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Nitridation reaction of aluminum powder in flowing ammonia

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Abstract

AlN powder was prepared by the nitridation of metal Al in flowing NH_3. The effects of reaction temperature and the temperature gradient of the reaction zone on the nitridation of Al were investigated. Comparative analysis of products formed in different reaction zones and reaction temperatures suggested that the nitridation reaction of liquid Al particles in flowing NH_3 was through the following mechanisms: NH_3 dissociated into reactive nitrogen (N) and hydrogen (H) radicals at the surface of Al particles. N reacted with Al to form AlN, while H promoted the decomposition of NH_3, which provided enough energy for the dissociation of NH_3. All of the experimental results had been discussed on the basis of this model, which indicated high reaction temperature or positive temperature gradient was favorable for the nitridation of Al.

Keywords: Al; AlN; Nitridation; Powder preparation

1. Introduction

Aluminum nitride (AlN) has been acknowledged as a very important ceramic material in industrial applications due to its high thermal conductivity, high electrical resistivity, low thermal expansion coefficient than alumina ceramics, good thermal shock resistance and good corrosion resistance.[1–6] There are two primary processes commercially used for the manufacture of AlN powder: (i) the direct nitridation of metallic aluminum in nitrogen (N_2), and (ii) the carbothermal reduction and nitridation of alumina. Comparatively the former method is known to have the advantages of simplicity and cost-effectiveness, but metallic Al tends to aggregate due to its lower melting point (660 °C) than the nitridation temperature. Another major obstacle is that a coherent nitride skin forms on the surface of metal Al in the absence of an additive and does not allow a complete nitridation. Extensive efforts have been taken to overcome these obstacles. Additive such as Mg[2] has been reported to be able to avoid a dense nitride layer, however residual impurities are difficult to avoid. In the development of direct nitridation, processes such as floating nitridation[1] and nitridation of Al vapor[3] have been developed to resolve such problems. A mixture of N_2 and ammonia (NH_3) instead of pure N_2 is sometime used to decrease the reaction temperature and to achieve a higher conversion of Al,[4,5] which is attributed to the lower N–H bond energies in NH_3 compared with the N–N bond energies in N_2; therefore, less energy is required to break bonds.[6] NH_3, however, is not stable at the temperatures where AlN is the only condensed phase. It decomposes according to

$$NH_3(g) = \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \tag{1}$$

at temperatures above 200–300 °C at atmospheric pressure. Once NH_3 decomposes into molecular N_2 and H_2, the reactivity with Al decreases. Chang et al.[6] have proved theoretically that the direct reaction of NH_3 with liquid Al was thermodynamically favored. Hoch et al.[7] has suggested that NH_3 gas should reach the oxide and react as NH_3 before it has a chance to decompose because of the fine particle size of the solid reactants. But he has also noted that this sequence of events should have to be tested in the reaction vessel. However, other researchers have pointed out that the dissociation of NH_3 occurring in parallel with nitridation should be

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carefully taken into account in studying the nitridation reaction. Huseby[8] has claimed that, with an NH_3 atmosphere heated to 727 °C, at equilibrium more than 99.9% of the NH_3 would dissociate and the dissociation occurred at surfaces. It has been found that at the contact of metallic iron with NH_3, not only direct nitridation with NH_3 but also dissociation of NH_3 into nitrogen and hydrogen gas molecules should occur on the surface, and larger specific surface of nanoparticles enhanced NH_3 dissociation.[9] Thus far, understanding of the nitridation reaction of Al in NH_3 has still been limited and no experiment is reported to investigate the reaction mechanisms, although it is important to understand the reaction mechanisms in order to improve the process for commercial application.

In the present study, the nitridation reaction of liquid Al particles in flowing NH_3 is investigated. NH_4Cl and KCl are used as the additives to ensure the complete nitridation of Al powder, which is discussed in detail in another paper.[10] In brief, NH_4Cl and KCl do not participate in the nitriding reaction as additives. NH_4Cl prevents the agglomeration of liquid Al particles and KCl avoids the formation of a dense nitride layer on the Al surface, so the large reaction area between Al and ammonia is ensured. Thus the nitridation fully proceeds as it can, without being interrupted by foreign factors (e.g. formation of passivate layer). Based on this, the main purpose of this paper is to determine the reaction mechanism between NH_3 and liquid Al particles. For this purpose, a special reactor with two reaction zones, whose temperature gradients are opposite, is used. The effect of the temperature gradient and the reaction temperature is also investigated to elucidate the reaction mechanism.

2. Thermodynamic considerations

The nitridation reaction of Al in flowing NH_3 can be written as

$$\mathrm{Al}(l) + \mathrm{NH_3}(g) = \mathrm{AlN}(s) + \frac{3}{2}\mathrm{H_2}(g) \tag{2}$$

If the ammonia decomposes previous to the nitridation reaction, the reaction can be written as

$$\mathrm{Al}(l) + \frac{1}{2}\mathrm{N_2}(g) + \frac{3}{2}\mathrm{H_2}(g) = \mathrm{AlN}(s) + \frac{3}{2}\mathrm{H_2}(g) \tag{3}$$

If the dissociation of NH_3 occurs at the surface of liquid Al particles in parallel with nitridation, it may be suggested as

$$\mathrm{Al}(l) + 2\mathrm{NH_3}(g) = \mathrm{AlN}(s) + \frac{1}{2}\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \tag{4}$$

The Gibbs free-energy changes for reactions (2)–(4) between 727 and 1727 °C are plotted in Fig. 1. The data on free energy of formation are obtained from the JANAF tables.[11] It can be seen from Fig. 1 that the free-energy change associated with reactions (4) is significantly more negative than reaction (2) and (3), and can provide a driving force for dissociation of NH_3 when in contact with Al, thus enhance its thermal dissociation into reactive nitrogen radicals (NH_2, NH, and N). The dissociation energies E_D of the N–H bonds in NH_3 molecule are 427, 375 and 356 kJ/mol, respectively (see Table 1). The free-energy changes associating with the dissociation reactions are somewhat lower than E_D according to Eq. (5), for $\Delta S^\circ > 0$.

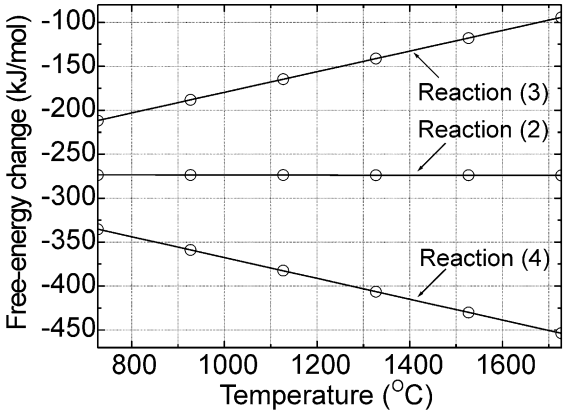

Fig. 1. Gibbs free-energy change for reactions (2)–(4) under isothermal conditions at 1 atm.

$$\Delta G^O = E_D - T\Delta S^O \tag{5}$$

It is obvious that only reaction (4) can provide enough energy for the dissociation of NH_3. According to thermodynamic calculations using ΔG° data of reaction (4) in Fig. 1, the necessary dissociation temperatures in equilibrium ($\Delta G = 0$) at atmosphere pressure are also listed in Table 1. It can be supposed that Al hardly be nitrided under atmosphere pressure if the reaction temperature is lower than 900 °C. Because $\Delta G^\circ < E_D$, the necessary nitridation temperature may be somewhat lower than the calculated in Table 1.

The free-energy change of reaction (4) is more negative at higher temperature, so it is expected that the conversion of Al increase with reaction temperature. Furthermore, since the dissociation of NH_3 is an endothermic and stepwise reaction, the temperature distribution in the reactor should be of important impact

Table 1
The dissociation energy (E_D) of N–H bonds in NH_3 molecule and the necessary dissociation temperatures according to reaction (4)

Reaction	E_D (kJ/mol)	Dissociation temperature (°C)
$NH_3(g) = NH_2(g) + H(g)$	427	1502
$NH_2(g) = NH(g) + H(g)$	375	1063
$NH(g) = N(g) + H(g)$	356	902

on the synthesis of AlN.[4,12] A positive temperature gradient can provide driving force for the stepwise dissociation of N–H bonds and thus the formations of reactive nitrogen radicals become more favorable. It is also predicted that the synthesis of AlN is favored with a positive gradient of reaction temperature. Thus the effects of the reaction temperature and the temperature gradient on the nitridation of Al powder in flowing NH_3 are studied in detail in the following section.

3. Experimental procedure

3.1. Reactor design

AlN was synthesized by reacting Al powder with NH_3 in an externally heated tube flow reactor (Fig. 2). The reactor was a corundum tube (10 cm inner diameter and 80 cm long) and had two sets of electric heater as illustrated in Fig. 2, similar to Ref. 12. Two Pt/Pt-Rh thermocouples were positioned 6 cm away from the center. Another thermocouple was used to measure the temperature profile (Fig. 3) in the reactor when the reaction temperatures measured by the two thermocouples are the same. Two corundum boats (each 11 cm long) were set in the different reaction zones (A and B) with opposite temperature gradients inside the tube, which were referred to the reaction zone A and B, respectively (see Figs. 2 and 3). That is, the boat in the reaction zone A had a negative temperature gradient and in the reaction zone B a positive one. When setting the boats, care must be taken to ensure the thermocouples locate above the middle of each boat, in order that the average reaction temperature could be measured accurately. NH_3 and N_2 were used as nitriding gas, respectively.

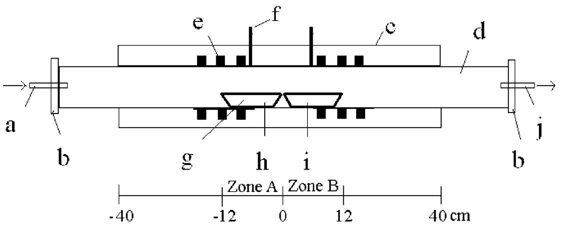

Fig. 2. Experimental apparatus for the synthesis of AlN powders and the temperature profile of the reactor. (a) NH_3-feeding tube, (b) water-cooling mantle, (c) furnace, (d) corundum tube reactor, (e) heater, (f) thermocouple, (g) corundum boat, (h) the reaction zone A, (i) the reaction zone B, (j) outlet.

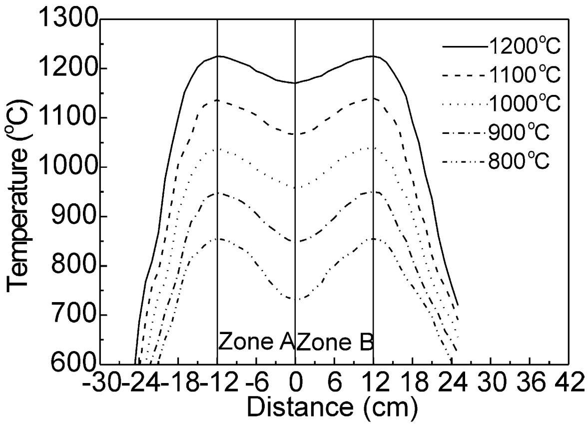

Fig. 3. Temperature profiles along the reactor axis at different reaction temperatures when the center of the reactor is taken as zero.

3.2. Procedure

Commercial Al powder (>99% pure, 100–200 mesh, BET surface area 0.65 m^2/g), NH_4Cl ($\geqslant$99.5% pure) and KCl ($\geqslant$99.5% pure) were ball-mixed (weight ratio of 1:1:1) for 48 h with stainless steel balls (powder/balls weight ratio of 1:10) in a plastic container, using acetone as media. After being dried at 80 °C, the resultant powders in one batch were placed in the boats in the reaction zone A and B, respectively. After NH_3 (>99% pure) gas was allowed to pass through the furnace for 1 h to remove most of the air in it, each batch was heated at 800–1200 °C for 5 h or at 1100 °C for 3 h in flowing NH_3 at the rate 0.6 l/min. The heating rate was 10 °C/min from room temperature to 600 °C, 7 °C/min from 600 to 800 °C and 5 °C /min from 800 °C to the setting temperature. Then the furnace was cooled down in the flow of NH_3 gas before products were collected from the boats. Similar procedures were used when N_2 (>99% pure) was used as the nitriding gas at 1000 °C except that the flow rate is 4 l/min, much higher than that of NH_3. Table 2 summarized the employed experimental conditions.

3.3. Characterization

The X-ray diffraction patterns of the resultant powders were obtained by an X-ray diffractometer (Model D/Max 2550V, Rigaku, Tokyo, Japan), using CuK_α radiation ($\lambda = 1.5418$ Å). The AlN crystallite diameters were determined from the Scherrer equation:[13]

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (6)$$

where λ was the wavelength and B was the broadening of a diffraction line due to the particle size effect measured at half of its maximum intensity. The specific surface area of the particles was obtained by BET (ASAP 2010, Micromeritics, USA). The average grain size was determined from the BET surface area assuming solid spherical grains and the theoretical density of 3.26 g/cm^3. The particle morphology and primary particle size were determined by a transmission electron microscopy (Model 200CX, Jeol, Tokyo, Japan). The size distribution of the agglomerate particles was measured by dynamic light scattering (Zeta Plus, Brookhaven,

Table 2
Summary of experimental conditions and results of XRD analysis

Exp. No.	T (°C)[a]	Reaction zone	XRD phase (wt.%)[b]	D_{XRD} (nm)	Remarks
1	800(5)	A	10AlN, 70Al, $Al_2O_3^t$, 20KCl		$\alpha = 8\%$
		B	10AlN, 40Al, 50KCl		$\alpha = 12\%$
2	900(5)	A	20AlN, 80Al, $Al_2O_3^t$	10	No residual KCl
		B	30AlN, 70Al	12	
3	1000(5)	A	60AlN, 40Al, $Al_2O_3^t$	12	Grey powder
		B	100AlN	12	White powder
4	1100(5)	A	AlN, $Al_2O_3^t$	13	
		B	100AlN	13	XRD Pure AlN
5	1200(5)	A	AlN, $Al_2O_3^t$	16	
		B	100AlN	15	XRD Pure AlN
6	1100(3)	A	85AlN, 15Al_2O_3, AlON	13	
		B	95AlN, $Al_2O_3^t$, 5AlON	12	
7	1000(5)	A	90AlN, 10Al_2O_3, AlON^t, KCl^t	35	Reacting with N_2 at high flow rate
		B	AlN,$Al_2O_3^t$, AlON^t, KCl^t	29	

Superscript t denotes trace amount.

[a] Numbers in parentheses indicate the time (in h) of nitriding at that temperature.

[b] Compositions are determined from the visual estimation of diffracted X-ray intensities.

NY, USA). The morphology of agglomerate particles was observed by the field emission scanning electronic microscopy (JSM-6700F, Jeol, Tokyo, Japan).

4. Results and discussion

4.1. Effect of the temperature gradient

Fig. 4a and b shows the X-ray diffraction patterns of the products synthesized in different reaction zones for comparison in the component phases. It is interesting that the resultant powders in the adjacent zones are distinct from each other as shown in Table 2, although they are synthesized under the same experiment conditions except for the temperature gradient. For nitridation at 1000 °C for 5 h in flowing NH_3 (Exp. No. 2), the resultant powder in zone B becomes white after the nitridation, indicating high AlN purity,[3] while it remains gray in zone A. XRD analysis proves that Al has been transformed completely to AlN in the reaction zone B while it remains a major phase in the final product in the reaction zone A. On the other hand, the residual Al is completely converted into AlN at 1100 °C in zone A, which is 100 °C higher than in zone B. Kimura et al.[4] have also found that AlN powder were only deposited in the zones with negative temperature gradients, which provided the driving force of the thermophoresis of AlN particles. These results suggest that it may be the temperature gradient that causes the difference between the products collected from the reaction zone A and B.

In addition, trace α-Al_2O_3 is formed in the reaction zone A (Fig. 4a), due to the water vapor brought in by additives.[14] Most of α-Al_2O_3 is converted into AlN at elevated temperatures ($\geqslant$1000 °C), but not all, because of the extreme stability of α-Al_2O_3.[7] In contrast no α-Al_2O_3 diffraction peaks appear in all cases in the reaction zone B (Fig. 4b). An experiment (No. 5) is conducted at 1100 °C for a shorter reaction time (3 h) in order to figure out the mechanism of the formation and the elimination of α-Al_2O_3. The intensity of the diffraction lines of α-Al_2O_3 is apparently stronger for the powders synthesized in both the reaction zone, especially in the reaction zone A (Fig. 4c). Besides, AlON is also detected, which is formed due to the same reason as that of α-Al_2O_3.[15] Both of α-Al_2O_3 and AlON are completely converted into AlN in the reaction zone B as the reaction time is prolonged, while trace α-Al_2O_3 remains as an impurity phase in the powders synthesized in the reaction zone A. The conversion temperature of α-Al_2O_3 into AlN in our study, especially in the reaction zone B, is much lower than that having been reported.[7,16]

These XRD analysis results provide clues to possible process mechanism for the reaction of Al in flowing NH_3. It seems that ammonia is much more reactive in the reaction zone B than in A, for the positive thermal gradient provides successive driving force for the dissociation of N–H bonds in NH_3 molecule. As a result, the temperature of the complete conversion of Al is lower and the time of the conversion of α-Al_2O_3 is shorter in the reaction zone with a positive thermal gradient. It can also be concluded that NH_3 does not (or seldom) decompose into N_2 and H_2 before it reaches the

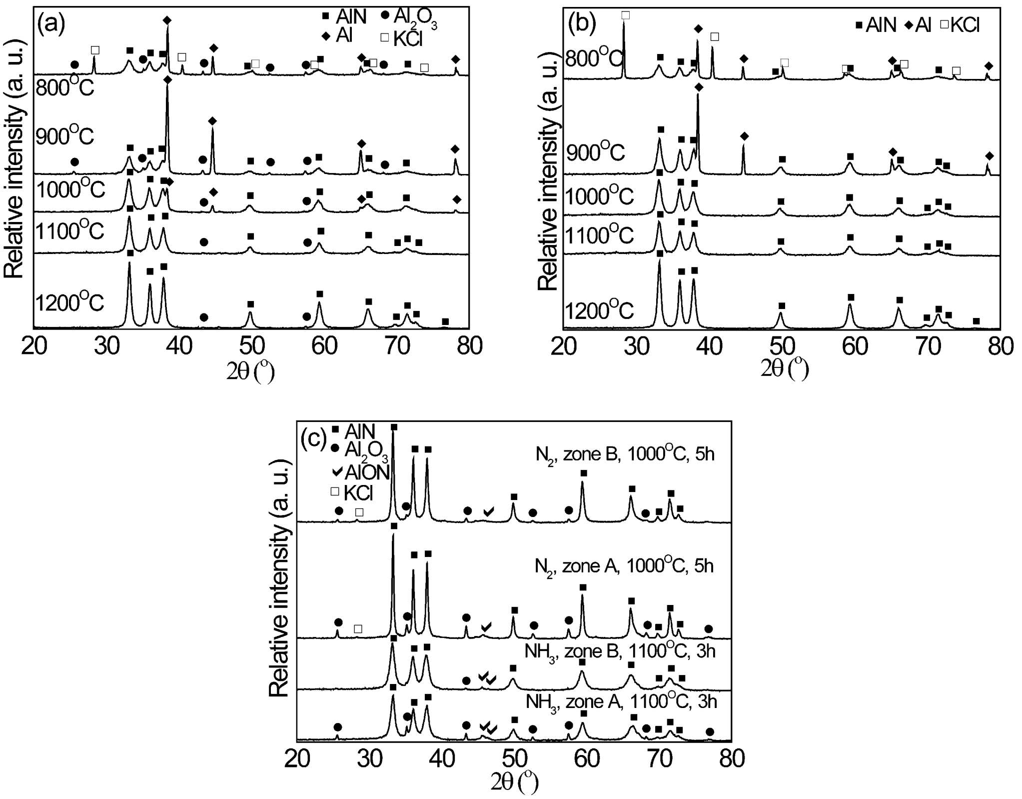

Fig. 4. X-ray diffraction patterns of the resultant powders synthesized (a) in the reaction zone A and (b) in the reaction zone B for 5 h in flowing NH_3, and (c) at 1100 °C for 3 h in flowing NH_3 or at 1000 °C for 5 h in flowing N_2.

surface of Al powder. Otherwise, the temperature gradients in the different reaction zones shouldn't have such a significant impact on the conversion of Al powder as revealed above. In order to exclude the possibility that the synthesis of AlN in zone A has an influence on AlN synthesis in zone B, we have conducted the experiments at the same reaction conditions by using only one boat in zone A or B and gotten the same results. Comparative experiment is also conducted in nitrogen gas (see Section 4.3).

4.2. *Effect of reaction temperature*

As proposed above, the nitridation of liquid Al particles through reaction (4) is more favored at higher reaction temperature, which is confirmed by the results of Exp. Nos. 1–5 (Table 2), with the reaction temperature varying from 800 to 1200 °C. At 800 °C, the conversion rate (α) of Al is less than 15% (Table 2), consistent with the prediction from the thermodynamics. It is 12% in zone B, higher than 8% in zone A. It seems the nitridation in zone B is favored. Furthermore, the KCl additive does not evaporate completely as the temperature is too low. The conversion rate α is below 30% even when the reaction temperature is raised to 900 °C. Still, the yield of AlN is higher in zone B at 900 °C. The XRD patterns (Fig. 4b) show that complete nitridation is realized at 1000 °C in the reaction zone B, while only 60% Al is nitrided in zone A, which means the Al powder can fully convert to AlN at lower temperature if the temperature gradient is positive. XRD find no impurity in the products obtained at temperatures $\geqslant 1000$ °C in zone B. Full conversion of Al is realized at temperatures $\geqslant 1100$ °C in zone A (Fig. 4a), although there are trace Al_2O_3 remaining in the AlN powders. At either case, the full conversion temperature is lower than reported[3,4] or at least equal to.[6]

All XRD peaks are broadened, corresponding to the characteristic of nanocrystallites. The degree of crystallinity is apparently higher at 1200 °C as all diffraction peaks become sharper. The AlN crystallite diameters calculated from the Scherrer Eq. (6) are listed in Table 2. Because high purity AlN is only obtained in the reaction zone B, the discussions below are limited to the powder collected from zone B.

Fig. 5 shows the lattice parameters (a and c) of the synthesized AlN, plotted against the reaction temperature. Here a and c are calculated from d of the diffraction lines of AlN. It can be seen that the lattice parameters decrease with increasing reaction temperature, which is explained that the higher reaction temperature enhances NH_3 dissociation and decreases the nitrogen content of AlN obtained.[9] According to Fig. 1, the dissociation of NH_3 is favored at high temperature if it dissociates through reaction (4).

It can be seen from TEM pictures that the AlN particles synthesized at 1000 °C for 5 h in the reaction zone B are near spherical and most of the particles fall in the size range of 10–20 nm with a mean value of 13.5 nm (Fig. 6a), which is in agreement with the crystallite size calculated from the Scherrer equation. Selected-area electron diffraction pattern (Fig. 6) indicates that the AlN particles are polycrystalline and in hexagonal structure. The grain size increases slightly at 1100 °C as observed by TEM. For AlN powder synthesized at 1200 °C, sphere or ellipse particles consisting of 20–45 nm crystalline are observed (Fig. 6b), indicating a rapid coarsening of AlN crystallite above 1100 °C. This value is apparently larger than that calculated from the broadening of XRD peaks (Table 2). The intensity of electron diffraction cycles in Fig. 6b is stronger than that in Fig. 6a, suggesting a better crystallinity of AlN synthesized at higher reaction temperature.

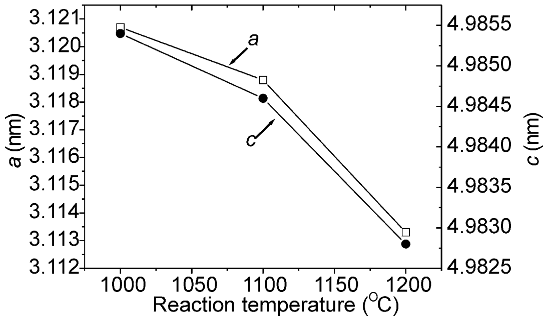

Fig. 5. The effect of reaction temperature on the lattice constants (□ *a*, • *c*) of AlN synthesized in the reaction zone B.

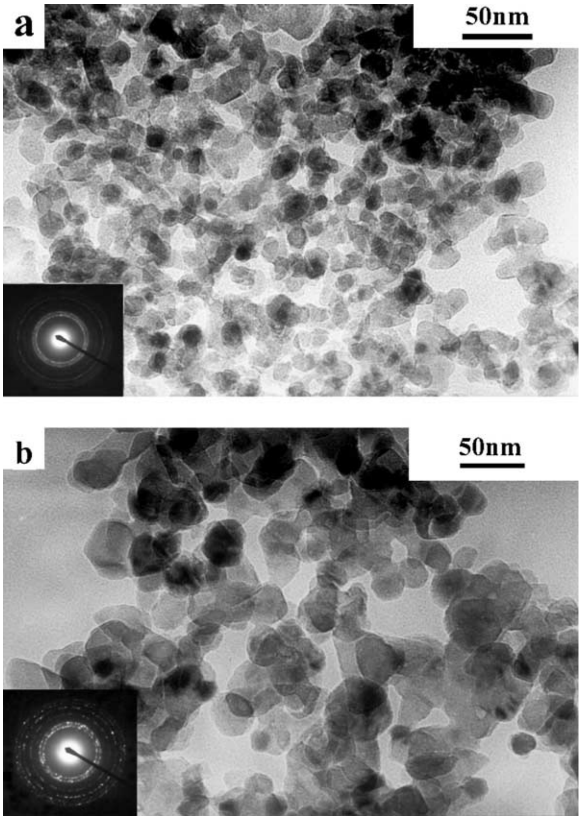

Fig. 6. TEM images of AlN particles synthesized at (a) 1000 °C and (b) 1200 °C for 5 h in the reaction zone B in flowing NH_3.

Fig. 7 shows the SEM picture of AlN powder synthesized at 1100 °C, indicating that particles are heavily agglomerated. The aggregates are composed of grains less than 100 nm in diameter, whose specific surface area is measured to be 42 m^2/g and the average grain diameter is 44 nm, while the mean diameter of the agglomerate particles is 3.90 µm determined by dynamic light scattering. The agglomeration of AlN grains is due to the coarseness of the starting Al powder.[17] Fig. 8 shows the effect of temperature on the AlN microstructure, wherein the grain size is calculated from the BET surface area and the particle size is determined by dynamic light scattering. It can be seen that both grain diameter and agglomerate particle size increase with the increasing reaction temperature. Grain diameter increases gradually with temperature, from 32 nm at 1000 °C

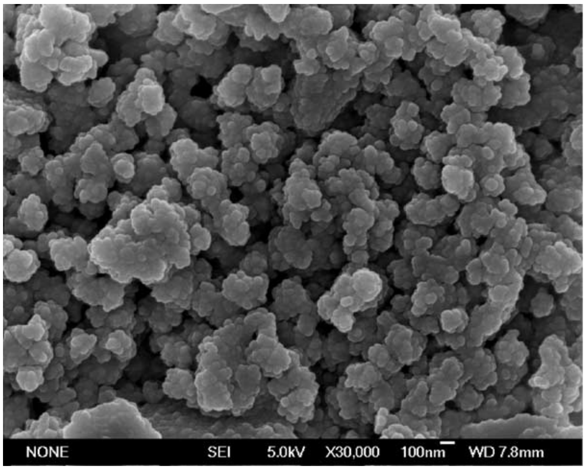

Fig. 7. FE-SEM images of AlN powders synthesized at 1100 °C for 5 h in the reaction zone B in flowing NH_3.

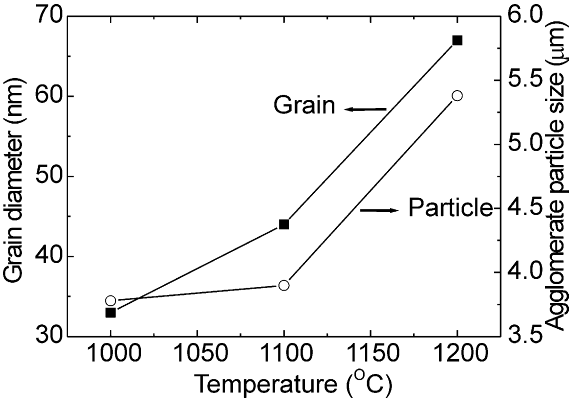

Fig. 8. Comparison of the grain (■) and agglomerate particle (○) size between the powders synthesized at different reaction temperatures for 5 h in the reaction zone B in flowing NH_3.

Table 3
Gibbs free-energies changes of reactions (4), (8), (9) and (10) at different reaction temperatures

Reaction	Gibbs free-energies changes (kJ/mol) at temperature (°C)					
	727	927	1127	1327	1527	1727
(8)	847.0	776.3	704.8	632.8	560.3	487.6
(9)	−624.0	−587.4	−551.0	−514.3	−477.6	−440.8
(10)	−558.4	−547.6	−536.3	−524.7	−512.7	−500.4
(4) = (8) + (9) + (10)	−335.4	−358.8	−382.5	−406.3	−430.0	−453.7

to 44 nm at 1100 °C, and finally reaches 67 nm at 1200 °C. The agglomerate particle size is 3.78 μm at 1000 °C. It does not change much at 1100 °C. Significant growth on agglomerate particles is observed above 1100 °C, due to the sintering of AlN powder at high temperature,[3] accompanied by the coarsening of AlN crystallite seen by TEM.

From the analysis above, the nitridation of liquid Al particles is more complete and the dissociation of NH_3 is enhanced at higher reaction temperature. In addition, the resultant AlN particles have a higher crystallinity, indicating that the formation of AlN is promoted at high temperature. The grain and agglomerate particle size of AlN also increase with reaction temperature. The particle size of AlN as synthesized is comparative to AlN synthesized using plasma processes.[18,19]

4.3. Using nitrogen as the nitriding gas

The nitridation of Al is also carried out using nitrogen as the nitriding gas at 1000 °C (Exp. No. 7 in Table 2). The overall reaction is given by

$$\mathrm{Al}(l) + \frac{1}{2}\mathrm{N_2}(g) = \mathrm{AlN}(s) \tag{7}$$

whose free-energy change is the same as the reaction (3) if NH_3 decomposes before the nitridation reaction occurs. Accordingly, the resultant powder should have the same compositions as revealed by Exp. No. 3 (Table 2). However, XRD analysis shows that Al powder has been converted into AlN completely, except for trace α-Al_2O_3 and AlON (Fig. 4c), and there is no distinguished difference between the products from different reaction zones. This is consistent with the above-mentioned assumption that ammonia does not (or seldom) decompose before reaching the surface of liquid Al particles.

Note that the use of nitrogen as nitriding gas instead of ammonia results in a higher AlN yield at zone A under the same reaction conditions (Table 2). It is probably due to the much higher flow rate of N_2 than NH_3 used. This result is also in agreement with the report of Pratsinis et al.,[3] who studied nitridation of Al with ammonia and nitrogen: pure AlN was obtained at 1400 °C by increasing the nitrogen flow rate to 164 ml/min, and a mixture of AlN with Al was produced even at 1600 °C if the ammonia flow rate was as low as 100 ml/min.

4.4. Mechanism for the nitridation reaction of liquid Al particles by NH_3

From the thermodynamics and the analysis of experiment results, simplified model can be proposed to explain the reaction sequence of the nitridation process at 900–1200 °C in flowing NH_3. It proceeds firstly by the dissociation of NH_3 at the surface of liquid Al particles and formation of reactive nitrogen radicals (using N as the representative) and H radicals, according to reaction (8), whose free-energy change is positive, indicating that it cannot proceed spontaneously.

$$\mathrm{NH_3}(g) = \mathrm{N}(g) + 3\mathrm{H}(g) \tag{8}$$

Then N radicals react with liquid Al by diffusion into the Al particles [reaction (9)] and H radicals react with another NH_3 molecule to promote its decomposition [reaction (10)].

$$\mathrm{Al}(l) + \mathrm{N}(g) = \mathrm{AlN}(s) \tag{9}$$

$$\mathrm{NH_3}(g) + 3\mathrm{H}(g) = \frac{1}{2}\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \tag{10}$$

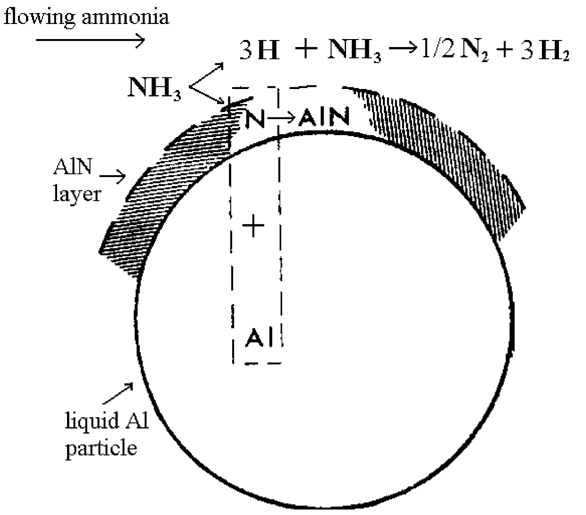

Fig. 9. Modeling of the nitridation reaction of liquid Al particles in flowing NH_3.

The free-energy changes of reactions (9) and (10) are negative and can provide enough energy for the dissociation of NH_3 (Table 3). Fig. 9 summarizes the whole reaction mechanism schematically. It can be concluded from Table 3 that as the reaction temperature become higher, or equally, the temperature gradient is positive, the free-energy change of reaction (4) is more negative, and thus the nitridation of liquid Al is more favored.

5. Conclusion

A model of the nitridation reaction of liquid Al particles in flowing NH_3 has been developed, which includes a series of basic steps:

$$\begin{array}{ll} \mathrm{NH_3}(g)=\mathrm{N}(g)+3\mathrm{H}(g) & \text{(occurring at the surface of liquid Al particles)} \\ \mathrm{Al}(l)+\mathrm{N}(g)=\mathrm{AlN}(s) & \text{(providing enough} \\ \mathrm{NH_3}(g)+3\mathrm{H}(g)=\frac{1}{2}\mathrm{N_2}(g)+3\mathrm{H_2}(g) & \text{energy for the dissociation of } \mathrm{NH_3}) \\ \hline \mathrm{Al}(l)+2\mathrm{NH_3}(g)=\mathrm{AlN}(s)+\frac{1}{2}\mathrm{N_2}(g)+3\mathrm{H_2}(g) & \end{array}$$

This model may be described as (i) the dissociation of NH_3 at the surface of fine liquid Al particles, (ii) the reaction between reactive nitrogen radicals and liquid Al, and (iii) the decomposition reaction of NH_3 promoted by reactive H radicals. The nitridation reaction is favored as the temperature gradient is positive or at higher reaction temperature.

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