



Article Synthesis of Aluminum Nitride Using Sodium Aluminate as Aluminum Source

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Abstract: At present, the carbothermal reduction and nitridation process is an important method for the large-scale preparation of aluminum nitride powder in industry, but the tremendous energy consumption caused by long-term high temperatures seriously restricts its practical application. To solve this problem, the (NaAlO₂+C) mixture with a mole ratio of NaAlO₂:C = 1:3 was prepared based on sodium aluminate and carbon black which has been ball milled with anhydrous ethanol as a grinding liquid. The crystal structure evolution and nitridation reaction behavior of sodium aluminate at 800–1600 °C under a nitrogen atmosphere in the presence of carbon were systematically studied employing XRD, SEM, and ICP-MS. The results showed that: high energy θ -Al₂O₃, η -Al₂O₃ can be excited by heating sodium aluminate to 1400 °C under a nitrogen atmosphere in the presence of carbon. The transformation process between sodium aluminate and aluminum nitride is carried out via the direct nitridation of θ -Al₂O₃, η -Al₂O₃. Benefiting from the direct nitridation of η -Al₂O₃ and θ -Al₂O₃, high-purity aluminum nitride powder with a particle size of 0.50 ± 0.18 µm was synthesized at 1400 °C. This work provides a new path for reduced energy consumption in the aluminum nitride industry.

Keywords: sodium aluminate; carbon black; carbon thermal reduction and nitridation; aluminum nitride powder

1. Introduction

Aluminum nitride (AlN) ceramics have been widely used in large-scale integrated circuits, semiconductor packaging, and optoelectronic devices because of their excellent thermal and electrical properties such as high thermal conductivity (theoretical value is 320 W·m⁻¹·k⁻¹), superior insulation (>10¹⁶ Ω/m), low dielectric constant (8.8 at 1 MHz), and dielectric loss (3–10 at 1 MHz), and thermal expansion coefficient (4.6 \times 10⁻⁶ k⁻¹ at 20–500 $^{\circ}$ C) comparable with that of silicon [1–6]. However, these properties of AlN ceramics can only be achieved based on AlN powder with high purity, small particle size, and narrow particle size distribution. So far, researchers have developed and adopted a variety of methods to synthesize AlN powder, including the direct nitridation process (DN) [7], carbothermal reduction and nitridation process (CRN) [8], self-propagating hightemperature synthesis process (SHS) [9], chemical vapor deposition (CVD) [10], suspension plasma spray process (SPS) [11] and other processes. Only the first two methods can be used to synthesize high-purity AlN powder in the industry: (1) direct nitridation of Al powder in the presence of nitrogen [12] and (2) carbothermal reduction-nitridation of Al_2O_3 powder and carbon black under a nitrogen atmosphere [13,14]. Comparatively, the AlN powder synthesized by the CRN process exhibits more excellent performance in terms of purity, sinterability, and stability against humidity [15]. However, the tremendous energy consumption caused by long-term high temperatures seriously restricts its application in industry. Hence, how to reduce the synthesis temperature has become an important research direction in the CRN process.



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). It is well known that the basic principle of the CRN process involves the conversion of Al_2O_3 and C under a nitrogen atmosphere into AlN, requiring a temperature above 1600 °C for several hours, as shown in Formula (1):

$$Al_2O_3(s) + 3C(s) + N_2(g) \xrightarrow{>1600 \, ^\circ C} 2AlN(s) + 3CO(g) \tag{1}$$

However, it is difficult to reduce the synthesis temperature of the CRN process by adjusting carbon and nitrogen sources due to the consideration of their cost and functionality. Therefore, the most promising way to decrease the synthesis temperature of the CRN process is to improve the reactivity of Al_2O_3 powder. Up to now, researchers have mainly adopted the following three methods to deal with Al₂O₃ powder: 1. Reduce the particle size of Al₂O₃ powder by plasma-assisted ball milling [16]. 2. Reduce the surface activation energy of Al_2O_3 powder by adding alkaline earth and rare earth compounds such as CaF₂, CaCO₃, Ca(OH)₂, Ca(OH)₂, CaC₂, Y₂O₃, Yb₂O₃, Y₂O₃-CaO, Y_2O_3 -CaO-Li₂O [17–20]. 3. Replace α -Al₂O₃ powders with hydrated alumina/transition alumina including Al(OH)₃, AlOOH, γ-Al₂O₃, δ-Al₂O₃, θ-Al₂O₃ [21–23]. However, the first two methods only realize the activation of the powder surface, while the inner part of the particles retains the crystal structure of α -Al₂O₃, and the hydrated alumina/ transitional alumina in the third method transforms to α -Al₂O₃ when the temperature exceeds 1200 °C. Therefore, the aluminum sources in the above methods were essentially α -Al₂O₃, and their effects in reducing the synthesis temperature were insignificant. To break through the limitation of α -Al₂O₃ on synthesis temperature constitutes a challenge. In recent years, Suehiro [24,25] and Yamakawa [26,27] systematically investigated the influence of aluminum source on the synthesis temperature using Al(OH)₃, AlOOH, γ -Al₂O₃, δ -Al₂O₃, α -Al₂O₃ as the aluminum source, and NH_3 - C_3H_8 as a reduction-nitridation agent. Their results not only confirmed that the crystal structure of the aluminum source had a significant influence on synthesis temperature but also verified that the hydrated alumina/transitional alumina reacts with ammonia (NH₃) directly before they transform into α -Al₂O₃. Hence, the hydrated alumina/transitional alumina was more easily nitridated than α -Al₂O₃. Although they synthesized pure AlN powder at 1200 °C, their method was not suitable for application in industry because it involved the usage of toxic NH₃. To synthesize AlN at low temperatures without NH₃, Chikami et al. [28] proposed to heat the transition alumina and carbon black under a nitrogen atmosphere with 2.45 GHz microwave radiation before the transition alumina completely transformed into α -Al₂O₃. However, since the microwave radiation could not maintain the stability of transition alumina and inhibit its transformation to α -Al₂O₃ effectively, so they did not synthesize pure AlN powder below 1400 °C. Therefore, keeping the crystal structure of Al_2O_3 in a high-energy state above 1200 °C is still a problem that restricts the low-temperature synthesis of AlN.

As we all know, sodium aluminate (NaAlO₂) is a kind of aluminum-containing compound with an unstable crystal structure at high temperatures, it usually decomposes and releases Na₂O above 1000 $^{\circ}$ C [29], The release of Na₂O leads to the collapse of the crystal structure of NaAlO₂, and the irregularly distributed oxygen atoms and aluminum atoms in the original crystal structure will form high-energy aluminas with poor coordination. If these high-energy aluminas can be generated at 1200 °C or even higher, and these high-energy aluminas react with nitrogen before they transform into α -Al₂O₃ at high temperatures, AlN powder can be obtained at a relatively low temperature. In this paper, $NaAlO_2$ and carbon black were milled in absolute ethanol to prepare the ($NaAlO_2+C$) mixture; the crystal structure evolution and nitridation reaction of NaAlO₂ with carbon black under a nitrogen atmosphere in the presence of carbon was systematically explored. The results illustrated that high energy θ -Al₂O₃, η -Al₂O₃ can be excited by heating sodium aluminate at 1400 °C under a nitrogen atmosphere. The transformation process between sodium aluminate and aluminum nitride is carried out via the direct nitridation of θ -Al₂O₃, η -Al₂O₃. Benefiting from the direct nitridation of η -Al₂O₃ and θ -Al₂O₃, aluminum nitride powder with a particle size of $0.50 \pm 0.18 \,\mu\text{m}$ was produced at 1400 °C. This work provides a theoretical basis for activating alumina activity at high temperatures, regulating the

nitridation reaction process, and reducing the energy consumption of the aluminum nitride industry.

2. Materials and Methods

2.1. Materials

The raw materials used in the experiment include sodium aluminate (analytically pure, D50 = 30 μ m, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China), alumina powder (CT3000SG, 99.8%, D50 = 500 nm, Qingdao Almatis Co., Ltd., Qingdao, China), carbon black (purity \geq 99.9%, D50 = 40 nm, Tianjin Ebory Chemical Co., Ltd., Tianjin, China); high purity nitrogen (purity \geq 99.999%, Beijing Huanyu Jinghui City Gas Technology Co., Ltd., Beijing, China); absolute ethanol (purity \geq 99%, Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China).

2.2. Experiments

Considering that it is easy for sodium aluminate to dissolve in water, great care should be taken when preparing the (NaAlO₂+C) mixture. In the experiment, NaAlO₂ and carbon black were mixed according to the mole ratio of NaAlO₂:C = 1:3, and the raw materials were milled in a polytetrafluoroethylene jar with corundum balls as the grinding medium and anhydrous ethanol as a solvent for 12 h. The mass ratio of grinding balls to raw materials is 10:1, and the additional amount of anhydrous ethanol is 2/3 of the total volume of mixed media. After milling, the slurry was separated from the corundum balls and dried in a vacuum oven at 80 °C for 6 h. Finally, the dried black solid was ground and passed through a 200-mesh sieve. The black powders obtained were (NaAlO₂+C) mixture. To avoid the hydration deterioration of sodium aluminate due to its adsorption of water molecules in the air, the (NaAlO₂+C) mixture needs to be stored in a vacuum receiver to avoid contact with water.

As we all know that alkali compounds are harmful to some high-temperature furnace linings, the carbothermal reduction and nitridation experiments were carried out in a high-temperature tubular atmosphere furnace using graphite as lining. At first, a graphite boat loaded with (NaAlO₂+C) mixture was placed in a high-temperature tubular atmosphere furnace; then, the furnace was washed with high-purity nitrogen three times to remove residual oxygen in the furnace, end the procedure and cool down with the furnace after the (NaAlO₂+C) mixture was heated at a heating rate of 5 °C/min for 160, 180, 200, 220, 240, 260, 280, 300, and 320 min, respectively. The corresponding temperatures for different heating times were 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, and 1600 °C. The flow rate of nitrogen was 0.5 L/min. To investigate the nitriding reaction behavior of sodium aluminate under a flow rate of 0.5 L/min nitrogen flow, the (NaAlO₂+C) mixture was also heated to 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400 °C, 1500 °C and 1600 °C for 3 h, respectively. The reaction products were taken out from the furnace after the furnace cooled to room temperature, and the residual carbon black was removed by firing in a muffle furnace at 700 °C for 2 h.

For comparison, the alumina and carbon black with a mole ratio of Al_2O_3 :C = 1:3 were also mixed for 12 h in a polytetrafluoroethylene jar with corundum balls as grinding medium and absolute ethanol as grinding liquid, and then the dried (Al_2O_3+C) mixture was also fired at 1200, 1300, 1400, 1500, and 1600 °C with a heating rate of 5 °C/min for 3 h, respectively. After the reaction was finished and the furnace cooled to room temperature, the reaction products were taken out and fired at 700 °C for 2 h in a muffle furnace.

2.3. Characterization

The phase composition and contents of the (NaAlO₂+C) mixture and reaction products were characterized by an X-ray diffractometer (XRD, D8 Advance, Bruker, Karlsruhe, Germany) with a scanning angle of 10–90° and a scanning speed of 10°/min, Cu target. The nitriding yield of reaction products in the (NaAlO₂+C) system and (Al₂O₃+C) system fired at 800~1600 °C for 3 h were determined using the Rietveld method. The microstructure of

the (NaAlO₂+C) mixture and reaction products were characterized by scanning electron microscope (SEM, Nova Nano450, FEI, Brno, Czech), and the reaction products were treated with gold spraying before detection. To further evaluate the effect of reaction temperature on the particle size of synthesized AlN powder, the grain size of AlN powder was analyzed by Image J software, and 1000 grains were counted. The sodium contents of the (NaAlO₂+C) mixture fired at 1400, 1500, and 1600 °C for 3 h under a nitrogen atmosphere were detected by an inductively coupled plasma mass spectrometer (ICP-MS, 7900, Agilent, Palo Alto, CA, USA).

3. Results

3.1. $(NaAlO_2+C)$ Mixture

It is known that a well-dispersed (NaAlO₂+C) mixture is essential for synthesizing AlN powder in the CRN process. However, considering the poor chemical stability of NaAlO₂, the phase, and microstructure of NaAlO₂, carbon black, and (NaAlO₂+C) were characterized by XRD and SEM. Figure 1 displays the XRD patterns of the NaAlO₂, carbon black, and (NaAlO₂+C) mixture. It can be seen from the picture that the NaAlO₂ used in the experiment is β -NaAlO₂ (Figure 1A); the carbon black used in the experiment is amorphous carbon (Figure 1B); The diffraction peak detected in the $(NaAlO_2+C)$ mixture is also ascribed to β -NaAlO₂, which indicates that NaAlO₂ is stable in absolute ethanol (Figure 1C). Figure 2 shows the SEM images of the NaAlO₂, carbon black, and (NaAlO₂+C) mixture, respectively. It can be seen from the image that the NaAlO₂ is a bulk crystal with a diameter of 30 μ m (Figure 2a), and that carbon black is an aggregate of spherical particles with a diameter of about 40 nm (Figure 2b); the irregular white crystals with a particle size of $0.8 \,\mu\text{m}$ were isolated by spherical particles in the (NaAlO₂+C) mixture (Figure 2c). The EDS results show that the white particles are composed of Na, Al, and O elements, and the atomic ratio of Na to Al is close to 1:1, which is $NaAlO_2$ (spot 1 in Figure 2d). The chemical composition of spherical particles only contains C (spot 2 in Figure 2d), which is carbon black. The above results indicate that NaAlO₂ can maintain the stability of its crystal structure in absolute ethanol, and that a well-dispersed (NaAlO₂+C) mixture could be obtained by ball-milling NaAlO₂ and carbon black in absolute ethanol.



Figure 1. XRD patterns of NaAlO₂ (A), carbon black (B), and (NaAlO₂+C) mixture (C).



Figure 2. SEM images of NaAlO₂ (**a**), carbon black (**b**), (NaAlO₂+C) mixture (**c**), and EDS analysis of (NaAlO₂+C) mixture in Figure 2c (**d**).

3.2. Crystal Structure Evolution of Sodium Aluminate

Sodium aluminate is an aluminum-containing compound with an unstable crystal structure at high temperatures. It will undergo a series of physical and chemical reactions as the temperature increases, and the physical and chemical reaction will be more complex under a nitrogen atmosphere in the presence of carbon black. Figure 3 displays the XRD patterns of the $(NaAlO_2+C)$ mixture heated to different temperatures without soaking time. When heated to 800~1100 °C, the main phase in the reaction products is γ -NaAlO₂. As the temperature increases to 1200~1300 °C, γ -NaAlO₂ disappears, and a large quantity of $NaAl_5O_8$ ($\beta''-Al_2O_3$) and $NaAl_{11}O_{17}$ ($\beta-Al_2O_3$) are detected in the products. The diffraction peaks of β' -Al₂O₃ decline gradually with the temperature increase, while the peaks of β -Al₂O₃ do just the reverse. When heated to 1400 °C, only θ -Al₂O₃ and η -Al₂O₃ can be detected. When heated to $1500 \sim 1600 \circ C$, the phases in the reaction products are η -Al₂O₃ and θ -Al₂O₃, while a small amount of AlN begins to appear. Based on the above results, it can be deduced that the crystal structure of sodium aluminate is closely related to its heating temperature in the N_2 flow in the presence of carbon. The crystal structure evolution of sodium aluminate at 800~1600 °C under a nitrogen atmosphere in the presence of carbon black takes place in the following order. Firstly, β-NaAlO₂ undergoes a phase transformation at 800~1100 °C and generates γ -NaAlO₂. As the temperature increases to 1200–1300 °C, the Na₂O in γ -NaAlO₂ crystals begin to volatilize, and the residual Na, O, Al atoms in the crystal structure rearrange and form β'' -Al₂O₃ and β -Al₂O₃. When the temperature reaches 1400 °C, Na₂O is completely volatilized, and the residual O and Al atoms in the crystal structure rearrange and form η -Al₂O₃ and θ -Al₂O₃ with an irregular arrangement and in complete coordination. When the temperature is above 1400 °C, the O atoms in the η -Al₂O₃ and θ -Al₂O₃ begin to be replaced by N atoms. The crystal structure evolution of sodium aluminate in carbon-containing high-temperature N₂ flow illustrates that high energy θ -Al₂O₃ and η -Al₂O₃ can be activated from NaAlO₂ which has been fired at 1400 °C without soaking time under a nitrogen atmosphere.



Figure 3. XRD patterns of (NaAlO₂+C) mixture heated to 800~1600 °C without soaking time.

3.3. Nitriding Reaction

Figure 4 shows the XRD patterns of the (NaAlO₂+C) mixture fired at 800~1600 $^{\circ}$ C for 3 h. After being fired at 800–1100 °C, the reaction products only contain γ -NaAlO₂. After being fired at 1200 °C, γ-NaAlO₂ cannot be detected, while a large amount of η-Al₂O₃, θ -Al₂O₃, and α -Al₂O₃ appears. As the temperature increases to 1300 °C, θ -Al₂O₃ and η -Al₂O₃ become the main phases in the product, while a small amount of AlN also appears. when the temperature exceeds 1400 °C, AlN is the only phase in the reaction products, and the diffraction peak becomes stronger and sharper as the temperature increases. Combined with the XRD results in Figure 3, it can be concluded that the transformation process between NaAlO₂ and AlN is carried out via the direct nitridation of θ -Al₂O₃, η -Al₂O₃. In addition, the higher the synthesis temperature, the more thorough the nitride reaction, and the better the crystallization degree. As Figure 5 displays, the AlN powder synthesized at 1400 °C is ellipsoidal, with a grain size of $0.50 \pm 0.18 \,\mu\text{m}$. The AlN powder synthesized at 1500 °C becomes coarser, and the grain size is mainly $0.58 \pm 0.20 \ \mu\text{m}$. The AlN powder synthesized at 1600 °C is mostly tabular, and the grain size increase to 0.70 ± 0.25 µm. The particle size distribution of AlN powder becomes broader as the temperature increases. However, the grain size is larger and the crystallization is better, which is consistent with the XRD results in Figure 4.



Figure 4. XRD patterns of (NaAlO₂+C) mixture fired at 800~1600 °C for 3 h.



Figure 5. SEM images of the AlN powder synthesized at 1400~1600 °C for 3 h: (a) 1400 °C; (b) 1500 °C; (c) 1600 °C.

Figure 6 shows the XRD patterns of the (Al₂O₃+C) mixture fired at 1200~1600 °C for 3 h. It can be seen from the figure that only α -Al₂O₃ is detected in the product when the temperature is below 1300 °C. As the temperature increases to 1300~1500 °C, the AlN begins to appear, and its peak intensity becomes stronger as temperature increases, while the peak intensity of α -Al₂O₃ is weakened. When the temperature is above 1600 °C, α -Al₂O₃ disappears, and only AlN can be detected in the product. The above results show that the traditional CRN process is carried out through the direct nitridation of α -Al₂O₃; the synthesis temperature often needs to be 1600 °C or higher to realize the complete conversion of AlN.



Figure 6. XRD patterns of (Al₂O₃+C) mixture fired at 1200~1600 $^{\circ}$ C for 3 h.

For comparison, the Rietveld method was also used to analyze the nitriding yield of the (NaAlO₂+C) and (Al₂O₃+C) mixture after being fired at 800~1600 °C for 3 h. As

shown in Table 1 and Figure 7, there is no AlN formation in the (NaAlO₂+C) system below 1200 °C. When the temperature rises to 1300 °C, only 7.51 wt% AlN is formed in the product. When the temperature is above 1400 °C, NaAlO₂ is converted to AlN completely. In contrast, no AlN was generated in the (Al₂O₃+C) system below 1300 °C. However, when the temperature reaches 1400 °C, about 2.30 wt% AlN is produced. When the temperature rises to 1500 °C, the content of AlN in the reaction product further increases to 49.45 wt%. Continuing to increase the temperature to 1600 °C, the product contains AlN. Compared with the (Al₂O₃+C) mixture, the (NaAlO₂+C) mixture more easily produces AlN at lower temperatures, which indicates that high energy θ -Al₂O₃ and η -Al₂O₃ are more easily nitrided than α -Al₂O₃. The sodium contents of the AlN powder obtained from the (NaAlO₂+C) mixture which was fired at 1400, 1500, and 1600 °C have little difference; their contents were 96, 91, and 90 ppm, respectively.

Table 1. The nitriding yield (wt%) of the (NaAlO₂+C) and (Al₂O₃+C) mixture fired at 800~1600 $^{\circ}$ C for 3 h.

	800~1100 °C	1200 °C	1300 °C	1400 °C	1500 °C	1600 °C
NaAlO ₂ +C mixture Al ₂ O ₃ +C mixture	—	_	7.51	100	100	100
	—	—	—	2.30	49.45	100



Figure 7. The nitriding yield of the (NaAlO₂+C) and (Al₂O₃+C) mixture fired at 800~1600 $^{\circ}$ C for 3 h.

4. Discussion

Based on the above results, it can be concluded that high energy θ -Al₂O₃ and η -Al₂O₃ which have been activated from NaAlO₂ at 1300–1400 °C directly react with nitrogen to form AlN. The transformation process between NaAlO₂ and AlN is actually through the following three steps: 1. NaAlO₂ is activated as the temperature increase and produces high energy θ -Al₂O₃ and η -Al₂O₃; 2. High energy θ -Al₂O₃ and η -Al₂O₃ transform into intermediate phase Al-O-N; 3. The intermediate phase Al-O-N is further converted to AlN. Therefore, the crystal structure evolution of NaAlO₂ and the crystal structure of its activated products are very important for the nitriding reaction.

As we all know, NaAlO₂ is an aluminum-containing compound whose crystal structure is unstable at high temperatures. It will generate a series of physical and chemical reactions as the temperature increases under a nitrogen atmosphere in the presence of carbon black. As shown in Figure 3, β -NaAlO₂ transforms into γ -NaAlO₂ under the high temperature of 800–1100 °C, and the arrangement order of Na, Al, and O atoms in the crystal structure changes greatly, but the chemical composition of sodium aluminate does not change. When the temperature exceeds 1100 °C, the chemical bond in the crystal structure of γ -NaAlO₂ breaks under the action of high temperature and releases gaseous Na₂O; the residual Na atoms coordinate with Al and O atoms in the γ -NaAlO₂ forming β "-Al₂O₃ and β -Al₂O₃. When the temperature reaches 1400 °C, almost all the sodium volatilizes from NaAlO₂, while the residual Al and O atoms in the crystal structure coordinate to form η -Al₂O₃ and θ -Al₂O₃ with an irregular arrangement and incomplete coordination. If the temperature continues to rise, the O atoms in η -Al₂O₃ and θ -Al₂O₃ will be gradually replaced by N atoms and form AlN. However, since the substitution of nitrogen atoms is limited to the surface of the grain, the internal part of the grain remains as η -Al₂O₃ and θ -Al₂O₃ can be excited at 1400 °C under a nitrogen atmosphere in the presence of carbon, and the presence of Na atoms inhibits these high energy aluminas' transformation to α -Al₂O₃.

At the same time, the crystal structure of alumina will affect its transition to the intermediate Al-O-N phase. α -Al₂O₃ is the most stable phase of all aluminas, and belongs to the trigonal system. The O atoms in the crystal structure are hexagonal close packing, and the Al atoms are filled with 2/3 octahedral voids; hence, each Al atom coordinates with six adjacent O atoms to form $[AlO_6]$. η -Al₂O₃ belongs to the cubic system with a spinel lattice; the unit cell is made up of 32 O anions and 24 cations. However, only $21_{1/3}$ Al³⁺ ions are available for the cation positions in η -Al₂O₃; thus, 51% of Al atoms are coordinated as $[AlO_{61}, 36\%$ as $[AlO_4]$, and 13% as $[AlO_3]$ in η -Al₂O₃. θ -Al₂O₃ belongs to the monoclinic system with a distorted spinel lattice; Al ions occupy only one octahedral site and one tetrahedral site, which means 50% of Al atoms are coordinated in the form of [AlO₆], and 50% of Al atoms are coordinated in the form of $[AlO_4]$ [30]. Although the Al-O bond in $[AlO_4]$ is shorter and has a higher bond energy than the Al-O bond in $[AlO_6]$, the nitrogen atom replaces the oxygen atom in [AlO₄] and consumes less energy during the formation process of Al-O-N [31], (Figure 8). Hence, from the aspect of energy change, it is easier for η -Al₂O₃ and θ -Al₂O₃ to form Al-O-N at low temperatures, and the synthesis temperature of AlN powder is reduced.



Figure 8. Transformation of crystal structure during reduction and nitridation reduction.

In conclusion, the synthesis temperature of AlN can be reduced by using NaAlO₂ as the aluminum source. The conversion of NaAlO₂ to α -Al₂O₃ can be suppressed to the maximum extent by firing NaAlO₂ and carbon black under a nitrogen atmosphere in the presence of carbon at 1400 °C for 3 h, and the complete conversion of AlN can be achieved.

5. Conclusions

In conclusion, sodium aluminate and carbon black were used as raw materials to prepare a uniformly dispersed (NaAlO₂+C) mixture in absolute ethanol by ball milling, and the crystal structure evolution and nitriding reaction behavior of NaAlO₂ under a nitrogen atmosphere in the presence of carbon was systematically studied. The results showed that high energy θ -Al₂O₃, η -Al₂O₃ can be excited by heating NaAlO₂ to 1400 °C under a nitrogen atmosphere in the presence of carbon. NaAlO₂ transforms to AlN via the direct nitridation of θ -Al₂O₃, η -Al₂O₃. Benefiting from the direct nitridation of η -Al₂O₃ and θ -Al₂O₃, AlN powder with a particle size of 0.50 ± 0.18 µm was synthesized at 1400 °C. This work has great application prospects in reducing the energy consumption of the AlN powder industry.

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References

- Chiu, C.W. Highly Thermally Conductive Epoxy Composites with AlN/BN Hybrid Filler as Underfill Encapsulation Material for Electronic Packaging. *Polymers* 2022, 14, 2950.
- Hassan, S.; Ahmed, S.; Ali, M.; Fahad, S. Advanced Electrical Characterization of AlN/Si Based Heterogeneous Junction for Photonic Applications. *Mat. Sci. Semicon. Proc.* 2022, 138, 106292. [CrossRef]
- Matsumae, T.; Kurashima, Y.; Higurashi, E.; Nishizono, K.; Takagi, H. Room Temperature Bonding of Aluminum Nitride Ceramic and Semiconductor Substrate. *Ceram. Int.* 2020, 46, 1099–1118. [CrossRef]
- Shi, Z.M.; Qi, Z.B.; Zang, H.; Jiang, K.; Chen, Y.; Jia, Y.P.; Wu, T.; Zhang, S.L.; Sun, X.J.; Li, D.B. Point Defects in Monolayer h-AlN as Candidates for Single-Photon Emission. ACS Appl. Mater. Inter. 2021, 13, 37380–37387. [CrossRef]
- Zhang, D.; Mylsamy, G.; Yang, X.X.; Xie, Z.P.; Su, X.K.; Liang, F.; Yang, B.; Dai, Y.N. High Purity and Good Dispersity AlN Nanoparticles Synthesized by An Arc Discharge with Assistance of Direct Nitridation. *Ceram. Int.* 2021, 47, 16972–16979. [CrossRef]
- Kumar, P.; Kaur, D. Functional Bipolar Resistive Switching in AlN/Ni-Mn-In Based Magnetoelectric Heterostructure. *Nanotechnology* 2021, 32, 445704–445713. [CrossRef]
- Rogers, S.; Dargusch, M.; Kent, D. Impacts of Temperature and Time on Direct Nitridation of Aluminium Powders for Preparation of AlN Reinforcement. *Materials* 2023, 16, 1583. [CrossRef]
- Chu, A.M.; Zhao, Y.P.; Ud-din, R.; Hu, H.R.; Zhi, Q.; Wang, Z.R. Carbon-containing Droplet Combustion–Carbothermal Synthesis of Well-Distributed AlN Nanometer Powders. J. Am. Chem. Soc. 2022, 105, 5999–6006. [CrossRef]
- 9. Wei, Z.L.; Zhang, Z.J.; Zhang, X.Y.; Li, Z.Y.; Li, T.; Hu, J.B.; Xu, S.J.; Shi, Z.Q. Preparation of Unidirectional Porous AlN Ceramics via The Combination of Freeze Casting and Combustion Synthesis. J. Mater. Sci. Technol. 2022, 100, 161–168. [CrossRef]
- McLeod, A.J.; Ueda, S.T.; Lee, P.C.; Spiegelman, J.; Kanjolia, R.; Moinpour, M.; Wooddruff, J.; Kummel, A.C. Pulsed Chemical Vapor Deposition for Crystalline Aluminum Nitride Thin Films and Buffer Layers on Silicon and Silicon Carbide. *Thin Solid Films* 2023, 768, 139717. [CrossRef]
- 11. Barandehfard, F.; Aluha, J.; Ntho, T.A.; Gitzhofer, F. Synthesizing AlN Coatings Using Suspension Plasma Spraying: Effect of Promotional Additives and Aluminum Powder Particle Size. *J. Therm. Spray. Techn.* **2022**, *31*, 2091–2111. [CrossRef]
- Lee, K.B.; Kim, J.J.; Shim, C.H.; Kim, Y.H.; Choi, H.J.; Ahn, J.P. Low-temperature Synthesis of High-Purity AlN from Al Powder. J. Mater. Res. Technol. 2022, 21, 4526–4536. [CrossRef]

- 13. Xu, Y.L.; Zhou, Z.Q.; Chen, X.M.; Han, C.C.; Yang, B.; Xu, B.Q.; Liu, D.C. Ultrafine AlN Synthesis by Alumina Carbothermal Reduction under Vacuum: Mechanism and Experimental Study. *Powder Technol.* **2021**, *377*, 843–846. [CrossRef]
- Liu, L.; He, B.Y.; Chen, X.M.; Zhao, Z.Q.; Yin, Q.; Xu, P.L.; Yang, B.; Xu, B.Q.; Liu, D.C. Thermodynamic and Kinetic Analyses of Vacuum Synthesis of AlN by The Alumina Carbothermal Reduction Nitridation Method. J. Am. Chem. Soc. 2022, 105, 3850–3861. [CrossRef]
- 15. Wen, Q.; Wang, P.; Zheng, J.W.; Ying, Y.; Yu, J.; Li, W.C.; Che, S.L.; Qiao, L. Carbothermal Reduction Synthesis of Aluminum Nitride from Al(OH)₃/C/PVB Slurries Prepared by Three-Roll Mixing. *Materials* **2021**, *14*, 1386. [CrossRef]
- 16. Liu, Z.J.; Dai, L.Y.; Yang, D.Z.; Wang, S.; Zhang, B.J.; Wang, W.C.; Cheng, T.H. Synthesis of Aluminum Nitride Powders from a Plasma-Assisted Ball Milled Precursor Through Carbothermal Reaction. *Mater. Res. Bull.* **2015**, *61*, 152–158. [CrossRef]
- 17. Ide, T.; Komeya, K.; Tatami, J.; Meguro, T.; Naito, M.; Hotta, T. Effect of Y₂O₃ Addition on Synthesis of AlN Powder by Carbothermal Reduction-Nitridation of Al₂O₃. *J. Ceram. Soc. Jpn.* **2001**, *109*, 372–375. [CrossRef]
- 18. Nie, G.L.; Sheng, P.F.; Li, Y.H.; Bao, Y.W.; Wu, S.H. Preparation of a Hydrolysis-Resistant Coating on AlN Powder Surface and Its Effect on Thermal Conductivity of AlN. *Rare Metal Mat. Eng.* **2021**, *50*, 1904–1909.
- 19. Ide, T.; Komeya, K.; Meguro, T.; Tatami, J. Synthesis of AlN Powder by Carbothermal Reduction-Nitridation of Various Al₂O₃ Powders with CaF₂. *J. Am. Chem. Soc.* **1999**, *82*, 2993–2998. [CrossRef]
- 20. Molisani, A.L.; Yoshimura, H.N. Low-temperature Synthesis of AlN Powder with Multicomponent Additive Systems by Carbothermal Reduction–Nitridation Method. *Mater. Res. Bull.* **2010**, *45*, 733–738. [CrossRef]
- Jung, W.S. Synthesis of Aluminum Nitride Powder from δ-alumina Nanopowders under a Mixed Gas Flow of Nitrogen and Hydrogen. *Ceram. Int.* 2012, 38, 871–874. [CrossRef]
- 22. Hermawan, A.; Son, H.; Asakura, Y.; Mori, T.; Yin, S. Synthesis of Morphology Controllable Aluminum Nitride by Direct Nitridation of γ-AlOOH in the Presence of N₂H₄ and Their Sintering Behavior. *J. Asian Ceram. Soc.* **2018**, *6*, 63–69. [CrossRef]
- Lin, S.M.; Yu, Y.L.; Zhong, M.F.; Yang, H.; Qiu, Y.C. The Activation Mechanism of Oxalic Acid on γ-alumina and the Formation of α-alumina. *Ceram. Int.* 2021, 47, 26869–26876. [CrossRef]
- 24. Suehiro, T.; Hirosaki, N.; Komeya, K. Synthesis and Sintering Properties of Aluminium Nitride Nanopowder Prepared by the Gas-Reduction–Nitridation method. *Nanotechnology* **2003**, *14*, 487–491. [CrossRef]
- 25. Suehiro, T.; Hirosaki, N.; Terao, R.; Tatami, J.; Meguro, T.; Komeya, K. Synthesis of Aluminum Nitride Nanopowder by Gas-Reduction-Nitridation Method. *J. Am. Chem. Soc.* **2010**, *86*, 1046–1048. [CrossRef]
- Yamakawa, T.; Tatami, J.; Komeya, K.; Meguro, T. Synthesis of AlN Powder from Al(OH)₃ by Reduction–Nitridation in a Mixture of NH₃–C₃H₈ Gas. J. Eur. Ceram. Soc. 2006, 26, 2413–2418. [CrossRef]
- 27. Yamakawa, T.; Tatami, J.; Wakihara, T.; Komeya, K.; Yokouchi, M. Synthesis of AlN Nanopowder from γ-Al₂O₃ by Reduction– Nitridation in a Mixture of NH₃–C₃H₈. *J. Am. Chem. Soc.* **2010**, *89*, 171–175.
- 28. Chikami, H.; Fukushima, J.; Hayashi, Y.; Takizawa, H.; Blendell, J. Low-Temperature Synthesis of Aluminum Nitride from Transition Alumina by Microwave Processing. J. Am. Chem. Soc. 2016, 99, 3540–3545. [CrossRef]
- Näfe, H. Relationship between the Sodium Oxide Activity of Ceramic (Na-β+β")-Alumina and the Sodium Activity in The Ambience of The Materia. *Int. J. Mater Res.* 2022, 94, 962–966. [CrossRef]
- Zhou, R.S.; Snyder, R.L. Structures and Transformation Mechanisms of the η, γ and θ-Transition Aluminas. *Acta Crystallogr. B* 1991, 47, 617–630. [CrossRef]
- Min, X.M.; Daiand, Y.; Nan, C.W. Structures of γ-Al₂O₃ and AlON Studied by 27Al NMR and Quantum Chemistry Calculations. *Acta Met. Sin-Engl.* 1999, 12, 372–376.

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