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## Communications

### Synthesis of Aluminium Nitride Whiskers from Basic Dicarboxylate Aluminium(III) Complexes in an N<sub>2</sub> Atmosphere

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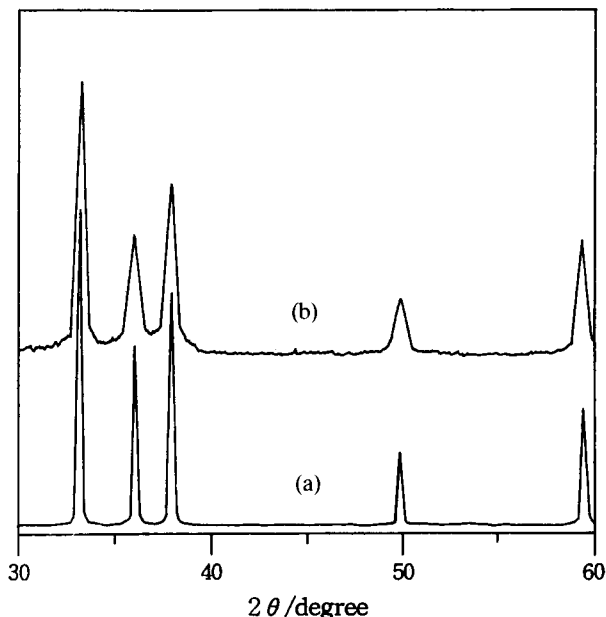
Aluminium nitride (AlN) is one of the most promising non-oxide materials for thermomechanical and electronic ceramics applications because of its high thermal conductivity, high electric resistivity, high mechanical strength, and relatively low dielectric constant and loss.<sup>1,2</sup> Its electronic applications include heat sinks, hybrid substrates, and semiconductor packages.<sup>3,4</sup> AlN powders can be prepared by a variety of methods.<sup>5</sup> Two of the common synthetic methods have been extensively employed for commercial powders: The direct nitridation of metallic aluminium with either N<sub>2</sub> or NH<sub>3</sub> and carbothermal reduction and nitridation (CRN) of  $\alpha$ -alumina with a source of carbon in an N<sub>2</sub> atmosphere. The latter method is known to be superior to the former in properties of the AlN powder produced but involves the preparation of an intimate alumina-carbon mixture and the reaction temperature above 1400 °C. We reported in previous papers<sup>6,7</sup> that the AlN powder can be obtained using one of basic dicarboxylate Al(III) complexes with an empirical formula of Al(OH)(succinate)·xH<sub>2</sub>O (hereafter it will be called as AS) as a precursor. The powders produced are nano-sized and their particle size depends on the calcination temperature and time. Our method may be called as a modified CRN method because the formation of AlN takes place *via* a mixture of  $\gamma$ -alumina and carbon which is formed by pyrolysis of AS in an N<sub>2</sub> atmosphere.<sup>6</sup> The method is more favorable than the conventional CRN method in the point that it is not necessary to add any carbon source to the precursor powder.

In recent years, AlN whiskers have been suggested for use as a filler in polymers to increase the thermal conductivity.<sup>4</sup> High thermal conductivity polymers have a wide variety of applications, from sealants and potting com-

pounds for electronic applications to heat-dissipating structural, adhesive, or insulating materials. Despite the great potential application of the AlN whiskers, studies on the synthesis have been very limited. Kim *et al.*<sup>8</sup> and Chung *et al.*<sup>9</sup> prepared the whiskers by the self-propagating high-temperature synthesis (SHS) method using metallic aluminium. And Caceres and Schmid<sup>10</sup> prepared them by the CRN method using alumina with a particle size of < 15  $\mu$ m and recarbulizing coke at 1800 °C under flowing nitrogen.

In this communication we report that our modified CRN method has another favorable characteristics than the conventional CRN method, that is, that AlN whiskers are easily prepared from Al(III) complexes at much lower temperature without mixing them any carbon source.

The AS powder was calcined at 1500 °C for 20 h in an N<sub>2</sub> atmosphere without mixing it with any carbon source in an alumina crucible using the reactor described in a previous paper.<sup>6</sup> And then the residual carbon was removed by heating the calcine at 700 °C for 1 h in air. The whiskers obtained were characterized by X-ray diffraction (XRD) patterns (recorded on a Rigaku DMX-2500 diffractometer with CuK $\alpha$  radiation operating at 40 kV and 50 mA) and scanning electron micrographs. As shown in Figure 1(a), the XRD patterns confirmed that the whiskers were only crystalline AlN. The scanning electron micrographs of the whiskers are shown in Figure 2. Most of the whiskers take shape of well-defined six-sided prismatic needles with a diameter around *ca.* 1  $\mu$ m and have planar and smooth surfaces. No droplets were observed at the whisker tips, as in the whiskers produced by Caceres and Schmid.<sup>10</sup> On the basis of no formation of droplets they suggested that the whiskers grew by the vapor-liquid-solid (VLS) mechanism.



**Figure 1.** XRD patterns of samples obtained by calcination of (hydroxo)succinato)Al(III) at 1500 °C (a) and 1250 °C (b) for 20 h in an  $N_2$  atmosphere.

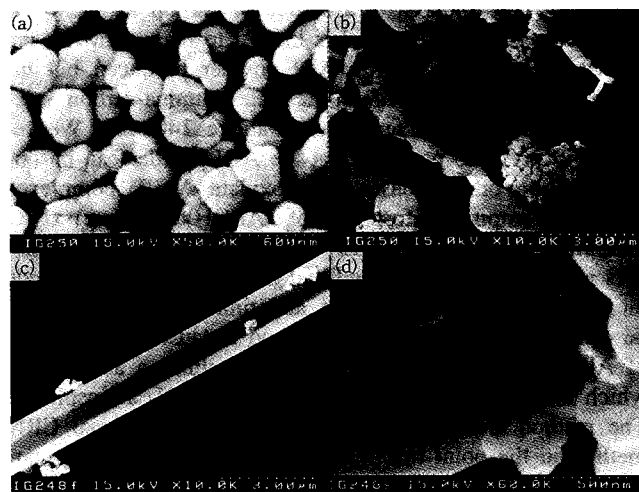


**Figure 2.** Scanning electron micrographs of AlN whiskers obtained by calcination of (hydroxo)succinato)Al(III) at 1500 °C for 20 h in an  $N_2$  atmosphere.

When  $Al(OH)(glutarate) \cdot xH_2O$  (hereafter it will be called as AG)<sup>11</sup> was used instead of AS, the whiskers were prepared by calcining it at 1500 °C for 3 h in an  $N_2$  atmosphere. The fact that the formation of AlN whisker is easier for AG than for AS may be due to the difference in the amount of carbon produced by pyrolysis of the complexes. Note that the pyrolysis of 2 mol of AS and AG complexes in an  $N_2$  atmosphere gives 4 and 5 mol of carbon, respectively.

On the other hand, when a mixture of  $\alpha$ -alumina and carbon black was heated at 1500 °C for > 20 h in an  $N_2$  atmosphere, no formation of the whiskers was found. The  $\alpha$ -alumina powders were obtained by firing AS at 1200 °C in air and their mean particle size was *ca.* 40 nm, which was much smaller than that of  $\alpha$ -alumina used by Caceres and Schmid.<sup>10</sup> Comparing results of ours and Caceres and Schmid,<sup>10</sup> it is estimated that the relatively low temperature of the whisker formation in this study is attributed to the nano-scaled size of AlN powder prepared from basic dicarboxylate Al(III) complexes and/or the highly intimate mixing of  $\gamma$ -alumina with carbon at the molecular level through the pyrolysis of the Al(III) complexes. Considering that the choice of carbon powder has a strong influence on the formation of TiC whiskers *via* the VLS mechanism,<sup>12</sup> we cannot rule out the possibility that the carbon produced by pyrolysis of Al(III) complexes is more favorable for the formation of AlN whiskers than any other source of carbon.

The process of the formation and growth of AlN whiskers from AlN powders can be explained by scanning electron micrographs (Figure 3) of the sample, which was obtained by calcination of AS at 1500 °C for 10 h in an  $N_2$  atmosphere. Primary particles (Figure 3(a)) are transformed into incomplete whiskers consisting of grown crystal particles (Figure 3(b)) and then the whiskers in the zigzag form are straightened, resulting in the formation of six-sided prismatic needles (Figure 3(c)). It is obvious from Figure 3(d) that the whiskers become longer by diffusion of nano-scaled particles adhered to the planar surface into the whisker. Besides the prismatic whiskers, the star-like and plate-like whiskers were also observed, as reported by Caceres



**Figure 3.** Scanning electron micrographs showing the process of formation of AlN whiskers from AlN powders. The sample was obtained by calcination of (hydroxo)succinato)Al(III) at 1500 °C for 10 h in an  $N_2$  atmosphere.

and Schmid.<sup>10</sup>

In the case of the sample obtained by calcining AS at 1250 °C for 20 h, there were no detectable peaks other than the peaks assigned to AlN in an XRD pattern, as shown in Figure 1(b). Each peak in Figure 1(b) is much broader than in Figure 1(a), but in the <sup>27</sup>Al magic-angle spinning (MAS) NMR spectrum only one peak at 114 ppm which is assigned to AlN<sup>13</sup> had almost the same linewidth (1.2 kHz) as that of the sample prepared at 1500 °C for 20 h. No whiskers were formed in the sample, indicating that the calcination temperature is very important for formation of AlN whisker. More detailed studies on the nucleation and growth of AlN whisker from basic dicarboxylate Al(III) complexes are in progress in order to elucidate the whisker growth mechanism, determine the optimum conditions for whisker growth, and synthesize larger single crystals.

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### References

- Slack, G. A. *J. Phys. Chem. Solids* **1973**, *34*, 321.
- Strite, S.; Morkoç, H. *J. Vac. Sci. Technol. B* **1992**, *10*, 1237.

- Sheppard, L. M. *Am. Ceram. Soc. Bull.* **1991**, *70*, 849.
- Mroz, T. J. *Am. Ceram. Soc. Bull.* **1994**, *73*, 77.
- Selvaduray, G.; Sheet, L. *Mater. Sci. Technol.* **1993**, *9*, 463.
- Jung, W.-S.; Ahn, S.-K. *J. Mater. Chem.* **1994**, *4*, 949.
- Ahn, S.-K.; Jung, W.-S.; Kim, D. J. *J. Korean Chem. Soc.* **1993**, *37*, 165.
- Lee, K.-J.; Jang, Y.-S.; Kim, S.-Y.; Kim, Y.-S. *J. Korean Ceram. Soc.* **1995**, *32*, 931.
- Lee, W.-C.; Tu, C.-L.; Weng, C.-Y.; Chung, S.-L. *J. Mater. Res.* **1995**, *10*, 774.
- Caceres, P. G.; Schmid, H. K. *J. Am. Ceram. Soc.* **1994**, *77*, 977.
- The AG complex was prepared by the same method as described in Ref. 6. Its empirical formula was determined by thermal analysis, gravimetry, IR, <sup>27</sup>Al MAS NMR and <sup>13</sup>C CP/MAS NMR spectroscopy. Details on synthesis of AlN using AG will be in preparation for publication.
- Ahlén, N.; Johnsson, M.; Nygren, M. *J. Am. Ceram. Soc.* **1996**, *79*, 2803.
- Dupree, R.; Lewis, M. H.; Smith, M. E. *J. Appl. Crystallogr.* **1988**, *21*, 109.

## The Multinuclear NMR Study for the Coordination Number of the La(III) Complex of Triethylenetetraaminehexaacetic Acid(TTHA) in Aqueous Solution

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Lanthanide complexes of polyaminopolycarboxylic acids are being employed extensively in magnetic resonance as MRI contrast reagents and as shift reagents for alkali metal nuclei.<sup>1</sup> Although many ligands have been used for these purposes, the most useful of these ligands is triethylenetetraaminehexaacetic acid (TTHA).<sup>2</sup> On the other hand, only are there two diamagnetic nuclei, lanthanum(<sup>139</sup>La<sup>3+</sup>) and lutetium(<sup>175</sup>Lu<sup>3+</sup>), in lanthanides for the study of the coordination properties of cations especially for the NMR spectroscopy study. Although trivalent lutetium(<sup>175</sup>Lu<sup>3+</sup>) has I=7/2 and 97.41% of natural abundance, its nuclear quadrupole moment(Q) is about 27 times bigger than that of lanthanum(<sup>139</sup>La<sup>3+</sup>) (quadrupole moments are 5.68 and 0.21 barns, respectively).<sup>3</sup> Since the NMR linewidth ( $\nu_{1/2}$ ) is proportional to the square of quadrupole moment, we can easily predict the linewidth of Lu to be several 10<sup>4</sup>-10<sup>5</sup> Hz in terms of known <sup>139</sup>La linewidth.<sup>4</sup> From this practical point of view, lanthanum(<sup>139</sup>La<sup>3+</sup>), which has I=7/2 and 99.1% of natural abundance, appears to be only one of the NMR plausible nuclei in lanthanides. In practice, lanthanum(III) cations already have been proposed as model for Ca<sup>2+</sup> binding sites to study coordination properties in proteins<sup>5</sup> and <sup>139</sup>La

NMR has been used for the analytical tool of relevant nucleus.<sup>3</sup>

In order to understand the interplay between polydentate coordination of the ligand with lanthanum and the availability of charged carboxyl sidechains acting as cation attractors, the determination of complex structure is prerequisite. It has been previously known using <sup>1</sup>H NMR that EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid) have 6 coordination numbers (2 nitrogens and 4 carboxylates) and 7 coordination numbers (3 nitrogens and 4 carboxylates) with alkaline earth and diamagnetic lanthanide cations (La<sup>3+</sup>, Lu<sup>3+</sup>, and Y<sup>3+</sup>), respectively.<sup>6</sup> However, in the case of TTHA complex, the structure has never been studied completely and even the coordination number is still controversial. More specifically, there are two proposals: one with eight coordination number (4 nitrogens and 4 carboxylates)<sup>7</sup> and the other involving six coordination number (2 nitrogens and 4 carboxylates).<sup>4</sup> The fact that TTHA ligand can not donate all 10 possible donor atoms is well supported by the ligand-induced <sup>139</sup>La NMR chemical shift.<sup>4</sup>

The present communication reports the results of the <sup>1</sup>H