. SEM photographs of aluminum hydroxide precipitated by the hydroysis of Al(O-sec-C₄H₉)₃.
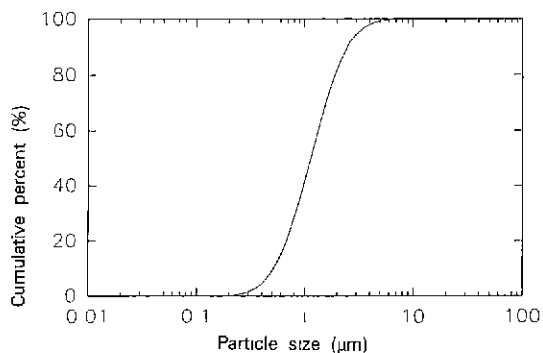
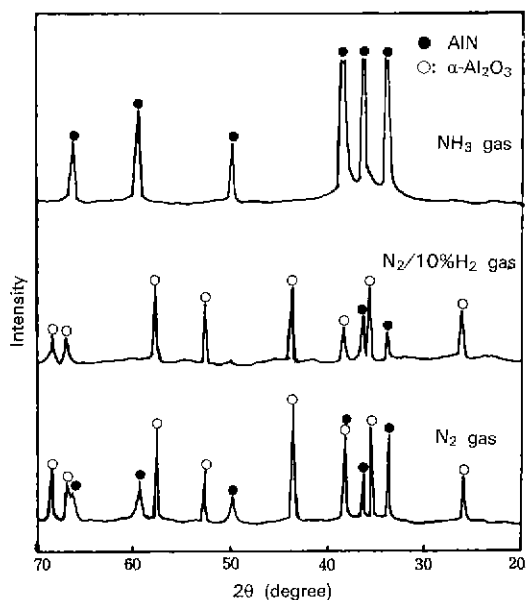Fig. 3. Cumulative distribution for particle size analysis of aluminum hydroxide.

Fig. 4. XRD patterns representing the effect of reaction gases on nitridation reaction at 1400℃ for 5 h.

Fig. 5. Relative intensity of main peaks of Al_2O_3 and AlN in the XRD patterns vs. reaction temperatures.

3.2.1. Effect of reaction gas on nitridation reaction

After the prepared $Al(OH)_3$ and carbon were mixed by ball milling, the powder mixture was subjected to the carbothermal reduction-nitridation in flowing reaction gas at 1400℃ for 5 hours. At this time, to investigate the effect of reaction gas on nitridation, three kinds of reaction gases-N_2 gas, gas mixture of $N_2/10\%H_2$, and NH_3 gas-were selected.

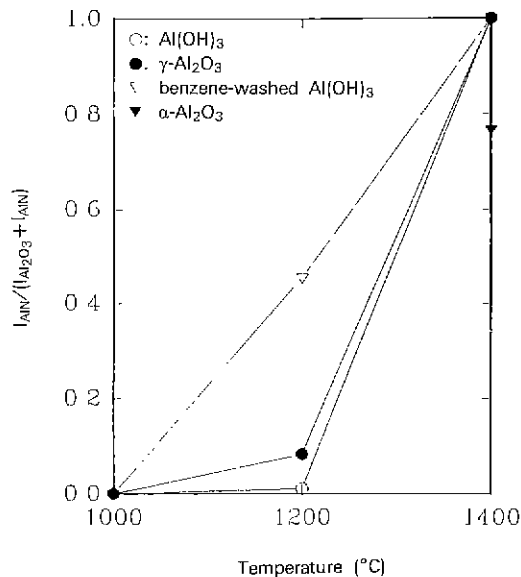Fig. 4 shows XRD patterns of samples produced by the variation of reaction gas. When N_2 gas or gas mix-

ture of $N_2/10\%H_2$ was used, AlN peaks were detected but mainly α-Al_2O_3 remained. On the other hand, only AlN single-phase existed when NH_3 gas was used. It is assumed that the reaction was promoted by the decomposition[11] of NH_3 as it would create an environment of highly reactive nitrogen species.

From this result, NH_3 gas was found to have good reactivity and this gas was used in subsequent experiments.

3.2.2. Effect of starting material on nitridation reaction

To investigate the effect of starting material on nitridation reaction, $Al(OH)_3$, benzene-washed $Al(OH)_3$, calcined γ-Al_2O_3 or α-Al_2O_3, were selected as the starting material. These powder and carbon were mixed by ball milling, respectively. The powder mixtures then were subjected to the carbothermal reduction-nitridation in flowing NH_3 gas at 1000℃ and 1200℃ for 10 hours and at 1400℃ for 5 hours.

Fig. 5 shows the nitridation degree of starting materials plotted against temperatures. The nitridation degree used in this paper is defined as relative intensity ($I_{AlN(100)}/I_{Al_2O_3(112)}+I_{AlN(100)}$) of main peak of AlN and α-Al_2O_3 in the XRD patterns. At 1000℃, AlN was not for-
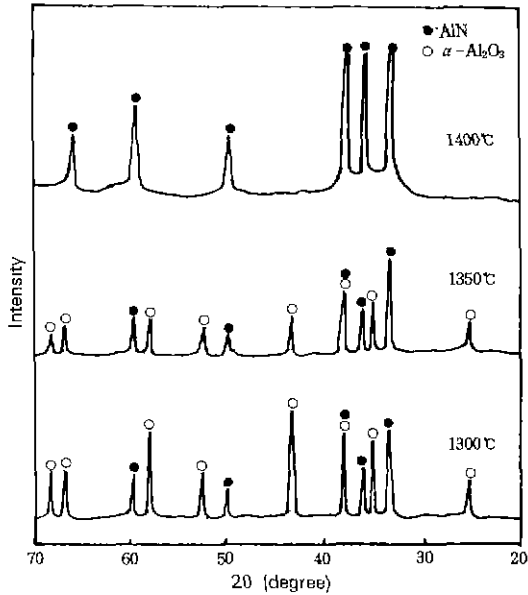
Fig. 6. XRD patterns of carbothermally nitrided produ-
cts from benzene-washed Al(OH)₃ and carbon
at various reaction temperatures for 5 h.

Fig. 7. XRD patterns of carbothermally nitrided produ-
cts from addition of carbon before the hydroly-
sis of alkoxide at various reaction temperatures
for 5 h.

med at all. But, at 1200℃, AlN was formed only for
benzene-washed Al(OH)₃. At 1400℃, nitridation reac-
tion was not completed for α-Al₂O₃ only. As this result
shows, nitridation reaction was promoted when ben-
zene-washed Al(OH)₃ was used as the starting material.
This behavior suggests that nitridation reaction was
favored by the elimination of the weakly bonded water
molecule from the gel through washing in nonpolar
organic solvent, benzene[8].

Benzene-washed Al(OH)₃ and NH₃ gas were deter-
mined to correspond to optimum conditions for syn-
thesis of AlN in this process from the above-mentioned
results. The XRD patterns of synthesized powder with
the optimum condition at 1300℃, 1350℃ and 1400℃
are shown in Fig. 6, and this figure shows that AlN
single-phase was obtained at 1400℃.

3.3. Addition of carbon before the hydrolysis of alko-xide

For uniformly mixed starting powders, the mixture
of Al(OH)₃ and carbon was prepared by the hydrolysis
of alkoxide in the presence of dispersed carbon pow-
der.

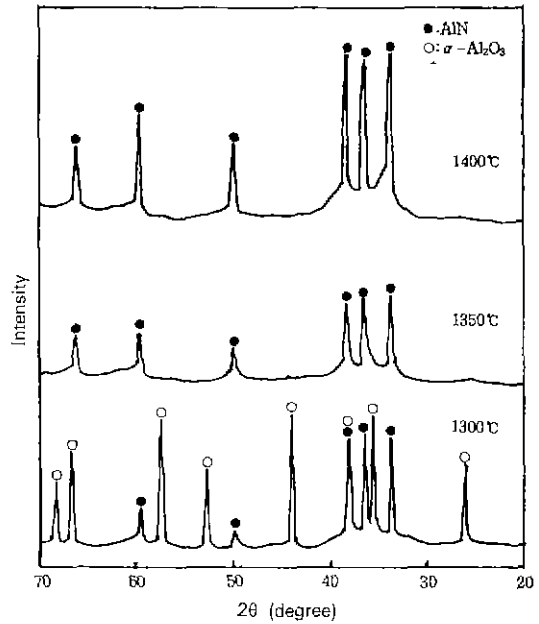Fig. 7 shows the XRD patterns of samples produced

by the carbothermal reduction-nitridation of the mix-
ture in flowing NH₃ gas at 1300℃, 1350℃ and 1400℃
for 5 hours. AlN single-phase was observed at 1350℃.
Thus, nitridation reaction was completed at 50℃ lower
than in mixing Al(OH)₃ with carbon by ball mill. This
result might be due to the fine grain size of starting
mixture and the uniform mixing.

3.4. Using furfuryl alcohol and polyacrylonitrile as reducing agent

Oxide powders with ultrafine particle size and mini-
mal agglomeration can be made by controlled precipi-
tation of oxide precursors followed by calcination. How-
ever, non-oxide precursor is usually not precipitated
directly, and the very high reaction temperature nee-
ded to make non-oxide can cause growth and aggrega-
tion of particles during reaction. To solve this problem,
Silverman[13] reported new synthesis process. This pro-
cess was to trap colloidally dispersed particle of an
oxide precursor by an in situ polymerization in the
dispersion medium and then heat the resulting compo-
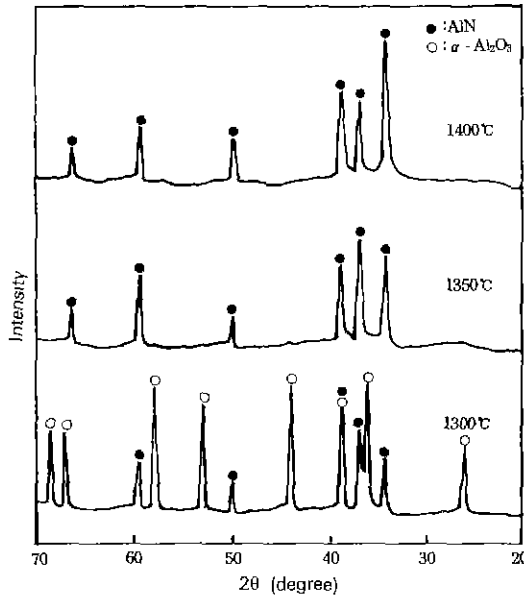site to pyrolyze the polymer and carbothermally reduce

Fig. 8. XRD patterns of carbothormally nitrided produ-
cts from Al(OH)₃/poly(furfuryl alcohol) compo-
site powder at various reaction temperatures
for 5 h.

Fig. 9. XRD patterns of carbothermally nitrided produ-
cts from Al(OH)₃ and polyacrylonitrile at various
reaction temperatures for 5 h.

the entrapped particle. The polymer thus acts both to
isolate the particles during reduction, limiting growth
and agglomeration, and to serve as the carbon source
for reduction.

Al(OH)₃/furfuryl alcohol system was chosen to make
Al(OH)₃/polymer composite. Al(OH)₃ powders disperse
in dilute nitric acid to form a sol. Furfuryl alcohol poly-
merization is acid catalyzed. Furfuryl alcohol was dis-
solved in sol which began to darken because of the
polymerization of the furfuryl alcohol.

Fig. 8 shows XRD patterns of samples produced by
the carbothermal reduction-nitridation of the Al(OH)₃
/poly(furfuryl alcohol) composite powder in flowing
NH₃ gas at 1300℃, 1350℃ and 1400℃ for 5 hours.
AlN single-phase was observed at 1350℃. It is assu-
med that the reduction effect was improved by trapped
Al(OH)₃ particle in glassy carbon[12], which was made
by the pyrolysis of polymer obtained by the polymeri-
zation of furfuryl alcohol.

Secondly, Al(OH)₃/polyacrylonitrile (PAN) system[14]
was subjected to carbothermal reduction-nitridation
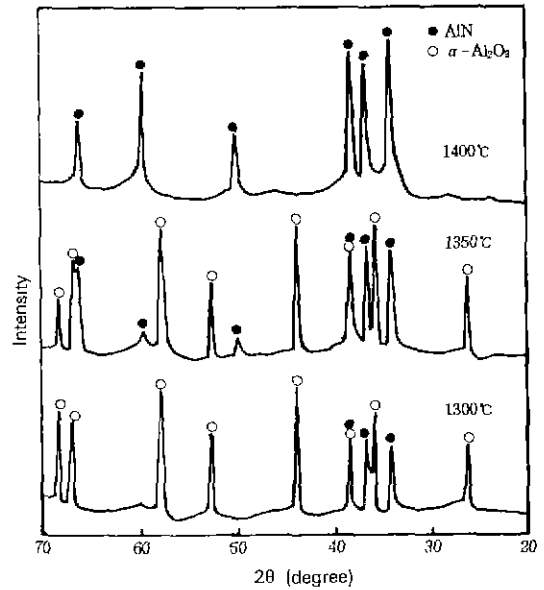process under NH₃ gas at 1300℃, 1350℃ and 1400℃
for 5 hours.

Fig. 9 shows XRD patterns of samples produced by
this process. At 1350℃, XRD patterns revealed high
concentration of AlN and α-Al₂O₃ in the reduced and
nitrided material. However, Al(OH)₃ was completely
converted to AlN at 1400℃.

From these result, it can be concluded that the trap-
ping of Al(OH)₃ particle in glassy carbon formed by
using furfuryl alcohol increases the contact area and
improves the reduction effect, and makes it possible
to synthesize AlN at lower temperature than in using
PAN.

3.5. Effect of reaction time on nitridation reaction

From the results up to now, the addition of carbon
before the hydrolysis of alkoxide and using furfuryl
alcohol as a reducing agent, were selected to investi-
gate the effect of reaction time on nitridation reaction.
The samples prepared by these processes were subjec-
ted to carbothermal reduction-nitridation at 1350℃ and
XRD analysis.

Fig. 10 shows the nitridation degree of samples plot-
ted against time. In using the addition of carbon before
the hydrolysis of alkoxide, nitridation rate was slow;
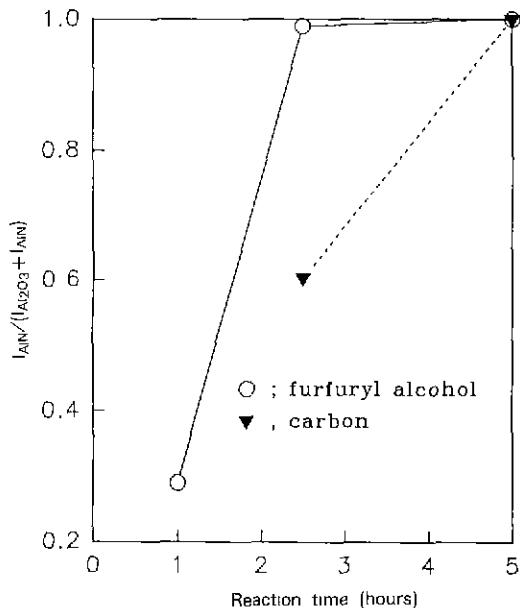Nitridation reaction took 5 hours to complete. Howe-

Fig. 10. Relative intensity of main peaks of Al_2O_3 and AlN in the XRD patterns vs. reaction time at 1350°C.

Fig. 11. XRD patterns of carbothermally nitrided products from Al(OH)$_3$-reducing agent and Al(OH)$_3$-reducing agent-CaF$_2$ system.
(a) $^+$Al(OH)$_3$-carbon-CaF$_2$ at 1350°C for 2.5 h
(b) $^-$Al(OH)$_3$-carbon at 1350°C for 2.5 h
(c) Al(OH)$_3$-PAN-CaF$_2$ at 1400°C for 2.5 h
(d) Al(OH)$_3$-PAN at 1400°C for 2.5 h
(e) Al(OH)$_3$-furfuryl alcohol-CaF$_2$ at 1350°C for 1.5 h
(f) Al(OH)$_3$-furfuryl alcohol at 1350°C for 1.5 h
($^+$: produced by the addition of carbon before the hydrolysis of alkoxide)

ver, the nitridation rate in using furfuryl alcohol was about 2 times as fast as that of using the addition of carbon before the hydrolysis of alkoxide. This behavior might be due to improved reduction effect in using furfuryl alcohol for reasons previously mentioned.

3.6. Effect of additive, CaF$_2$ on nitridation reaction

When AlN powder was synthesized from the Al$_2$O$_3$-C-N$_2$ system, the apparent activation energy was reduced to 190 kcal/mol from 250 kcal/mol by the addition of CaF$_2$[15]. CaF$_2$ was not only an excellent nitridation promoter but also strongly affect AlN grain morphologies providing spherical AlN particles.

Addition of additive, CaF$_2$ could show some additional effect; decrease in impurities such as oxygen in AlN grains can be expected, and furthermore presence of Ca-compounds, may contribute to the densification promotion in AlN sintering.

Fig. 11 shows the effect of additive, CaF$_2$ on nitridation reaction rate for the preparation of AlN from the Al(OH)$_3$-reducing agent-NH$_3$ system. The effect of CaF$_2$ appeared to be influenced by the kind of reducing agent. If CaF$_2$ was added when carbon was used as
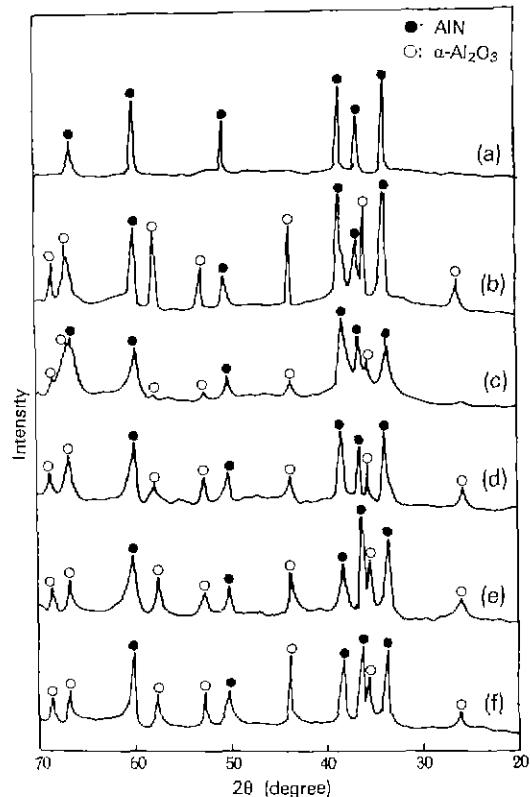
a reducing agent, nitridation reaction was promoted and completed within 2.5 hours at 1350°C. If CaF$_2$ was added when PAN was used as a reducing agent, XRD patterns show relative intensities of AlN to α-Al$_2$O$_3$ increased suggesting nitridation rate is promoted. On the other hand, no effect of CaF$_2$ on the nitridation reaction was observed when furfuryl alcohol was used.

This result might be due to inhibition of the reaction between Al(OH)$_3$ with CaF$_2$ by the trapping of Al(OH)$_3$ in a polymer matrix when furfuryl alcohol is used.
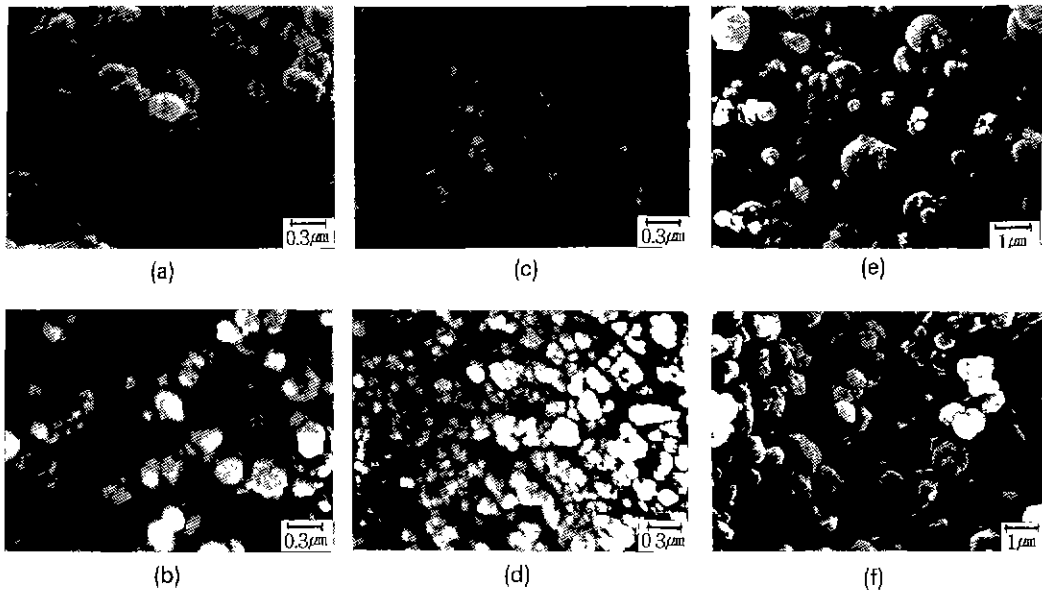
Fig. 12. SEM photographs of AlN produced from Al(OH)$_3$-reducing agent and Al(OH)$_3$-reducing agent-CaF$_2$ system.

(a) Al(OH)$_3$-carbon (by ball milling), 1400℃

(b) Al(OH)$_3$/poly (furfuryl alcohol) composite powder, 1350℃

(c) $^+$Al(OH)$_3$-carbon, 1350℃

(d) $^+$Al(OH)$_3$-carbon-CaF$_2$, 1350℃

(e) Al(OH)$_3$-PAN, 1350℃

(f) Al(OH)$_3$-PAN-CaF$_2$, 1350℃

($^+$: produced by the addition of carbon before the hydrolysis of alkoxide)

3.7. SEM observation of prepared AlN powder

The SEM photographs in Fig. 12 shows the particle size, shape and the state of agglomeration of AlN powder produced by several processes used in this study.

In AlN powder produced from the mixing Al(OH)$_3$ and carbon by ball mill, particle size was about 0.2~0.3 μm and agglomeration of spherical particles were observed. But, when carbon was added before the hydrolysis of alkoxide, AlN powder with particle size of smaller than 0.1 μm and a narrow particle size distribution was obtained. Also, the particles had spherical shape and slightly agglomerated. When AlN powder was produced by using furfuryl alcohol as a reducing agent, particle size distribution was narrow and shape was spherical, although particle size was about 0.3 μm. On the other hand, in PAN, large particles were observed and particle size distribution was broad.

In case of CaF$_2$ addition, particles grew and agglomerated. When CaF$_2$ was added to the mixture prepa-

red by the addition of carbon before the hydrolysis of alkoxide, spherical particles were obtained but the particle size became larger and particles agglomerated. But when CaF$_2$ was added to the sample obtained when PAN was used as the reducing agent, the particle size became larger, its distribution became narrow and the particles with polyhedral shape were obtained.

4. Conclusion

AlN powder was synthesized by the carbothermal reduction-nitridation of Al(OH)$_3$ prepared by sol-gel method, and the effect of experimental variables on nitridation reaction was also investigated. Conclusions obtained from this study as follows.

(1) Preparation of monodisperse, spherical Al(OH)$_3$ having the mean particle size of 1 μm from Al(O-sec-C$_4$H$_9$)$_3$ was made possible by the controlled hydrolysis in the mixed solvent consisting n-octanol and acetonit-

rile. The preparation condition obtained are as follows; ASB/H_2O molar ratio, 1 : 4; hydrolysis water adding rate, 0.5 ml/min; aging temperature, 25℃ ; and aging time, 5 hours.

(2) NH_3 gas was the most effective reaction gas for the synthesis of AlN. Among starting materials such as Al(OH)$_3$, benzene-washed Al(OH)$_3$, γ-Al$_2$O$_3$ and α-Al$_2$O$_3$, benzene-washed Al(OH)$_3$ had the lowest starting temperature of nitridation reaction.

(3) In the addition of carbon before the hydrolysis of alkoxide, AlN powder with uniform particle size (0.1 μm below) was synthesized at lower temperature (1350 ℃, 5 hours) than in the mixture of benzene-washed Al(OH)$_3$ and carbon by ball mill.

(4) When furfuryl alcohol was used as the reducing agent rather than polyacryonitrile, nitridation reaction proceeded fast and completed in 2.5 hours at 1350℃.

(5) When additive, CaF$_2$ was used, reaction rate was not affected when furfuryl alcohol was used as the reducing agent, but accelerated when carbon and poly-acrylonitrile was used as the reducing agent.

Acknowledgement

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