# Preparation of Aluminum Nitride Powders and Whiskers Using Aluminum(III) Salts as a Precursor

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## ABSTRACT

Aluminum nitride (AlN) powders were synthesized by using a mixture of an aluminum nitrate or sulfate salt and carbon (mole ratio of $Al^{3+}$ to carbon=1 : 30). The AlN was obtained by calcining the mixture under a flow of nitrogen in the temperature range 1100–1600°C and then burning out the residual carbon. The process of conversion of the salt to AlN was monitored by XRD and $^{27}Al$ magic-angle spinning (MAS) NMR spectroscopy. The salt decomposed to γ-alumina and then converted to AlN without phase transition from γ- to α-alumina. $^{27}Al$ MAS NMR spectroscopy shows that the formation of AlN commenced at 1100°C. AlN powders obtained from the sulfate salt were superior to those from the nitrate salt in terms of homogeneity and crystallinity. A very small amount of AlN whiskers was obtained by calcining a mixture of an aluminum sulfate salt and carbon at 1150°C for 40 h, and the growth of the whiskers is well explained by the particle-to-particle self-assembly mechanism.

*Key words : Aluminum nitride, Aluminum(III) salts, Whisker, Growth mechanism, $^{27}Al$ MAS NMR*

## 1. Introduction

**A**luminum nitride (AlN) has many attractive properties, including high thermal conductivity, low coefficient of thermal expansion that closely matches that of silicon, high electrical resistivity, and good mechanical strength. Thus it has attracted extensive interests for applications as electrical packaging material and as components in the structural composites.[1] There are two primary processes commercially used for the manufacture of AlN powder : (i) the direct nitridation of metallic aluminum and (ii) the carbothermal reduction and nitridation (CRN) of alumina under a flow of nitrogen.[2] The latter method is known to be superior to the former method in terms of purity, stability against humidity, and sinterability of the AlN powder produced. For the conventional CRN method the intimate mixing of the alumina with carbon powders is essential to the complete transformation of alumina to AlN. Several modified CRN methods were suggested to improve the intimate mixing. One of these methods is to use aluminum(III) complexes as a precursor, which are prepared from the reaction between organic ligands and aluminum(III) compounds such as aluminum alkoxides and salts in solution.[3-8]

In the present work, we report the synthesis of AlN powders and whiskers by the conventional CRN method using a mixture of carbon and an aluminum(III) salt such as aluminum nitrate and sulfate salts. The process of conversion of the salts to AlN was monitored by XRD and $^{27}Al$ magic-angle spinning (MAS) NMR spectroscopy. The growth mechanism of AlN whiskers was suggested on the basis of change in their morphologies.

## 2. Experimental

Charcoal was added to aqueous aluminum(III) nitrate or sulfate solution (mole ratio of $Al^{3+}$ to charcoal=1 : 30) and stirred. Each mixture was evaporated to dryness and was put in the graphite boat. The boat was placed into the alumina tube at the room temperature. The mixture powder was calcined at the reaction temperature (1100 to 1600°C) under a flow of nitrogen. The ramp rate was 5°C/min. The residual carbon was removed by burning out at 700°C for 1 h in air.

The products obtained were characterized by powder X-Ray Diffraction (XRD) using a Rigaku DMX-2500 diffractometer with Cu-Kα radiation operating 40 kV and 50 mA. High-resolution $^{27}Al$ magic-angle spinning (MAS) NMR spectra were recorded at ambient temperature using a Varian Unity INOVA 600 spectrometer running at 156.3 MHz. The zirconia rotor used as sample chamber was spun at 14 kHz during data collection. Chemical shifts (δ) were referenced to 1 M aqueous aluminum nitrate solution. The morphology of the AlN products was investigated by scanning electron microscopy (SEM, Hitachi S-4100).

## 3. Results and Discussion

Fig. 1 shows X-Ray Diffraction (XRD) patterns of samples

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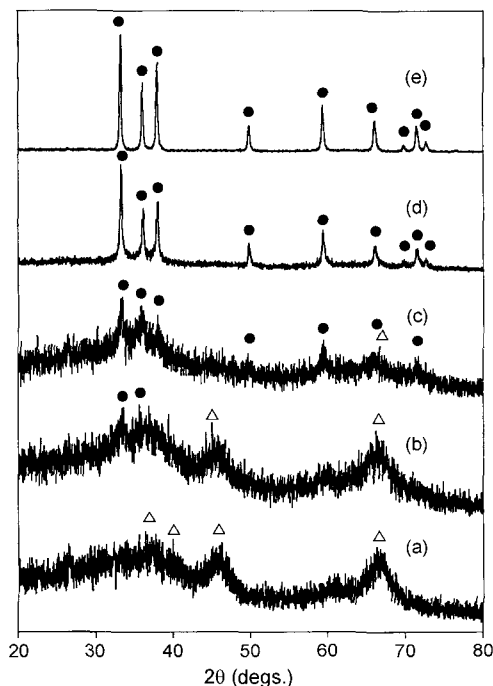
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**Fig. 1.** XRD patterns of powders obtained by calcination of a mixture of aluminum nitrate and carbon (mole ratio= 1 : 30) at various temperatures for 5 h : (a) 1100°C, (b) 1200°C, (c) 1250°C, (d) 1300°C, and (e) 1400°C. (● : AlN, △ : γ-alumina).



**Fig. 2.** XRD patterns of powders obtained by calcination of a mixture of aluminum sulfate and carbon (mole ratio= 1 : 30) at various temperatures for 5 h : (a) 1100°C, (b) 1200°C, (c) 1250°C, (d) 1300°C, and (e) 1400°C. (● : AlN, □ : α-alumina, △ : γ-alumina).

synthesized by calcining a mixture of aluminum nitrate and carbon at different reaction temperatures for 5 h. The sample calcined at 1100°C is γ-alumina. In the sample calcined at 1200°C weak diffraction peaks to assigned to AlN are detected together with those assigned to γ-alumina. The temperature (1200°C) at which the formation of AlN commences is the same as that for the case of basic dicarboxylate Al(III) complexes $Al(OH)(C_{n+2}H_{2n}O_4) \cdot xH_2O$.[5-7] With increasing the reaction temperature the peaks assigned to γ-alumina decrease and the peaks to assigned to AlN increase. In the case of the samples calcined above 1300°C, there are no detectable peaks other than the peaks assigned to AlN. It is inferred from this observation that AlN is synthesized directly from γ-alumina without phase transition from γ- to α-alumina, as in the case of the synthesis of AlN from the basic dicarboxylate Al(III) complexes.[5-7] But γ-alumina was partly converted to α-alumina if the mole ratio of carbon to aluminum nitrate was lower than 30. The overall variation in XRD patterns with the calcination temperature is very similar to that for $(NH_4)$-$[Al(edta)] \cdot 2H_2O$.[8]

Fig. 2 shows X-Ray Diffraction (XRD) patterns of samples synthesized by calcining a mixture of aluminum sulfate and carbon at different reaction temperatures for 5 h. The sample calcined at 1100°C is γ-alumina, as for aluminum nitrate, but their peaks are more distinct than those for aluminum nitrate. In the sample calcined at 1200°C intense diffraction peaks to assigned to AlN are detected together with those assigned to γ- and α-alumina. With increasing
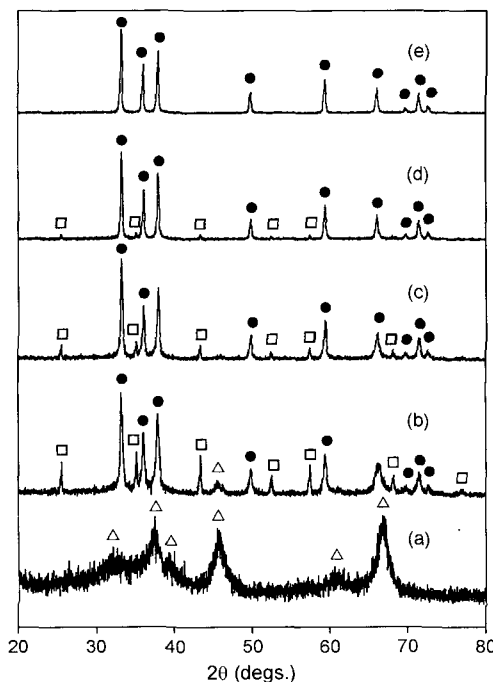
the reaction temperature the peaks assigned to γ- and α-alumina decrease and the peaks to assigned to AlN increase. In the case of the samples calcined above 1400°C, there are no detectable peaks other than the peaks assigned to AlN. The formation of α-alumina phase indicates that the mole ratio of carbon to aluminum sulfate should be higher than 30 for the sake of complete conversion of γ-alumina to AlN without γ- α alumina phase transition.

Solid-state NMR spectroscopy might be a more powerful probe than XRD in characterizing less crystalline materials because the latter provides little information about the central-metal distribution owing lack of long-range order. The chemical shift of $^{27}$Al NMR is sensitive to the local coordination at the Al nucleus.[9,10] For octahedrally coordinated $AlO_6$ groups, chemical shifts of about −10 to +20 ppm are observed, while five-coordinated $AlO_5$ groups resonate between +30 and +40 ppm, and tetrahedrally coordinated $AlO_4$ groups resonate between +50 and +80 ppm.[9]

Fig. 3 shows $^{27}$Al MAS NMR spectra of samples synthesized by calcining a mixture of aluminum sulfate and carbon at different reaction temperatures for 5 h. The spectrum (Fig. 3(a)) of the sample obtained at 1100°C shows that there are three peaks at 11, 67, and 114 ppm. Two peaks at 11 and 67 ppm are due to γ-alumina, where the two peaks are readily assigned to six-coordinate $(AlO_6)$ and four-coordinate $(AlO_4)$ aluminum, respectively.[11] The very weak peak at 114 ppm is assigned to AlN.[10] A very small amount of AlN is hard to be detected by XRD because very weak diffraction peaks of the AlN are overshadowed by intense
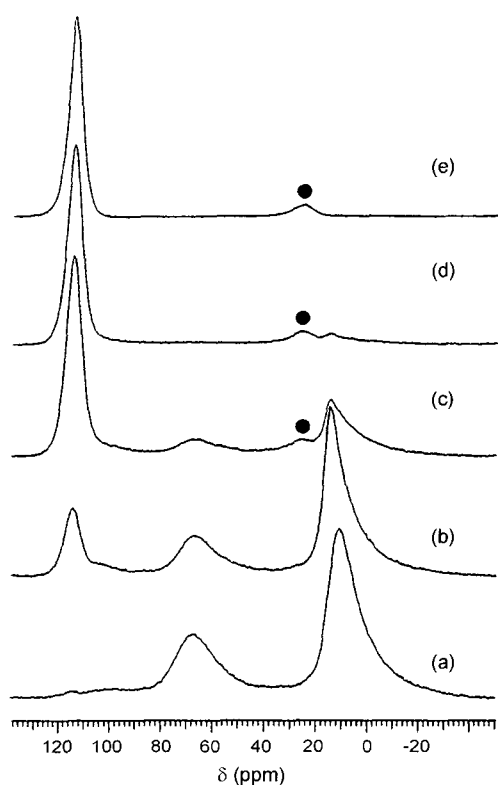
Fig. 3. $^{27}$Al MAS NMR spectra of powders obtained by calcination of a mixture of aluminum sulfate and carbon (mole ratio=1 : 30) at various temperatures for 5 h : (a) 1100°C, (b) 1150°C, (c) 1200°C, (d) 1300°C, and (e) 1400°C. The peaks marked by closed circles are signals due to spinning sidebands.
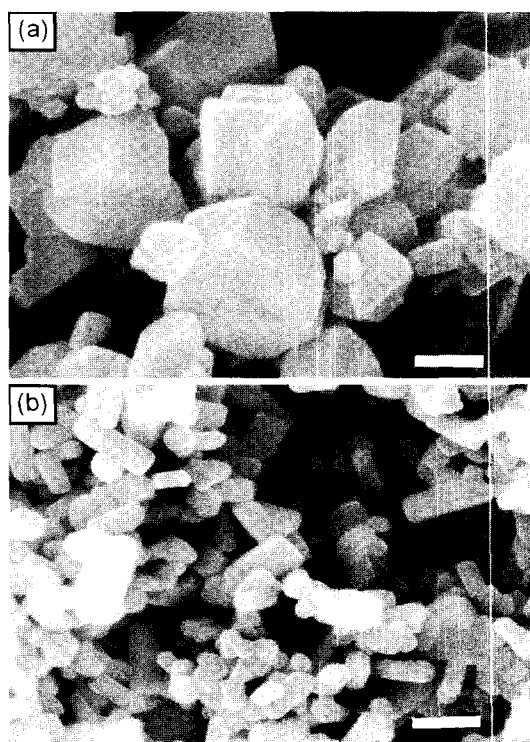


Fig. 4. SEM micrographs of AlN powders obtained by calcination of a mixture of aluminum nitrate (a) or sulfate (b) and carbon (mole ratio of $Al^{3+}$ to carbon=1 : 30) under a flow of nitrogen at 1500°C for 5 h (bar=300 nm).

peaks of γ-alumina. In the spectrum of the sample calcined at 1150°C the relatively intense peak at 114 ppm is observed, and the peak corresponding to six-coordinate $AlO_6$ aluminum is down-field shifted by $ca.$ 4 ppm and the ratio $(I_6/I_4)$ of intensity $(I_6)$ of $AlO_6$-aluminum peak to intensity $(I_4)$ of $AlO_4$-aluminum peak is higher for the sample obtained at 1150°C than for the sample obtained at 1100°C because $AlO_6$-aluminum peak of α-alumina is overlapped with that of γ-alumina. As the calcination temperature reaches at 1200°C, AlN peak becomes intense abruptly and alumina peaks diminish in intensity. In the case of samples above 1400°C, only AlN peak is observed, as expected from their XRD patterns. The AlN peak becomes more narrow with increasing temperature because of increase in crystallinity.

The morphology of AlN powders obtained at 1500°C was observed by SEM. The powders (Fig. 4(a)) obtained from aluminum nitrate are very agglomerated with faceted particles and their homogeneity in size is very poor. But as shown in Fig. 4(b), AlN particles obtained from aluminum sulfate are relatively homogeneous in size and shape, and are hexagonal rods, reflecting the wurtzite structure for the AlN crystal habit. The rods have an aspect ratio higher than 3. Such rod-shaped AlN particles were also synthesized from the reaction of $AlF_3$ and

ammonia.[12] The rods became larger with increasing the reaction temperature.

It is known that it is very difficult to synthesize AlN whiskers by the CRN method without using any catalyst.[13] It was reported in a previous paper[14] that the AlN whiskers were synthesized by calcining a (glutarato)(hydroxo)aluminum(III) complex without mixing any catalyst under a flow of nitrogen. The sample prepared by calcining a mixture of aluminum sulfate and carbon at 1150°C for 40 h contained a very small amount of AlN whiskers. Fig. 5(a) shows the beginning step ($i.e.$, particle-to-particle self-assembling step) in formation of the whisker. The whisker is matured to a hexagonal prism (Fig. 5(c)) via coalescence of AlN particles (Fig. 5(b)). In the case of well-dispersed nanometer-sized AlN particles AlN whiskers grow through both the particle-to-particle connection and the solid diffusion of the particle.[14] Up to date, the growth of AlN whiskers obtained by the CRN method has been mainly explained by the vapor-liquid-solid (VLS) mechanism.[13,15]

The formation of the AlN whiskers is known to be catalyzed by the sapphire.[8] The polished side of (0001) sapphire was put downward on the top of the powder, which was obtained by calcining a mixture of aluminum sulfate and carbon at 500°C for 2 h in flowing nitrogen and milling the calcined product in an agate mortar and pestle, and then nitridated at 1500°C for 5 h in flowing nitrogen. Unfortunately no AlN whiskers were found on the polished side of the sapphire because no AlN epitaxy, which may act as a
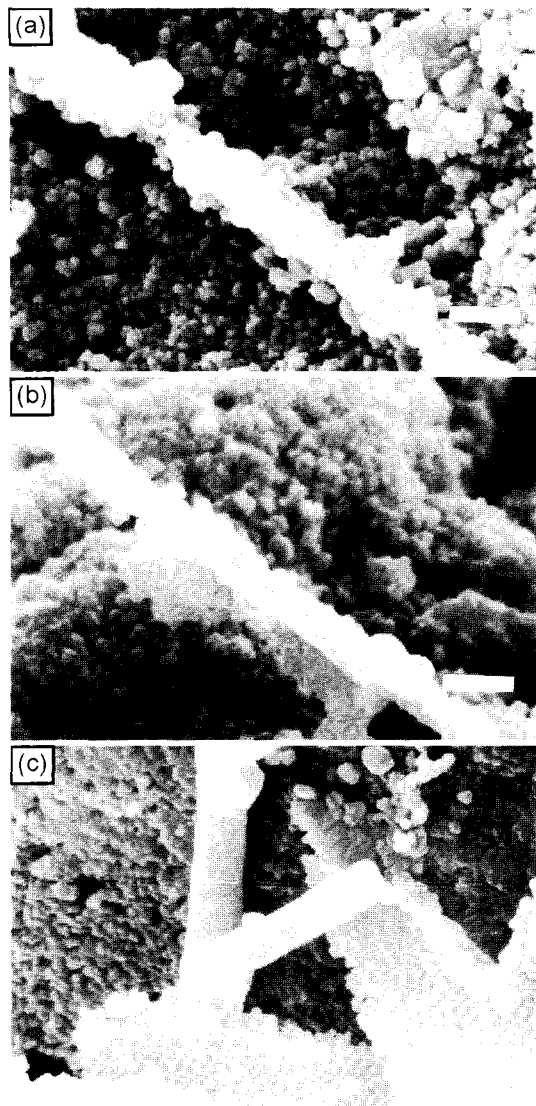
**Fig. 5.** SEM micrographs of AlN whiskers obtained by calcination of a mixture of aluminum sulfate and carbon (mole ratio of $Al^{3+}$ to carbon=1 : 30) under a flow of nitrogen at 1150°C for 40 h (bar=300 nm). The self-assembled AlN particles (a) are matured to a hexagonal prismatic whisker (c) via coalescence of particles (b).
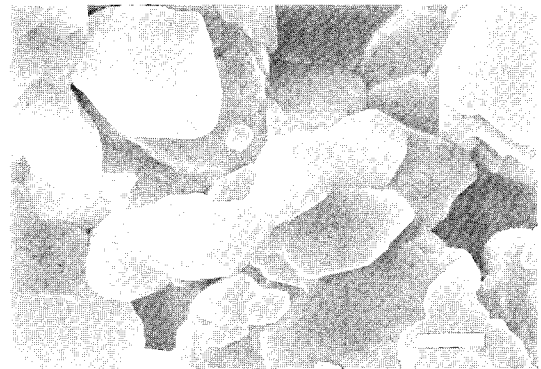


**Fig. 6.** SEM micrograph of a polished side obtained by calcining (0001) sapphire embedded in a mixture of aluminum sulfate and carbon (mole ratio of $Al^{3+}$ to carbon=1 : 30) under a flow of nitrogen at 1500°C for 5 h (bar=1 μm).

The temperature (1100°C) at which the formation of AlN commences was not revealed by XRD but by ^{27}Al MAS NMR spectroscopy. The AlN particles obtained from the sulfate salt were rod-shaped and homogeneous in size, while those obtained from the nitrate salt were very agglomerate and inhomogeneous in size. AlN whiskers were obtained by prolonged calcination of a mixture of aluminum sulfate and carbon at relatively low temperature and the whiskers were grown through the particle-to-particle self-assembly.

## Acknowledgements

seed for growth of the whisker, was grown, as shown in Fig. 6 and the AlN particles are too large to connect (self-assemble) for the whisker growth.[14]

## 4. Conclusions

Aluminum nitride (AlN) powders and whiskers were synthesized by the conventional CRN method using an aluminum nitrate or sulfate salt. As evidenced by XRD and ^{27}Al MAS NMR spectroscopy, the salt decomposed to γ-alumina, and the carbothermal reduction and nitridation of γ-alumina led to the formation of AlN without γ- to α-alumina phase transition. ^{27}Al MAS NMR spectroscopy was proved to be a powerful tool in detecting a small amount of AlN.

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