

Synthesis of Nanocrystalline Aluminum Nitride by Nitridation of δ -Al₂O₃ Nanoparticles in Flowing Ammonia

Qinghong Zhang and Lian Gao*,[†]

State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Nanocrystalline aluminum nitride (AIN) with surface area more than 30 m^2/g was synthesized by nitridation of nanosized δ -Al₂O₃ particles using NH₃ as a reacting gas. The resulting powders were characterized by CHN elemental analysis, X-ray diffraction (XRD), Fourier transform infrared spectra, X-ray photoelectron spectra, field-emission scanning electron microscopy, transmission electron microscopy, and Brunauer-Emmett-Teller surface area techniques. It was found that nanocrystalline δ -Al₂O₃ was converted into AlN completely (by XRD) at 1350°-1400°C within 5.0 h in a single-step synthesis process. The complete nitridation of nanosized alumina at relatively lower temperatures was attributed to the lack of coarsening of the initial δ -Al₂O₃ powder. The effect of precursor powder types on the conversion was also investigated, and it was found that α -Al₂O₃ was hard to convert to AlN under the same conditions.

I. Introduction

THE importance of nanocrystalline powders has been known for many years in powder metallurgy, ceramics, catalysis, and other fields. It is common knowledge that ultrafine powders have better sinterability, and some possess higher catalytic activity, or higher dispersability. Unfortunately, unlike wellinvestigated nanocrystalline oxides, the preparation of nanocrystalline nitrides is more difficult as the preparation generally proceeds at high temperatures, which also undergoes dynamic growth and agglomeration of the resulting nitride particles. Among nitrides, aluminum nitride (AlN) has attracted much interest in recent years, particularly in the electronics industry as a substrate material, because of its high intrinsic thermal conductivity $(320 \text{ W} \cdot (\text{m} \cdot \text{K})^{-1})$, high electrical insulation, and thermal expansion coefficient close to that of silicon.¹ In addition, AlN has been added to polymers as a filler in a powder or fiber form to modify the thermal properties of electronic-packaging materials.^{2,3}

Commercial AlN powder is currently produced via the direct nitridation of aluminum metal or the carbothermal reduction–nitridation of alumina.⁴ Aluminum metal melts at a temperature much lower than its nitridation temperature with N₂. The AlN crust on liquid droplets of Al prevents the unreacted Al core from further nitridation, and thus a complete conversion to AlN powder is difficult to achieve in this process. For the carbothermal reduction–nitridation of alumina, there are also some disadvantages such as a relatively high nitriding temperature (higher than 1600°C) as well as an additional postoxidation step necessary to remove the excessive carbon.^{5–7} Recently, some new methods such as pulsed laser ablation,⁸ carbothermal synthesis,⁹ electrochemical method,¹⁰ low-temper-

ature nitridation of metallic aluminum,11 organo-metallic precursors, and vapor synthesis were reported to prepare nanocrystalline AlN.¹²⁻¹⁵ Other routes such as self-propagating high-temperature synthesis or combustion synthesis generally produced micrometer-sized aluminum nitride particles and whiskers.¹⁶⁻¹⁹ In addition, alumina could be transformed into AlN in flowing ammonia or a mixture of N₂/NH₃ over long time periods, and the conversion could be carried out at 1400°C in the presence of CaF₂ as additives.²⁰ Hoch and Nair²¹ reported that up to 80% of the amorphous alumina was converted to AlN at 1200°C for 24 h, and the rest of the starting material was transformed to α -Al₂O₃. Rocherulle *et al.*²² demonstrated that pure aluminum nitride powder was produced by reacting alumina (~1 μ m) with ammonia at 1300°C for 48 h. For carbothermal synthesis of AlN, Keramont Corporation observed that nitridation parameters were very dependent on the type of alumina/carbon used: a temperature difference as much as 200°C might be observed in requirements for nitridation using different types of alumina.¹ So, for the Al₂O₃–NH₃ system, using alumina nanoparticles instead of alumina of 1 µm size for the nitridation reaction may shorten the reaction time, and also much finer AlN powders are expected. A modified carbothermal reduction method was also developed, and it focused on more homogeneous mixing of alumina with carbon.^{23,24} More recently, Komeya et al. reported a novel process for synthesizing spherical or fibrous AlN powder by reduction-nitridation of Al_2O_3 of particle diameter 0.91 and 5.8 µm using NH₃-C₃H₈ as reactant gases,²⁵⁻²⁷ and a small amount of crystalline aluminum oxide still remained in their products.^{25,27} The gaseous carbon source derived from the pyrolysis of C₃H₈ stimulated the nitridation reaction to take place at a lower temperature compared with the conventional carbothermal reaction.²⁵ Haussonne et al.²⁸ reported an interesting process by heating the mixture of aluminum powder with lithium salts in nitrogen at temperatures ranging from 800° to 1200°C, and they obtained pure aluminum nitride with a specific surface area up to $17.51 \text{ m}^2/\text{g}$ at 940°C.

For the gas-solid reaction, it is expected that the temperature may decrease and the time for complete reaction may be shortened significantly using finer solid particles as a precursor. Recently, alumina nanoparticles in crystalline phase or amorphous state have been commercially available, and their conversion to aluminum nitride may be carried out at a relatively low temperature within a shorter time. The present work aims to establish a method to obtain a pure and ultrafine AlN powder via a carbon-free and cost-effective synthesis technique. Ultrafine and pure (by X-ray diffraction (XRD)) AlN powder with a specific surface area of more than 30 m²/g was obtained by this one step process. The complete nitridation of nanosized Al₂O₃ was carried out in flowing NH₃ at temperatures lower than the sintering temperature of fine alumina powder.

Manuscript No. 20732. Received July 1, 2005; approved July 27, 2005. *Member, American Ceramic Society.

[†]Author to whom correspondence should be addressed. e-mail: liangaoc@online.sh.ch

II. Experimental Procedure

Three kinds of Al_2O_3 powder were used for the nitridation reaction: One is the laboratory synthesized amorphous Al_2O_3 , and

N. Jacobson-contributing editor

the others are the commercial nanocrystalline $\delta\text{-Al}_2\text{O}_3$ and α-Al₂O₃. For the preparation of amorphous Al₂O₃ powder, 0.1M Al₂(SO₄)₃ solution was neutralized with 0.4M NaAlO₂ solution isovolumetrically at room temperature, and then the precipitate was separated from the mother solution by filtration and washed with distilled water several times. The thoroughly washed precipitate was dried at 110°C for 24 h and subsequently calcined at 800°C for 2 h to remove the undesired water for the nitridation reaction. The XRD result showed that the powder after calcination at 800°C was amorphous, having a Brunauer-Emmett-Teller (BET) specific surface area of 86 m²/g. Assuming all particles are spherical, the value of the specific surface area corresponds to a primary particle size of 16 nm. A commercially available spherical δ-Al₂O₃ powder (Aluminium Oxide C, Degussa, Frankfurt, Germany) with a surface area of 95.6 m^2/g and an average primary particle size of 13 nm was used as a nanocrystalline precursor. For comparison, the commercial α-Al₂O₃ powder (Al₂O₃ Type-HFF25, Shanghai Zhongyuan Chem. Ltd. Co., Shanghai, China) with a BET specific surface area of 25.0 m^2/g was also used as a precursor for synthesizing AlN. It was found that nanocrystalline δ -Al₂O₃ powder was converted into AlN more easily than the others, so δ -Al₂O₃ powder was used as a precursor to investigate the effects of the processing parameters on the conversion of Al₂O₃ into AlN and the crystallite size of the resultant AlN.

Two grams of alumina was placed in a high-purity alumina boat and set in an alumina tube furnace (inner diameter of 90 mm) with air-tight end gaskets. The reactor was flushed with argon to eliminate oxygen in the system during the heating-up period. As the temperature reached 900°C, a gas of NH₃ (99.9% purity) was introduced from the extremity of the reactor, at a flow rate of 1 L/min (stp). The pressure in the alumina tube was slightly higher than 1 atm, which permitted removal of the reactant and product gases from the exit side of the furnace tube. The NH₃ was adsorbed with a water pool before the waste gas was released into air. The furnace was heated to the experimental reaction temperature (1200°–1500°C) at a rate of 8°C/min, and the reaction temperature was held subsequently for 2–5 h. Then, the sample was cooled to room temperature at a rate of 6°C/min in an ammonia atmosphere.

The powder phase composition was identified by XRD (Model D/max 2550V, Rigaku Co., Tokyo, Japan), operated at 40 kV and 100 mA using CuK α ($\lambda = 1.5406$ A) radiation. Elemental analysis for carbon (C), hydrogen (H), and nitrogen (N) contents in the nitrided powder was carried out using a Perkin Elmer CHN analyzer (Model 2400-II, Boston, MA), and oxygen was introduced for complete combustion of the nanocrystalline nitride powder. CHN elemental analysis was very effective in quantitatively determining the nitrogen content in the nanocrystalline InN powder.²⁹ The morphology and the crystallite size of the resulting nitrides were observed using a transmission electron microscope (TEM) (Model 200CX, JEOL, Tokyo, Japan) as well as a field-emission scanning electron microscope (FE-SEM) (Model JSM-6700F, JEOL). The BET specific surface area measurement was performed using a nitrogen adsorption apparatus (Model ASAP2010, Micromeritics Instruments, Norcross, GA). Simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses of the sample were performed in air using a thermal analyzer (Model STA 449C, Netzsch Inc., Selb, Germany) at the rate of $5^{\circ}C/min$. Using a Noclet Series NEXUS Fourier transform infrared (FTIR) spectrometer (NEXUS, Nicolet, Madison, WI), absorption spectra were collected on the samples in the spectral range of 400–4000 cm⁻¹ using the KBr pellet method. The X-ray photoemission spectroscopy (XPS) analysis was performed using a Microlab MK II XPS surface analyzer (VG Scientific Ltd., East Grinstead, U.K.) using MgKa X-ray irradiation. The peak positions were calibrated with respect to the position of C 1s carbon contamination peak usually located at about 284.6 eV, when observed without charging effects. The chemical composition after ionic cleaning of the surface was determined by quantification of the corresponding photoelectron peaks.

III. Results and Discussion

(1) Effect of Precursor Oxides on Conversion of Al_2O_3 to AlN

When amorphous Al_2O_3 and α - Al_2O_3 were nitrided both at 1400°C for 2 h, the amorphous alumina with a specific surface area of 82 m²/g predominantly converted in aluminum nitride, and the remaining amorphous parts crystallized to α -Al₂O₃ (Fig. 1(d)). The conversion of α -Al₂O₃ powder with a surface area of 25.0 m^2/g was much lower than that of amorphous Al₂O₃, and only very weak peaks of hexagonal AlN (100) were detected in its XRD patterns as shown in Fig. 1(b). Hoch and Nair²¹ also reported difficulty in the conversion of α -Al₂O₃ to AlN. They found that increasing the nitridation temperatures of amorphous alumina generally crystallized more amorphous Al_2O_3 to α - Al_2O_3 rather than forming higher concentrations of AlN.²¹ By comparison, the nanocrystalline δ-Al₂O₃ converted into AlN almost completely and a very small peak corresponding to the residual α -Al₂O₃ was detected by XRD (Fig. 1(c)). The presence of α -Al₂O₃ is because of δ - α transformation of alumina, which also indicates that the reaction time of 2 h is not enough for complete conversion to AlN. For a longer nitridation (such as 5 h), no α -Al₂O₃ was detected by XRD in the samples (refer to Fig. 2). The commercial nanocrystalline δ -Al₂O₃ powder consists of very fine (13 nm) nanoparticles and does not coarsen in NH3 gas, which should promote the formation of AlN at relatively low temperatures for a shorter time. Coalescence of Al₂O₃ particles not only limits the ammonia availability but also reduces the gas-solid interface area significantly, thus greatly retarding the nitridation reaction. Besides the effect of Al_2O_3 particle size on nitridation reaction, the relative stability of different phases of alumina should also be taken into account. Hoch and Nair²¹ calculated the free energies of reaction and the equilibrium water vapor pressure for different types of alumina (amorphous and α -Al₂O₃), and they concluded that amorphous alumina can react with NH₃ at a higher partial pressure of water (0.027 vs 0.0075 atm at 1400°C). This means that the amorphous alumina may be nitrided with a higher yield. δ -Al₂O₃ is a mesostable phase compared with α -Al₂O₃, and a more stable phase than amorphous alumina. Owing to these considerations, amorphous alumina may display a higher nitridation rate than the others. However, amorphous alumina crystallizes and the particles grow at very high temperatures (Fig. 1(d)). The crystallization rate is relatively fast, and crystallization into α -Al₂O₃ reduces the speed of the subsequent nitridation. So, we conclude that the absence of coalescence and the mesostable phase of δ -Al₂O₃ are responsible for the complete conversion to AlN in a much shorter time.



Fig. 1. X-ray diffraction patterns of (a) α -Al₂O₃ powder, (b) α -Al₂O₃ powder after nitridation, (c) δ -Al₂O₃ after nitridation, and (d) amorphous Al₂O₃ after nitridation at 1400°C for 2 h in flowing NH₃ gas.



Fig. 2. X-ray diffraction patterns of nanosized δ -Al₂O₃ after nitridation at (a) 1200°C, (b) 1300°C, (c) 1350°C, and (d) 1400°C for 5 h, using a commercial nanosized δ -Al₂O₃ (aluminum oxide C, Degussa) as starting material.

To consider gas-solid reaction kinetics, the whole reaction will be considered:

$$Al_2O_3(s) + 2NH_3(g) \rightarrow 2AlN(s)) + 3H_2O(g)$$
(1)

However, ammonia readily decomposes at high temperatures and consequently, the reaction may be better represented as follows⁷

$$Al_2O_3(s) + N_2(g) + 3H_2(g) \rightarrow 2AlN(s) + 3H_2O(g)$$
 (2)

Thermodynamically, it is quite unlikely that reaction (2) will proceed to the right as a very low equilibrium partial pressure of H_2O is needed to be maintained for the above reaction.²¹ However, ammonia may reach reaction sites and react as NH_3 before it decomposes, especially when very fine alumina is used (such as 13 nm δ -Al₂O₃ and amorphous alumina) as starting materials. Al₂O₃ powder with a high specific surface area may absorb more NH₃ molecules, and some of them may react with the oxide before the decomposition of NH₃. Moreover, the ultrafine crystallite size of initial precursor aids in mass transfer in the boundary layer and mass transfer by diffusion in the product layer. At higher temperatures, δ -Al₂O₃ powder may transform



Fig. 3. Specific surface area of δ -Al₂O₃ powder calcined at various temperatures in (\bullet) NH₃ gas and (\blacktriangle) air.

to α -Al₂O₃ and exaggregated growth may occur, which reduces the speed of the nitriding reaction and results in an incomplete nitridation at 1500°C.

(2) Influence of Reaction Temperature on Nitridation of Nanocrystalline δ -Al₂O₃

Figure 2 shows the powder XRD patterns of nanocrystalline δ-Al₂O₃ powder after nitridation at different temperatures for 5 h. When δ -Al₂O₃ powder was calcined in NH₃ at 1200°C for 5 h, it neither transformed into α -Al₂O₃ nor converted into crystalline AlN. However, some nitrogen (5.09 wt%) was detected in this sample (see Table I), suggesting adsorption of nitrogen species and/or formation of Al-N layers on the δ-Al₂O₃ surfaces. The adsorption of both NH₃ and the Al-N layers may inhibit $\delta - \alpha$ transformation and prevent exaggerated growth during further nitridation at a high temperature, which is similar to that observed for oxide nanoparticles with a higher thermal stability. 30,31 After nitridation at 1200°C, $\delta\text{-Al}_2O_3$ also retained a specific surface area as high as 82.7 m^2/g as presented in Fig. 3, which suggests its high thermal stability in NH₃. For the sample nitrided at 1300°C for 5 h, it transformed into α -Al₂O₃ partially (Fig. 2(b)), accompanied by a significant decrease of surface area and increase of nitrogen content (7.03 wt%) compared with the sample nitrided at 1200°C. All XRD peaks for the powder obtained by nitridation of commercial δ -Al₂O₃ powder at 1350 or 1400°C for 5 h may be attributed to the hexagonal

Table I. Conversion of Nanocrystalline Al₂O₃ Powders to AlN at Different Temperatures in Flowing NH₃ Gas

Sample	Starting materials	T (°C)	Time (h)	Phase	Crystallite size (nm) [†]	N (wt%) ^{\ddagger}	H (wt%) [‡]	O (wt%)§
A	δ-Al ₂ O ₃	1200	5	δ-Al ₂ O ₃	13	5.09	< 0.3	40.04
В	δ -Al ₂ O ₃	1300	5	δ -Al ₂ O ₃ α -Al ₂ O ₃	14 (δ -Al ₂ O ₃) 95 (α -Al ₂ O ₃)	7.03	0.41	37.36
С	δ-Al ₂ O ₃	1350	5	AIÑ	39	28.88	0.49	7.26
D	$\delta - Al_2 O_3$	1400	2	AlN	40	29.07	0.50	6.99
E	$\delta - Al_2O_3$	1400	5	AlN	43	30.44	0.45	5.11
F	δ -Al ₂ O ₃	1500	5	AlN, α-Al ₂ O ₃	54 (AlN) >100 (Al ₂ O ₃)	23.97	< 0.3	14.02
G	α -Al ₂ O ₃	1400	2	α -Al ₂ O ₃ AlN(trace)	91 (Al_2O_3)	1.23	< 0.3	45.36
Η	α -Al ₂ O ₃	1400	5	α -Al ₂ O ₃ AlN	65 (AlN) >100 (Al ₂ O ₃)	4.75	< 0.3	40.51
Ι	Amor. Al ₂ O ₃	1400	2	AlN α-Al ₂ O ₃	39 (AlN) 72 (Al ₂ O ₃)	24.34	< 0.3	13.04

[†]The crystallite size is calculated from the broadening of XRD peaks at $d_{104} = 2.552$ Å for α -Al₂O₃ and $d_{100} = 2.695$ Å for AlN, respectively. [‡]The nitrogen and hydrogen contents were analyzed by a CHN elemental analyzer, H contents in samples C–E are close to 0.5 wt%, indicating that the surfaces of AlN particles were hydroxylated after its exposure to air. [§]Balanced concentration by assuming that the oxidation state of O, N, and Al is -2, -3, and +3, respectively. AlN, aluminum nitride; XRD, X-ray diffraction.



500 nm



Fig. 4. X-ray diffraction patterns of nanosized $\delta\text{-Al}_2O_3$ after nitridation at 1500°C for (a) 2 h and (b) 5 h.

phase of AlN (Figs. 2(c) and (d)). The conversion of δ -Al₂O₃ into AlN was very sensitive to the nitridation temperature and reaction time, and pure AlN powder could be prepared only in a relatively narrow temperature range. As shown in Fig. 4, when the nitridation temperature was as high as 1500°C, the conversion of Al₂O₃ into AlN was not complete, and some α-Al₂O₃ remained in the product. This temperature was higher than the sintering temperature (1350°C) of fine alumina powder,³² and sintered powder had low reactivity and also as encountered diffusion limitations with respect to ammonia's to make inability contact with unreacted core of alumina. Figure 5 shows brightfield TEM images and electron diffraction (ED) patterns of nanocrystalline δ-Al₂O₃ after nitridation at 1500°C for 5 h. The sample consisted of primary particles 40-100 nm in size (Fig. 5(a)) and spherical particles of much larger size (>500 nm, Fig. 5(b)). The ED patterns in Fig. 5(b) indicate that the larger particles consist of α -Al₂O₃. The result suggests that the temperature of 1500°C is too high to prepare nanocrystalline AlN because of the sintering and exaggeration of α -Al₂O₃ particles. As given in Table I, the calculated crystallite size of AlN based on the broadening of XRD peaks is also much finer than that of α -Al₂O₃, also suggesting larger particles attributable to α -Al₂O₃.

It is notable that the growth of Al₂O₃ nanoparticles in the flowing NH_3 gas is much slower than that in air (see Fig. 3). The specific areas of samples calcined at 1200°C both in the flowing NH₃ gas and in air show a slight decrease. However, after calcination at 1300°C, the specific surface area decreased significantly, especially in air. As shown in Fig. 2(b), after calcination at 1300°C in NH₃ gas, the major δ -Al₂O₃ transformed into α -Al₂O₃ at this temperature. The δ - α transformation as well as the discontinuous growth of particles during the transformation may be responsible for the lowering of the specific surface area. AlN powders obtained by nitridation of δ -Al₂O₃ have specific surface areas of around 30 m²/g, which is higher than the value of 11 m²/g reported by Rocherulle *et al.*,²² who used Al₂O₃ of 1 µm size as starting materials. As-prepared nanocrystalline aluminum nitride powders with high surface areas have potential, and have promising applications in low-temperature sinterable ceramics and as additives for electron packaging materials. Moreover, this nitridation reaction takes place under atmospheric pressure for a remarkably reduced time (less than 5 h in the present work versus 48 h in the previous work²²). Both methods make this route attractive for industrial production of ultrafine AIN on a large scale, although a more effective gassolid reactor is necessary for economic considerations.

(3) Morphology of the Synthesized AlN

The resulting AlN particles are predominantly spherical, having a diameter range of 60-150 nm, as shown by the SEM images in



Fig. 5. Transmission electron microscope micrograph of nanocrystalline δ -Al₂O₃ after nitridation at 1500°C for 5 h in flowing NH₃ gas: (a) aluminum nitride particles and (b) the sintered α -Al₂O₃ particles in this sample. X-ray diffraction result shows that it was nitrided partially and some amount of α -Al₂O₃ existed in the nitrided powder. The electron diffraction (ED) patterns labeled a, b, and c are assigned (1 -1 -1), (0 1 -1) and (1 0 -2) crystallographic planes of α -Al₂O₃, respectively.

Fig. 6. The particle size of AlN obtained by nitridation of δ -Al₂O₃ nanoparticles at 1350°C for 5 h is finer than that obtained at 1400°C for 5 h. The AlN powders prepared by our method are uniform and very fine. In contrast, Sheppard¹ found that the commercial AlN was 800 nm or above in size, and Kim *et al.*³³ reported that they produced AlN 400 nm in size (by TEM) by nitridation of aluminum alkoxide hydrazide with NH₃ at 1300°C.

Figure 7 shows the characteristic TEM images corresponding to representative samples. For the AlN powder obtained by ammonolysis of an oxide precursor at 1350°C for 5 h, spherical crystalline particles with 30-50 nm in size were observed, which is much larger than that of δ -Al₂O₃ nanoparticles, because of the growth of nanoparticles at high temperatures. AlN obtained at higher temperatures generally had a larger particle size. For example, the AlN prepared by the nitridation of δ -Al₂O₃ nanoparticles at 1400°C for 5 h had a diameter of 40-80 nm. The calculated diffusion rate inside the reacting particles was in the range 8-20 nm/h at 1350°-1400°C. This means that for one Al_2O_3 particle having a radius of 500 nm, a nitridation time as long as 25-62.5 h is needed. The reported value of 48 h at 1300°C fell in this range.²² As demonstrated above, when the temperature was elevated to 1500°C, was incomplete nitridation of alumina was observed. This temperature is close to the sintering temperature of fine alumina powder, and some extremely coarse particles (1 µm) were also found in its TEM micrograph. The sintering as well as the associated lower reactivity and the retarded diffusion of reactive gas to the core of larger particles



Fig. 6. Scanning electron microscope images of phase-pure aluminum nitride obtained by nitridation of nanosized δ -Al₂O₃ calcined at (a) 1350°C for 5 h and (b) 1400°C for 5 h in a NH₃ gas flow, respectively.

were responsible for incomplete nitridation of fine alumina at higher temperature (1500° C). The employment of finer alumina particles instead of larger particles lowers the nitridation temperature and shortens the nitridation time, which is beneficial for formation of the nanocrystalline nitrides.

(4) Nitrogen Contents and Crystallite Size in the Nanocrystalline AlN Powders and the Thermal Stability of Nanocrystalline AlN

The problem encountered in the nitridation of oxide particles to nitride is oxygen contamination. In the present work, the CHN elemental analysis method was used to determine the nitrogen content in nanocrystalline nitride. Only about 5 mg was needed for this CHN analysis. Table I summarizes the results with respect to nitrogen contents, phase composition, and crystallite size of the nitrided powders obtained by nitridation of δ -Al₂O₃ powder at different temperatures for 2-5 h. All samples were exposed to air, and no special passivation for the fresh surface of nanocrystalline AlN was carried out prior to CHN element analysis and thermogravimetry (TG)-DSC analysis. The nitrogen content of AlN powder was 30.44 wt% (detected by CHN elemental analysis), slightly lower than the theoretical value of 34.15 wt% for AlN. As shown in Fig. 8, TG and DSC were used to investigate the thermal stability of the resulting nanocrystalline AlN powder in air and to calibrate the result of the CHN elemental analysis. A strong exothermal peak at 1103°C is detected in its DSC curve, which was attributable to the oxidation



Fig. 7. Transmission electron microscope micrographs of (a) nanocrystalline δ -Al₂O₃ and the resulting aluminum nitride powders prepared by a nitridation oxide precursor at (b) 1350°C and (c) 1400°C for 5 h in a NH₃ gas flow.

of AlN to Al_2O_3 in air. The TG curve shows a strong weight increase (19.7 wt%) in the range 885° -1165°C, which is associated with the oxidation of AlN in air. The value of weight increase from TG analysis is also slightly lower than the theoretical weight increase of pure AlN (24.3 wt%) and consistent with the nitrogen content listed in Table I.

Infrared absorption spectra obtained on the δ -Al₂O₃ and the nitrided samples are shown in Fig. 9. Overall, the IR spectra collected on these samples were very different. An intense vibration at 3600 cm⁻¹ was observed in δ -Al₂O₃ powder, which is because of the stretching vibration of the water molecules, suggesting the presence of adsorbed water on the surface of δ -Al₂O₃. After heat treatment at high temperatures, the intensity of this vibration reduced, and shifted to 3440 cm⁻¹, which is attributable to N–H stretching vibration.^{33–35} This result



Fig.8. Thermogravimetry–differential scanning calorimetry curves (in air) of the aluminum nitride powder prepared by nitridation of nanocrystalline δ -Al₂O₃ at 1400°C for 5 h.

indicates the formation of N–H bands on the resulting AlN nanoparticles. For δ -Al₂O₃ nanoparticles, the absorption peaks at 820, 740, and 600 cm⁻¹ correspond to Al–O linkages.^{33,36} For the sample after nitridation at 1200°C for 5 h, both the bands 820 and 600 cm⁻¹ are reduced to the shoulder peaks, and a new band at 700 cm⁻¹ is observed. The change of IR spectra suggests the structural evolution of δ -Al₂O₃ nanoparticles although few changes are observed in its XRD patterns as well as the specific surface area. The band at 700 cm⁻¹ is assigned to Al–N linkages,³³ demonstrating the formation of Al–N linkages, which is also supported by the nitrogen content result (Table I). When δ -Al₂O₃ nanoparticles were nitrided at 1350°–1400°C, the peak at 700 cm⁻¹ was much stronger and sharper, and the shoulder at 600 cm⁻¹ disappeared completely for the sample after nitridation at 1400°C. The IR spectra are very similar to those of AlN nanocrystals reported by Panchula and Ying.³⁵ However, the shoulder band centered at 740 cm⁻¹ is observed for both phase pure (by XRD) AlN, indicating the existence of Al–O linkages.³⁶

Figure 10 shows typical survey scans of nanocrystalline AlN prepared by nitridation of nanocrystalline δ -Al₂O₃ at 1400°C for 5 h. The XPS survey scans were recorded after Ar⁺ bombardment for 3 min. The XPS spectra show the appearance of the O 1s photoelectron peak with a strong intensity, indicating the predominance of aluminum oxide in the surface and sub-surface regions. Based on the XPS spectra, the estimated atomic percentages are as follows: C 24.59 at.% (internal standard for the normalization of binding energy), O 30.12 atom%, N 13.32 at.%, and Al 31.97 at.%. The atomic sum of oxygen and nitro-



Fig.9. Comparison of infrared absorption spectra collected on δ -Al₂O₃ nanoparticles and the nitrided samples in NH₃ for 5 h.



Fig. 10. X-ray photoemission spectroscopy survey spectrum of aluminum nitride powder prepared by nitridation of nanocrystalline δ -Al₂O₃ at 1400°C for 5 h.

gen is higher than the amount for the chemical equilibrium for Al by assuming that aluminum exists as Al₂O₃ and AlN, suggesting that some AlOOH also occurs in the surface and subsurface regions. The photoelectron escape depth value for AlN is $\lambda = 2.45 \text{ nm}^{37}$; if oxygen is homogeneously distributed throughout the XPS escape depth with a concentration of 30.12 at.%, one can calculate mean oxygen concentrations as high as 10.23 wt% for AlN nanocrystals of 40 nm diameter. The calculated value from XPS is much higher than the oxygen content in some samples listed in Table I, which suggests that the oxygen exists in ultrathin thickness at the surface rather than in AlN lattices or as unreacted Al₂O₃ cores. The surface layers of Al₂O₃ and AlOOH aware from the surface hydrolysis of AlN (especially its nanocrystals) after the ultrafine AlN powders were exposed to air, because of its high reactivity to air.^{22,35} So, we conclude the oxygen exists as ultrathin layers on the surface of as-prepared AlN, and special precautions should be taken to prevent it from hydrolyzing³⁵ as the oxygen contamination in AlN powder and ceramics may decrease the thermal conductivity of alumi-num nitride materials.^{35,38} The sintering behavior of as-prepared ultrafine AlN powders and the effect of oxygen content on the thermal conductivity of the sintered AlN ceramics are being investigated, and some sintering parameters should be optimized according to Jackson's published work.39

IV. Conclusions

A novel route for the preparation of nanocrystalline AlN powder via nitridation reaction of nanocrystalline δ -Al₂O₃ is presented. Nanocrystalline AlN powder of 30-60 nm crystallite size and with a specific surface area of $30 \text{ m}^2/\text{g}$ was obtained by nitridation of the commercially available nanocrystalline δ-Al₂O₃ at temperatures ranging from 1350° to 1400°C for 2-5 h. The remarkably reduced nitriding time (48 h were necessary in a previous work) makes this method attractive for the industrial production of ultrafine AlN on a large scale. The degree of conversion to nitride was very sensitive to the preparative parameters, especially the nitriding temperature. The resultant AlN was less agglomerated and uniform in particle size but some oxygen was found to exist on the surfaces, which may have a detrimental effect on the thermal conductivity of sintered AlN ceramics. Both the finer crystallite size and the higher thermal stability of δ -Al₂O₃ are beneficial for the formation of AlN at temperatures lower than the sintering temperature of fine Al₂O₃.

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