

Synthesis of aluminum nitride by a modified carbothermal reduction and nitridation method using basic dicarboxylate Al(III) complexes $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ ($n = 3, 6, 8$)

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Received 16 March 2000; received in revised form 2 June 2000; accepted 11 June 2000

Abstract

Aluminum nitride (AlN) particles and whiskers were synthesized by using basic dicarboxylate Al(III) complexes $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ ($n = 3, 6, 8$) as a precursor. AlN was obtained by calcining the glutarate complex ($n = 3$, AG) without further additions of carbon source under flowing nitrogen in the temperature range 1200–1500°C and then burning out the residual carbon. In contrast, for suberate ($n = 6$, ASu) and sebacate ($n = 8$, ASe) complexes additional carbon was required for their complete conversion to AlN. The process of conversion of AG to AlN was investigated by ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance, infrared spectroscopy, and X-ray diffraction. The complex began to decompose at ca. 400°C and then turned into γ -alumina at temperature above 600°C. Finally, the γ -alumina was converted to AlN without γ - α alumina phase transformation. The morphology of AlN powders was very similar to that of the precursor, indicating that conversion of alumina to AlN during the carbothermal reduction and nitridation does not proceed through gaseous intermediates but through solid-state Al–oxynitride compounds. The AlN powders obtained consisted of ultrafine particles or mixtures of particles and whiskers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: AlN; Calcination; Powders-chemical preparation; Whiskers

1. Introduction

Aluminum nitride (AlN) is predominantly used as an electronic and structural ceramic.¹ The attractive properties of AlN for electronic applications include its high thermal conductivity, high electrical resistivity, a thermal expansion coefficient close to that of silicon, and a low dielectric constant. 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 Comparatively the latter method is known to be more advantageous 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 achieve complete

transformation of alumina to AlN. Therefore several modified CRN methods were suggested to compensate for intimate mixing. One of these methods uses 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.^{3–7} The complexes are calcined to a homogeneous mixture of alumina and carbon powders at the beginning of the CRN process. If the amount of the carbon derived from the ligands is not sufficient for simultaneous reduction and nitridation of the alumina to AlN, organic compounds such as glucose and sugar are required to be added to the starting solution.^{3,4}

Recently we reported the synthesis of AlN powders via a modified CRN method starting from (hydroxo)(succinato)aluminum(III) complex (AS) as a precursor.⁶ This reaction system offers the following benefits: the easy-to-synthesize precursor and its high hydrolysis resistance, low nitridation temperature, ultrafine AlN powder, and no need of any additional carbon source. In this report we chose glutaric, suberic,

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and sebacic acids as ligands in order to investigate the effect of the carbon amount in dicarboxylic acid ligands on the reaction process and the morphology of AlN produced. Finally the results were compared with those obtained with other Al(III) complexes such as AS and (adipato)(hydroxo)aluminum(III) (AA).^{6,7}

2. Experimental

2.1. Synthesis

The synthesis method for the basic dicarboxylate Al(III) complexes $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ ($n=3, 6, 8$) was the same as that⁶ for the AS complex with exception of using glutaric, suberic, and sebacic acids instead of succinic acid as a ligand. Amorphous as well as crystalline powders of the complexes were prepared in boiling solution and under very mild heating (ca. 40°C), respectively. For its complete conversion to AlN the glutarate complex (AG) needed not to be mixed with any additional carbon source, while suberate (ASu) and sebacate (ASe) complexes required to be mixed with carbon black (mole ratio=1:3) in a mortar. The following calcination step was performed under flowing nitrogen gas (200 ml/min) in two different ways: (i) the powder was calcined in a graphite crucible by placing it into an alumina tube furnace preheated to the calcination temperature (Q route) and (ii) the powder was placed in an alumina crucible at the room temperature and then heated in the alumina tube furnace to the calcination temperature (S route). In the latter route the heating rate was 5°C/min. The nitrogen gas used for CRN reaction was purified from oxygen contaminants by passing it through a mullite tube packed with carbon black at 900°C. The residual carbon was removed during a final heating step on air at 700°C for 1 h.

2.2. Characterization

IR spectra were recorded on a Jasco FT-IR 5300 spectrophotometer using KBr disks. TG and DTA curves of AG were measured on a Polymer Laboratories STA-1500 thermogravimetric analyzer. The calcined products were characterized by powder X-ray diffraction (XRD) using a Rigaku DMX-2500 diffractometer and $\text{Cu-K}\alpha$ radiation (40 kV/50 mA). The morphology of the AlN products was investigated by scanning electron microscopy (SEM, Hitachi S-4100). High-resolution ²⁷Al MAS and ¹³C CP/MAS NMR spectra were recorded at room temperature using a Varian Unity+300 spectrometer operating at 78.2 and 75.5 MHz, respectively. The Si_3N_4 rotor used as a sample chamber was spun at 5 kHz (6 and 7 kHz, if necessary to confirm spinning sidebands) during data collection. ²⁷Al and ¹³C chemical shifts are given with respect to 1 M AlCl_3

($\delta=0$ ppm) dissolved in water and methyl carbon ($\delta=17.3$ ppm) in hexamethylbenzene, respectively, as external standards. For the measurement of ²⁷Al MAS NMR spectra typically $\pi/6$ pulses of 2 μs were applied to excite the (1/2, -1/2) transition, and 64 free induction decays were accumulated with a recycle of 3 s. Carbon contents of end products, which were measured on Leco WR-12 carbon determinator, were <0.1 wt.%.

3. Results and discussion

3.1. Characterization of $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$

The IR and ¹³C CP/MAS NMR spectra of prepared $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ ($n=2, 3, 4, 6, 8$) compounds show similar patterns. The IR spectra exhibit the following common features: O–H stretching vibration band of hydroxyl groups appears near 3693 cm^{-1} and broad and strong bands assigned to asymmetric stretching vibrations of carboxylate groups in coordinated ligands occur near 1595 cm^{-1} , which is ca. 100 cm^{-1} lower than the C=O stretching frequency of free acids because of their coordination to aluminum(III) ions. The positions of these two bands vary with the Al(III) complexes in the range of $\pm 5\text{cm}^{-1}$. The ¹³C CP/MAS NMR spectra show that peaks can be divided into two regions. One is assigned to methylene carbons (21.6 and 37.0 ppm for $n=3$; 26.7 and 37.7 ppm for $n=6$; 26.9, 30.8, and 38.0 ppm for $n=8$) and the other is assigned to carboxylate carbons (181.7 ppm for $n=3$; 179.4 and 180.7 ppm for $n=6$; 179.4 and 180.9 ppm for $n=8$). The values of x in the empirical formulas of the Al(III) complexes were determined to be below 1 by gravimetry, considering that the complexes are converted to α -alumina during calcination at 1200°C in air.

All Al(III) complexes synthesized in boiling solution were amorphous and the morphology of their powders was observed by scanning electron microscopy (SEM). As shown in Fig. 1, AG powders were agglomerated with nearly spherical particles. The mean particle size was $\sim 0.5 \mu\text{m}$, which was 10 times larger than that of AS or AA complexes. Dispersed particles were obtained by no means, even if the boiling solution was exposed to the ultrasonic vibration. The ASu and ASe powders appeared as agglomerates of small particles. While the agglomerate size distribution of ASu powders was relatively narrow (mean size $\sim 1 \mu\text{m}$), the agglomerates of ASe powders are in the wide range of 1–8 μm . When Al(III) complexes were synthesized under the mild condition, they formed crystals, as shown in Fig. 2. Two common peaks at $2\theta=11.6$ and 17.4° were found in the XRD patterns of basic dicarboxylate Al(III) complexes.

The decomposition characteristics of the Al(III) complexes were investigated by TG/DTA methods using N_2 atmosphere. The complexes dehydrate and then

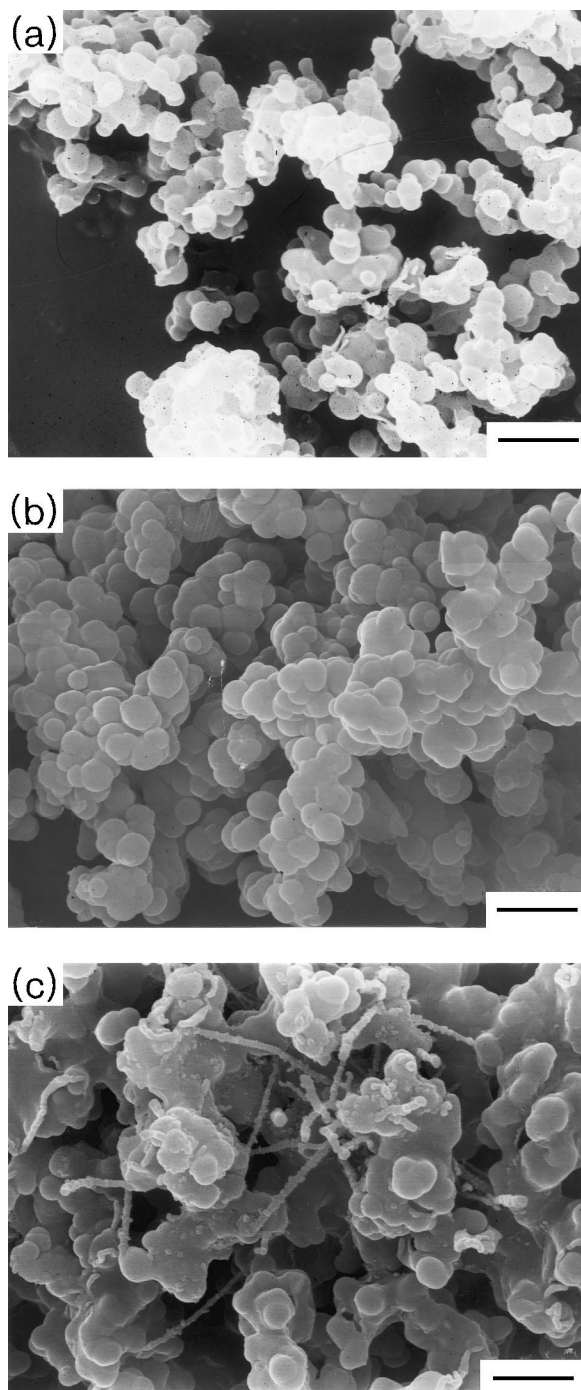
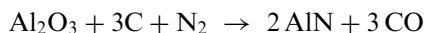


Fig. 1. SEM micrographs of (a) (glutarato)(hydroxo)aluminum(III) and (b) powders obtained by calcining it in air at 700°C for 2 h and (c) under a flow of nitrogen at 1300°C for 2 h (bar = 1.5 μm).

commence to decompose at ca. 400°C. The decomposition is accompanied by weight loss and the weight steadily decreases until the temperature reaches ~ 600°C. Further heating leads to a weight plateau due to the formation of an alumina/carbon mixture. The pyrolysis of 2 mol AG, ASu, and ASe complexes gives 1 mol of alumina and 5, 1.5, and 2 moles of carbon, respectively. The carbon contents in a series of basic dicarboxylate

Al(III) complexes $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ are not correlated to those in their products formed after CRN reaction: residual carbon content in the reaction products increases in the order $n=6 < 4 \approx 8 < 2 < 3$. Considering a CRN reaction is expressed by equation



it is expected that all Al(III) complexes except AS and AG need simultaneous carbon additions for their complete conversion to AlN.

3.2. Conversion of $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ to AlN

High-resolution ^{27}Al MAS NMR spectroscopy is a more powerful probe than XRD in investigating the carbothermic nitridation of ^{27}Al (III) complexes to AlN because firstly also amorphous phases, if they exist, can be identified, and secondly chemical shift of ^{27}Al NMR is sensitive to the local coordination at the Al nucleus.⁸ For octahedrally coordinated AlO_6 groups, chemical shifts of about -10 to +20 ppm are observed, while five-coordinated groups resonate between +30 and +40 ppm, and tetrahedrally coordinated AlO_4 resonate between +50 and +80 ppm.⁹ ^{27}Al MAS NMR spectra were measured in order to see whether there is any difference among Al(III) complexes in the process of their conversion to AlN.

Figs. 3 and 4 show ^{27}Al MAS NMR spectra of samples synthesized from AG at different calcination temperatures for 2 h (Q route). The samples were measured without removing the residual carbon because the burning out of carbon lead to spectral changes.¹⁰ In the spectrum of AG (Fig. 3), the centerband occurs at 3 ppm, indicating that Al^{3+} ion in the complex is six-coordinated. The spinning sidebands are much simpler than for AS,⁸ indicating that symmetry in chemical environment of Al^{3+} ion in AG is higher than that in AS. The lineshape of $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ ($n=4, 6, 8$) complexes is very similar to that of AS. At the decomposition temperature (ca. 400°C) of AG complex peaks assignable to three types of AlO_6 , AlO_5 , and AlO_4 aluminum atoms are observed. The lineshape is similar to that¹¹ of ρ -alumina formed by calcining gibbsite in vacuo at 200°C because the intensities of three peaks decrease in the order $\text{AlO}_6 > \text{AlO}_5 > \text{AlO}_4$. With increasing temperature in the range 400–700°C the relative intensities of aluminum atoms of AlO_4 and AlO_5 sites increase simultaneously. The NMR spectrum of the sample calcined at 700°C is similar to that for AA but very different from that for AS since the intensity of AlO_4 site is almost the same as that of AlO_6 site.⁸ Upon increasing temperature over 700°C, the relative intensity of aluminum atoms in AlO_6 sites increases as a consequence of the gradual transformation of aluminum

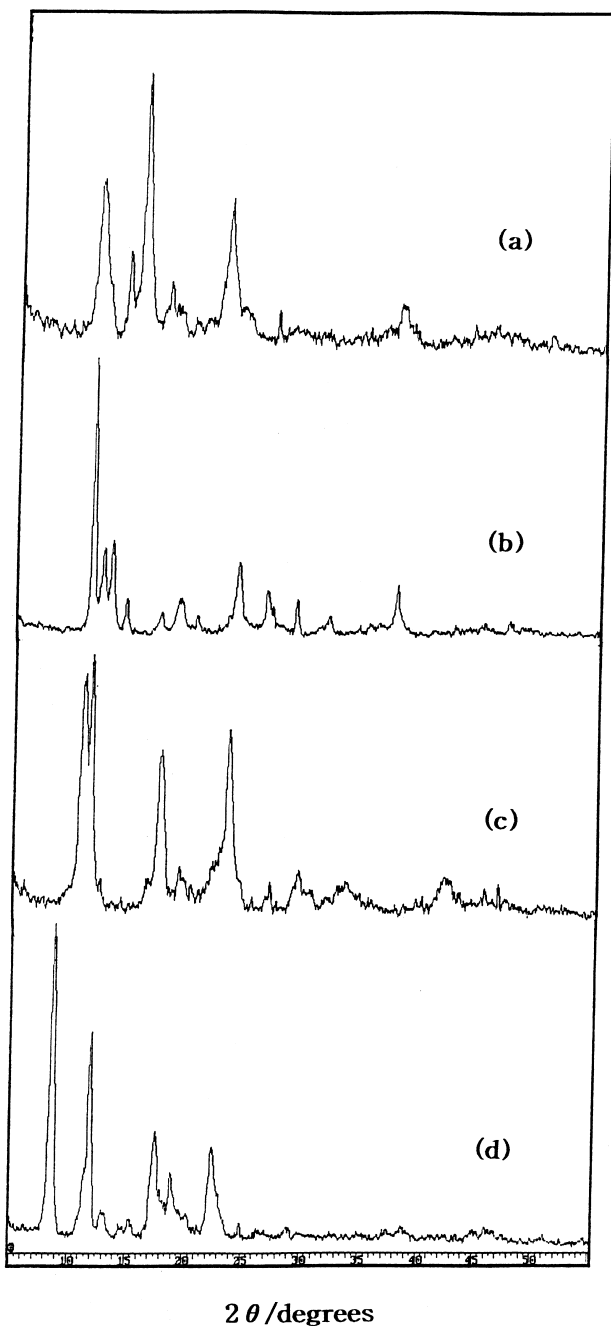


Fig. 2. XRD patterns of (a) (hydroxo)(succinato)aluminum(III), (b) (glutarato)(hydroxo)aluminum(III), (c) (adipato)(hydroxo)aluminum(III) and (d) (hydroxo)(suberato)aluminum(III).

atoms from AlO_5 sites into AlO_6 sites. The NMR spectrum of the sample calcined at 1100°C is close to that¹² of γ -alumina. Therefore it follows that basic dicarboxylate Al(III) complexes show a similar trend referring to relative intensity of three aluminum atoms as a function of calcination temperature in the range 400 – 1100°C but some differences referring to relative intensities at each calcination temperature. The factors determining the relative intensities are still open to question.

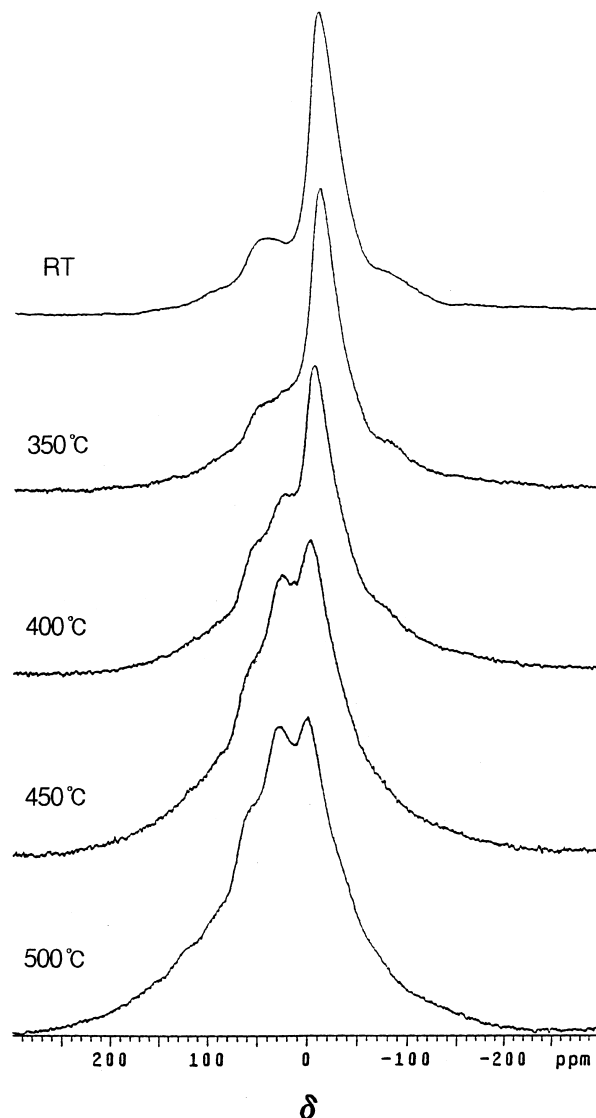


Fig. 3. ^{27}Al MAS NMR spectra of (glutarato)(hydroxo)aluminum(III) calcined under a flow of nitrogen from room temperature to 500°C for 2 h.

As shown in Fig. 4, NMR spectrum of the sample calcined at 1200°C exhibits three peaks with an AlN peak at 114 ppm. The AlN peak intensity abruptly increased for the sample calcined at 1300°C . At temperatures above 1400°C only the AlN peak was observed. This NMR spectroscopic study clearly shows that AlN is formed from γ -alumina without its transition to α -alumina. This finding is in accordance with earlier CRN-studies of aluminum(III) complexes,^{3,4,6} where thermal decomposition of the complexes resulted in an intimate mixture of γ -alumina with carbon at a molecular level. The transition of γ - to α -alumina may have been hindered by the residual carbon trapped in interstices of the γ -alumina lattice. It should be noted that AA, ASu, and ASe complexes gave a mixture of α -alumina and AlN, when they were directly calcined

under a flow of nitrogen at higher calcination temperatures without a prior mixing step with carbon. The CRN reaction of AG to AlN was also investigated by IR spectroscopy and XRD. In accordance with ^{27}Al

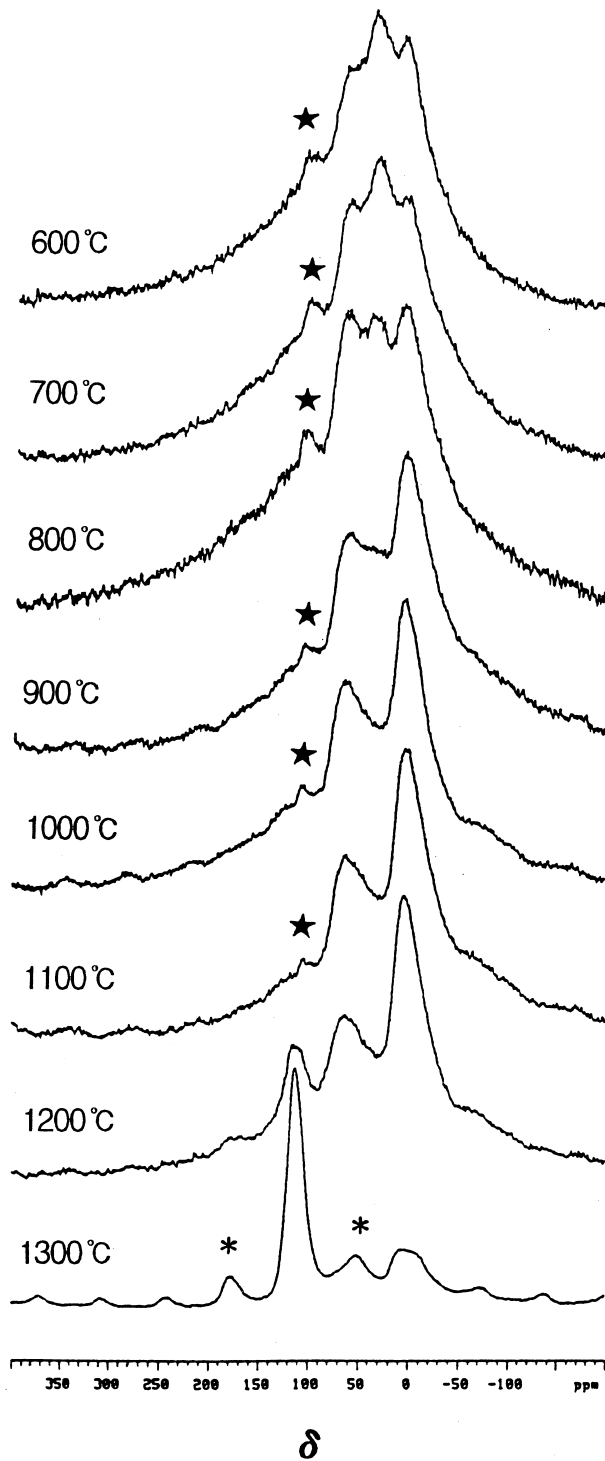


Fig. 4. ^{27}Al MAS NMR spectra of (glutarato)(hydroxo)aluminum(III) calcined under a flow of nitrogen in the temperature range 600–1300°C for 2 h (Q route). The peaks marked by stars and asterisks are signals due to Al in the Si_3N_4 rotor and the spinning sidebands, respectively.

MAS NMR spectroscopic results, it was found that there is no evidence on the formation of α -alumina.

The degree of nitridation (α) at various calcination temperatures in the range 1350–1500°C (S route) was also studied by measuring the weight loss accompanied by transformation of Al(III) complexes to AlN. As recently shown for AS,⁶ it can be estimated from the ratio of the weight of the sample after carbonization to the weight of the complexes used. Values of $\alpha=0$ and 1 mean that Al(III) complexes are completely transformed to alumina and AlN, respectively. The results obtained show that at each calcination temperature the value of α for AG is very similar to that for AS and α -values for ASu and ASe are a little lower than that for AS. The difference in the degree of nitridation indicates that the alumina/carbon mixture obtained by spontaneous pyrolysis of Al(III) complexes is much more homogeneous than the mechanical mixing employed in the conventional CRN method. In addition the study on the degree of nitridation reveals that for all Al(III) complexes a short dwell time at the higher calcination temperatures has kinetic preference over a long time at the lower calcination temperature.

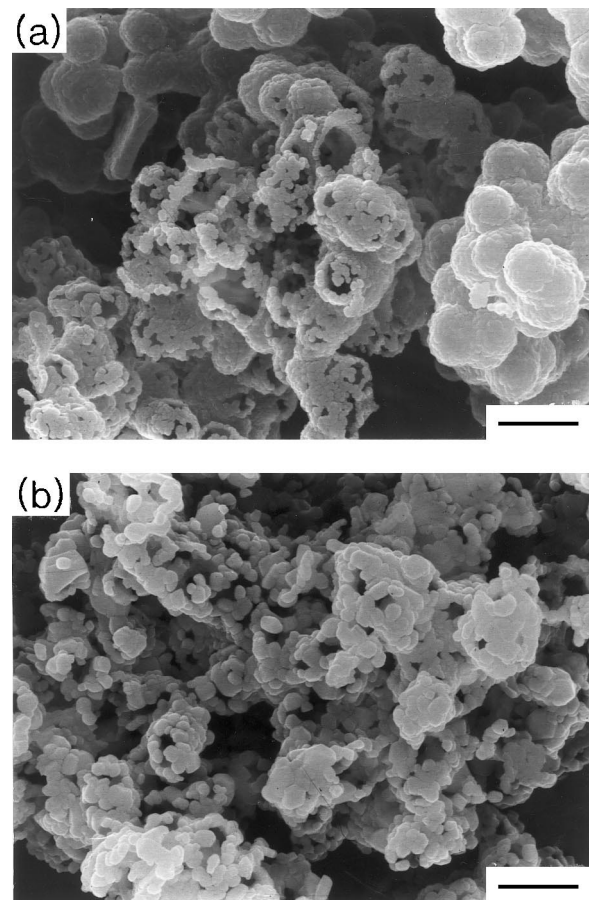


Fig. 5. SEM micrographs of AlN powders obtained by calcination of (glutarato)(hydroxo)aluminum(III) under a flow of nitrogen at (a) 1400 and (b) 1450°C for 15 h (S route) (bar = 1.5 μm).

3.3. Morphology of the synthesized AlN

The change in morphology of powders obtained by calcination of Al(III) complexes was investigated by SEM. Fig. 1 shows that the morphology of γ -alumina and AlN, which were prepared by calcination of AG in air at 700°C and under a flow of nitrogen at 1300°C for 2 h, respectively, is the same as that of AG. It thus appears that the morphology of Al(III) complexes is externally maintained on their conversion through γ -alumina to AlN. This maintenance strongly indicates that the nitridation reaction of γ -alumina to AlN proceeds through solid-state formed Al-oxynitride intermediates (AlO_xN_y).¹⁰ On the contrary with formation of gaseous intermediates, including aluminum vapor or volatile aluminum suboxides such as Al_2O and AlO ,^{13–17} maintenance in morphology can be excluded. Up to now maintenance in the morphology has been also reported for CRN reactions using aluminum citrate⁴ or alumina and $\text{Al}(\text{OH})_3$ ^{18,19} as a precursor.

It is believed that amorphous AlN powders formed at the initial stage are hollow and/or less dense, considering that the morphology of the amorphous AlN powders is externally the same as that of AG powders, in

spite the fact that formation of 1 mol AlN from 1 mol of AG complex is accompanied with a weight loss of 78%. Upon increasing the calcination temperature, AlN powders become more crystalline and denser, resulting in the fact that the AlN agglomerate transform into an aggregates with a mean diameter of $\sim 0.2 \mu\text{m}$ (Fig. 5). The observed change in morphology during conversion of ASu and ASe to AlN can be explained in the same way. Thus it follows that in the CRN method the morphology of AlN powders is controlled by that of the precursor.

As already known, fabrication of AlN whiskers by the CRN method is very difficult. However, the AlN whiskers have been fabricated by the conventional CRN method using a mixture of alumina and carbon together with droplets formed by a catalyst.^{20,21} In the previous paper,²² the authors reported that AlN whiskers also could be obtained by calcination of AS at temperatures much lower than in the conventional CRN method without using any catalyst. As shown in Fig. 1(c), for the sample obtained by calcination of AG at 1300°C for 2 h, beginning formation of AlN whiskers is observed. At higher calcination temperatures predominant formation of AlN whiskers with various shapes is observed, but

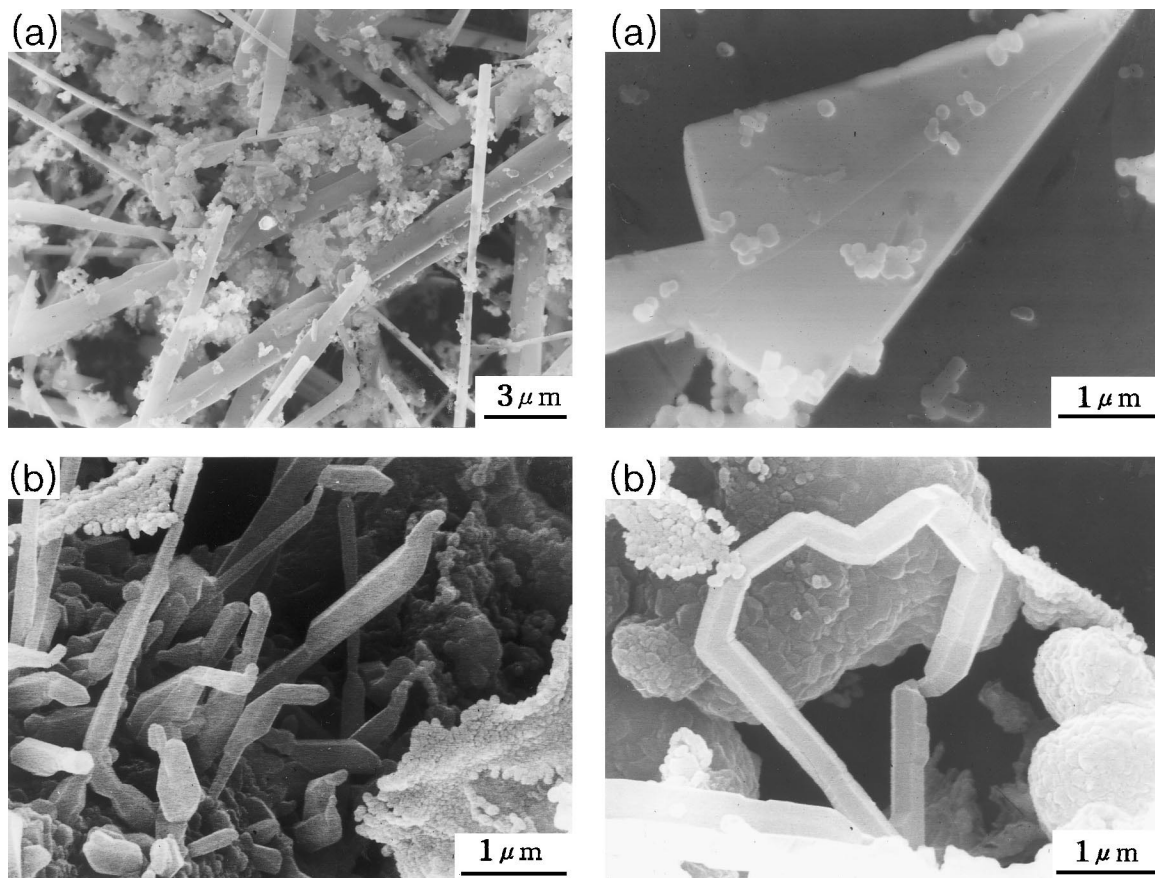


Fig. 6. SEM micrographs of AlN whiskers obtained by calcination of (a) (glutarato)(hydroxo)aluminum(III) and (b) a mixture of (hydroxo)(sebacato)aluminum(III) and carbon under a flow of nitrogen at 1500°C for 5 h (S route).

tips of whiskers did not show droplets (Fig. 6). The formation of AlN whiskers is easier using AS and AG instead of AA, ASu, and ASe as starting materials. Unfortunately the AlN powders obtained in this study always consisted of both particles and whiskers. To obtain AlN whiskers exclusively further detailed studies are necessary.

4. Conclusion

Aluminum nitride (AlN) particles and whiskers were synthesized by calcining basic dicarboxylate Al(III) complexes $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ ($n = 3, 6, 8$) under flowing nitrogen and removal of residual carbon in reaction products via oxidation on air. The carbon contents in a series of $\text{Al}(\text{OH})(\text{C}_{n+2}\text{H}_{2n}\text{O}_4) \cdot x\text{H}_2\text{O}$ complexes were found not to be correlated to those in their reaction products after calcination in a nitrogen atmosphere. The complexes of $n = 2$ and 3 are completely converted to AlN without using additional carbon and their nitridation kinetics are better than those of the complexes of $n = 4, 6$, and 8, which can be completely converted to AlN only after admixture of a carbon source. The reaction system using basic dicarboxylate Al(III) complexes as a precursor of AlN has common characteristics as follows: (a) the complexes decompose to a mixture of γ -alumina and carbon and then transform to AlN without γ - α alumina transition; (b) the morphology of AlN powders is very similar to that of the precursor; (c) AlN whiskers are more easily formed than using the conventional CRN method. The morphology of AlN powders obtained indicates that the conversion of alumina to AlN does not proceed through gaseous intermediates but through solid-state intermediates during the CRN process.

Acknowledgements

This research was supported by the Yeungnam University research grants in 1999.

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