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Effects of different aluminum sources and calcination temperatures on the synthesis of ultrafine AlN powder via carbothermal reduction nitridation

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AlN ultrafine powder was synthesized in N₂ via carbothermal reduction nitridation with different aluminum sources (i.e., Al(OH)₃, Al(NO₃)₃·9H₂O, and α -Al₂O₃) and high-activity nanocarbon black as raw materials. The effects of different aluminum sources, aluminum dosage, and calcination temperature on the phase composition and microstructure of the synthesized AlN powder were studied. Thermodynamic analysis of the reaction process was performed and the reaction mechanism of AlN powder was discussed. Results showed that fully nitrided phase-pure AlN powder was synthesized after incubating the precursor powder samples at 1500 °C for 2 hrs with Al(OH)₃ or Al(NO₃)₃·9H₂O as the aluminum source. At a 1 : 5 molar ratio of Al₂O₃/C, a weak Al₂O₃ diffraction peak was present in the AlN powder samples that were synthesized at 1550 °C with α -Al₂O₃ as the aluminum source. The quality of AlN powder samples that were synthesized with Al(NO₃)₃·9H₂O as the aluminum source was optimal relative to those of AlN powder samples that were synthesized with the two other aluminum sources. Flake-like particles (~ 100-300 nm) in the powder samples exhibited reduced agglomeration. Moreover, approximately spherical structures that were 0.5-1.0 µm in size formed between the flake-like particles. During carbothermal reduction nitriding, Al₂O₃ in the raw material first underwent carbothermal reduction to produce metallic aluminum vapor and aluminum low valence gas oxides (Al₂O), and then underwent further nitriding to form AlN.

Key words: AlN powder, Different aluminium sources, Synthesis, Phase composition, Mechanism.

Introduction

AlN ceramics possess high thermal conductivity (theoretical thermal conductivity of 319 W/(m·K)), low dielectric constant (approximately 8.8 at 1 MHz), high material strength at high temperatures, a coefficient of thermal expansion that matches that of silicon $(4.6 \times 10^{-6} \text{ K}^{-1} \text{ at } 20 \text{ }^{\circ}\text{C} \text{ to } 500 \text{ }^{\circ}\text{C})$, insulation (volume resistivity > $10^{14} \Omega \cdot \text{cm}$), non-toxicity, and other excellent physical properties [1-2]. Thus, AlN is an ideal electronic ceramic material with broad applications in substrates, electronic films, integrated circuits, electronic optics, microelectronics, and protective armor materials. Given its excellent physical properties and broad applications, AlN has attracted research interest worldwide [3-5].

To obtain AlN ceramics with comprehensive performance, the synthesis of high-purity AlN powder with small particle size, high sintering activity, and stable performance is critical. Present methods for AlN powder synthesis include aluminum powder direct nitriding [6-7], carbothermal reduction nitridation (CRN) [8-11], self-propagating high temperature synthesis [1214], and chemical vapor deposition [15-16]. Aluminum powder direct nitriding is a strong exothermic reaction that is difficult to control, thus leading to the low conversion rate of aluminum powder and vielding an unstable, low-quality product that easily agglomerates. Self-propagating high-temperature synthesis involves the self-heating and self-conduction synthesis of AlN powder using the high amount of heat that is released during aluminum powder nitriding. The main drawbacks of this method are similar to those of aluminum powder direct nitriding: given the fast reaction rate of the process, the reaction product easily agglomerates and the reaction is not completed, thus hindering the synthesis of high-quality powder. Chemical vapor deposition involves precipitating AlN powder from a gas phase by chemically reacting aluminum-volatile compounds with ammonia or other ammonia compounds. This method, however, has low production efficiency and produces hydrochloric acid by-products when inorganic aluminum is used as the raw material. These acidic by-products will corrode the production equipment. Meanwhile, organic aluminum raw materials are expensive and are therefore not conducive for large-scale industrial applications. By contrast, CRN is a simple process with a wide range of raw materials and low production cost. Moreover, CRN yields high-purity AlN powders with excellent particle size, stability, and sintering performance.

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Therefore, CRN has become the most important industrial production method for AlN powder. In conventional CRN, a powder mixture of Al₂O₃ and C at a molar ratio of 1:3 is heated at 1600 °C under a nitrogen atmosphere [17]. CRN, however, has drawbacks. For example, the commonly used Al₂O₃ and carbon raw materials are difficult to homogeneously combine. Moreover, the Al₂O₃ raw material has low reactivity; therefore, CRN requires high nitriding temperature and long reaction time, thus increasing the particle size of the synthesized AIN powder [18]. In recent years, considerable effort has been expended to improve CRN by reducing nitriding temperature. Chowdhury et al. obtained spherical AlN particles via the nitridation and the subsequent decarbonization of C@Al₂O₃ composite particles [19]. Molisani et al. utilized multicomponent additive systems as additives and synthesized AIN powders at low temperatures (1300 °C and 1400 °C) via CRN with an Al₂O₃:C molar ratio of 1:3 [10]. Qi et al. prepared hexagonal bipyramids via CRN using alumina and carbon as raw materials and with Fe₂O₃, SiO₂, and Na₂O as mineralizers under alternate gas pressures; they found that the growth of AlN hexagonal bipyramids is dominated by the vapor-solid mechanism [20]. Wang et al. investigated the effects of various additives on conversion fraction, weight loss, phase compositions, and surface morphology of spherical AlN granules during carbothermal synthesis [21]. These methods have high requirements for starting materials. Moreover, AlN powder morphology strongly depends on the morphology of the aluminum sources.

Several studies have shown that different aluminum sources, raw material ratio, and reaction temperatures are the key factors that affect the quality of AlN powder [22-24]. Although many researchers have used different starting materials and mixing methods, the homogeneous mixing and good bonding between aluminum and carbon are desirable to reduce the nitridation temperature and improve the properties of AlN powders. Unfortunately, the effects of different types and amounts of aluminum on AlN powder synthesis via CRN have not been extensively studied. In this study, AlN powder was produced via CRN with α -Al₂O₃, Al(OH)₃, and Al(NO₃)₃·9H₂O as aluminum sources. Carbon black with a high specific surface was used as the carbon source. The effects of different aluminum sources, aluminum source dosages, and reaction temperatures on the phase composition and microstructure of the synthesized AlN powder were studied. The reaction mechanism of AlN powder was analyzed in detail.

Experimental

Al(OH)₃ (purity: \geq 99.0%, $D_{50} = 8.76 \,\mu\text{m}$), α -Al₂O₃ (purity: $\geq 99.5\%$, $D_{50} = 6.53 \,\mu\text{m}$), Al(NO₃)₃·9H₂O (purity: \geq 99.0%), and carbon black (ash content: < 0.1%, particle size: < 40 nm) were used as the precursor materials for AlN powder. The preparation process of AlN powder is shown in Fig. 1. The raw materials of Al(OH)3 and carbon black were weighed based on the Al₂O₃/C molar ratio of 1:3, 1:4, 1:5,and 1:6. The raw materials were uniformly mixed in a grinding jar for 4 hrs using Al₂O₃ balls as the grinding body and anhydrous ethanol as the dispersing medium at a solid-liquid mass ratio of 1:2. The well-mixed starting materials were dried at 80 °C, sieved, transferred to a graphite crucible, and placed in a tube-atmosphere furnace. The materials were heated from room temperature to 1300 °C, 1400 °C, 1500 °C, 1550 °C, and 1600 °C at a rate of 10 °C·min⁻¹ under flowing nitrogen (purity: \geq 99.99%). The holding time at the desired temperature was 2 h. At the end of the holding time, the temperature was reduced to approximately 250 °C at a cooling rate of 10 °C ·min⁻¹. The furnace was cooled naturally and the carboncontaining AIN powder was obtained. Subsequently, the carbon-containing AIN powder was decarbonized in a box-type resistance furnace. The temperature was set to 650 °C and the holding time was 3 hrs. The superfine AIN powder was obtained after natural cooling to room temperature. Based on the best molar ratio of Al₂O₃/C that was optimized in the above experiment, AlN powder was synthesized in accordance with the above experimental procedure using α -Al₂O₃ or Al(NO₃)₃·9H₂O as the aluminum source. The phase composition of powder samples that were prepared at different calcination temperatures was analyzed using an X-ray diffractometer (XRD, TD-3500). The mass of the powder samples was weighed by an electronic analytical balance (accurate



Fig. 1. Preparation process of AlN powder.

to 0.1 mg) before and after synthesis, and the weight loss rate of the synthesis of the powder sample was calculated. The microstructure of the powder samples was analyzed using scanning electron microscopy (SEM, Quanta FEG 250).

Results and Discussion

Phase composition

The XRD patterns of the powder samples that were obtained at different temperatures with Al₂O₃/C molar ratios of 1:3, 1:4, 1:5, and 1:6 and with Al(OH)₃ as the aluminum source were shown in Figs. 2 to 5, revealing that both raw material ratio and reaction temperature greatly influenced the phase composition of the powder samples. At a Al₂O₃/C molar ratio of 1:3 (see Fig. 2), the XRD pattern of the powder sample after calcination at 1300 °C was dominated by an Al₂O₃ diffraction peak and did not contain an AlN diffraction peak. This result indicated that at this reaction temperature, Al(OH)₃ decomposed to Al₂O₃ products; however, the degree of reaction of Al₂O₃ to produce AlN was low at this low temperature. When the reaction temperature increased to 1400 °C, the XRD pattern of the synthesized powder samples did not significantly change. At the reaction temperature of 1500 °C, the XRD patterns of the powder samples exhibited mainly Al₂O₃ and AlN diffraction peaks, indicating that carbothermal reduction between the mixed materials produced more AIN products. As the reaction temperature increased, the diffraction peak of AlN was enhanced. Moreover, as the reaction temperature reached 1550 °C, the diffraction peak of AlN was enhanced and the diffraction peak of Al2O3 was weakened in the XRD pattern. When the reaction temperature reached 1600 °C, the characteristic diffraction peak of AIN existed in the powder sample, whereas that of Al₂O₃ disappeared. This indicated that the carbothermal reduction nitrification of the mixed raw materials for AlN formation was completed at 1600 °C. At an Al₂O₃/ C molar ratio of 1:4 (see Fig. 3), the effect of reaction temperature on the phase composition of the powder sample was similar to that shown in Fig. 2. Given the increased amount of carbon black in the mixed raw materials, the contact between the reactant raw material particles in the system was more sufficient, resulting in the formation of more AlN products in the system at a lower reaction temperature. At the reaction temperature of 1400 °C, the characteristic diffraction peaks of AlN existed in addition to the diffraction peak of Al₂O₃ in the XRD pattern of the powder sample. When the reaction temperature reached 1550 °C, only the diffraction peak of AlN existed in the XRD pattern of the powder sample, indicating that the synthesis of AlN was completed at this temperature. As the amount of carbon black increased in the mixed raw materials, the optimum reaction temperature



Fig. 2. XRD patterns of powder samples that were obtained at different temperatures and with $Al(OH)_3$ as the aluminum source at an Al_2O_3/C molar ratio of 1 : 3.



Fig. 3. XRD patterns of powder samples that were obtained at different temperatures and with $Al(OH)_3$ as the aluminum source at an Al_2O_3/C molar ratio of 1 : 4.

of AlN synthesis further decreased. At the Al₂O₃/C molar ratio of 1:5 (see Fig. 4), only the diffraction peaks of AlN were present in the XRD patterns of the powder samples that were synthesized at 1500 °C, indicating that the synthesis of the mixed raw materials to AlN was completed at 1500 °C. At the Al₂O₃/C molar ratio of 1:6 (see Fig. 5), the effect of the reaction temperature on the phase composition of the powder sample was similar to that shown in Fig. 4. Therefore, as shown in Fig. 5, the synthesis of AlN was already completed at 1500 °C. In summary, when Al(OH)₃ is selected as the aluminum source, decreasing the molar ratio of Al₂O₃/C decreases the optimum reaction temperature. Considering the reaction temperature and the factors of carbon removal during the later stage, the optimum reaction conditions are as follows: an Al₂O₃/C molar ratio of 1:5 and a reaction temperature of 1500 °C.



Fig. 4. XRD patterns of powder samples that were obtained at different temperatures and with $Al(OH)_3$ as the aluminum source at an Al_2O_3/C molar ratio of 1 : 5.



Fig. 5. XRD patterns of powder samples that were obtained at different temperatures and with $Al(OH)_3$ as the aluminum source at an Al_2O_3/C molar ratio of 1 : 6.

Fig. 6 shows the XRD patterns of the powder samples that were obtained at different temperatures with α -Al₂O₃ as the aluminum source at an Al₂O₃/C molar ratio of 1:5. The effect of reaction temperature on the phase composition of the powder sample is similar to that shown in Fig. 4. However, the reaction temperature increased because of the insufficient contact between the reactant particles that resulted from the larger particle size and lower activity of the α-Al₂O₃ raw material in the reaction system. At the reaction temperature of 1500 °C, the XRD pattern of the powder sample showed weak Al₂O₃ and strong AlN diffraction peaks, indicating that although numerous AIN particles formed in the system at this reaction temperature, a certain amount of Al₂O₃ raw material was not converted to AlN. When the reaction temperature increased to 1550 °C, the AlN diffraction peak was further enhanced;



Fig. 6. XRD patterns of powder samples that were obtained at different temperatures and with α -Al₂O₃ as the aluminum source at an Al₂O₃/C molar ratio of 1 : 5.



Fig. 7. XRD patterns of powder samples that were obtained at different temperatures and with $Al(NO_3)_3 \cdot 9H_2O$ as the aluminum source at an Al_2O_3/C molar ratio of 1:5.

the Al₂O₃ diffraction peak, however, remained weak. Based on the XRD patterns of the powder samples that were calcined at different temperatures and on previous studies [25], phase-pure AlN powder can be synthesized at a reaction temperature that is higher than 1550 °C and with α -Al₂O₃ as the aluminum source at an Al₂O₃/C molar ratio of 1:5 under the experimental conditions, Fig. 7 shows the XRD patterns of the powder samples that were obtained at different temperatures with an Al_2O_3/C molar ratio of 1 : 5 and with $Al(NO_3)_3$ · 9H₂O as the aluminum source. In Fig. 7, the trend of the diffraction peaks of the samples that were calcined at different temperatures is similar to that shown in Fig. 4. In the reaction system with Al(NO₃)₃·9H₂O as the aluminum source, Al(NO₃)₃·9H₂O was relatively unstable and easily decomposed to produce fine Al₂O₃ particles; therefore, the reactant feedstock produced a large

Reaction temperature	Al(OH) ₃				α -Al ₂ O ₃	Al(NO ₃) ₃ .9H ₂ O
	1:3	1:4	1:5	1:6	1:5	1:5
1300 °C	23.58	26.48	29.80	33.26	4.59	51.68
1400 °C	31.98	40.84	44.37	45.07	22.78	60.52
1500 °C	41.77	46.80	50.53	50.05	30.17	63.38
1550 °C	51.62	56.50	51.75	51.92	33.24	64.04
1600 °C	56.89	57.63	52.62	52.51		—

Table 1. Reaction mass weight loss rates of AIN powders that were synthesized at different temperatures with different aluminum sources (%)

Note: the ratio in the table refers to the molar ratio of Al_2O_3/C .

amount of AlN powder at a low temperature. When the reaction temperature was 1400 °C, the XRD pattern of the powder sample showed a strong AlN diffraction peak and a weak Al_2O_3 diffraction peak. This result indicated that carbothermal reduction occurred in the system at this temperature to produce a large amount of AlN powder. When the reaction temperature was 1500 °C, the XRD pattern of the powder sample only showed the AlN diffraction peak. The AlN diffraction peak gradually increased with calcination temperature. Comparing the XRD patterns of the powder samples that were calcined at different temperatures revealed that phase-pure AlN powder can be synthesized at 1500 °C for 2 hrs using Al(NO₃)₃·9H₂O as an aluminum source at an Al₂O₃/C molar ratio of 1 : 5.

Synthesis reaction weight loss rate

CO gas is produced when AlN powder is synthesized via CRN. The escape of CO gas will cause the mass loss of the sample. Given that the weight loss rate of the synthesis reaction can be calculated based on the weight change of the sample before and after calcination, the progress of the synthesis reaction of AlN powder can be assessed. The calculated mass weight loss rates are shown in Table 1.

Table 1 shows that when Al(OH)₃ was used as the aluminum source, the weight loss rate of the synthesis reaction of the sample tended to increase gradually as reaction temperature increased. This behavior indicated that the reaction process was significantly enhanced as the reaction temperature increased. At the same reaction temperature, the weight loss rate of the samples tended to gradually increase as the Al2O3/C molar ratio increased. When the molar ratio of Al_2O_3/C was 1:3, the actual weight loss rate at 1600 °C was 56.89%, which is close to the theoretical weight loss rate (57.29%). This result indicated that the synthesis reaction was completed at this reaction temperature. Moreover, this result is consistent with the previous XRD analysis. When the molar ratio of Al_2O_3/C was 1 : 4, the actual weight loss rates at 1550 °C and 1600 °C were 56.50% and 57.63%, respectively, which exceeded the theoretical weight loss rate (53.92%). When the molar ratios of Al_2O_3/C were 1 : 5 and 1:6, the actual weight loss rates at 1500 °C reached or exceeded the theoretical weight loss rate (50.93% and 48.25%). These results indicated that the synthesis reaction between the sample mixtures was completed at 1500 °C.

When α -Al₂O₃ was used as the aluminum source at an Al₂O₃/C molar ratio of 1 : 5, the actual weight loss rate increased as the temperature increased. At the reaction temperature of 1300 °C, the actual weight loss rate was approximately 4.59%, indicating that the reaction process was slow and produced a small amount of AIN powder at this temperature. When the reaction temperature reached 1550 °C, the reaction weight loss rate significantly increased to 33.24% but remained slightly lower than its theoretical value of 34.57%, indicating that a small amount of Al₂O₃ raw material remained in the system. This result is consistent with previous XRD results (see Fig. 6).

When Al(NO₃)₃ 9H₂O was used as the aluminum source at a reaction molar ratio of Al₂O₃/C of 1 : 5, the actual weight loss rates at 1500 °C and 1550 °C were 63.38% and 64.04%, respectively. The actual weight loss rate between these two samples was low at only 0.66%, indicating that the synthesis reaction in the system was completed at 1550 °C, which is consistent with the previous XRD analysis (see Fig. 7).

Microstructure

Fig. 8 shows the SEM images of the AlN powders that were synthesized at different reaction temperatures and with Al(OH)₃ as the aluminum source at an $Al_2O_3/$ C molar ratio of 1:5. As shown in Figs. 8(a) and 8(b), the powder sample that was prepared at 1500 °C was mainly composed of a crystalline structure that formed via the aggregation (stacking) of tabular grains. The sizes of the flake-like grains were mostly distributed between 100 and 300 nm. When the reaction temperature was 1550 °C, the morphology of the synthesized powder sample did not obviously change; however, the agglomeration or aggregation of the powder particles was intensified and hedgehog-like aggregates increased in number (Fig. 8(d)). As the reaction temperature increased to 1600 °C, elongated crystals appeared with the tabular grains. The elongated crystals were uniformly distributed in the synthetic product (Fig. 8(e)). Moreover, the aggregation of the powder samples was exacerbated and the hedgehog-like aggregates grew larger (Fig. 8(f)). Fig. 9 shows the SEM images of the

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Fig. 8. SEM images of AlN powders that were synthesized at different reaction temperatures and with $Al(OH)_3$ as the aluminum source at an Al_2O_3/C molar ratio of 1:5.

(a) 1500 °C, low magnification; (b) 1500 °C, high magnification; (c) 1550 °C, low magnification; (d) 1550 °C, high magnification;

(e) 1600 °C, low magnification; (f) 1600 °C, high magnification

AlN powders that were synthesized at 1550 °C and 1600 °C and with α -Al₂O₃ as the aluminum source at an Al_2O_3/C molar ratio of 1 : 5. As seen in Figs. 9(a) and 9(b), the powder sample that was prepared at 1500 °C is mainly composed of tabular grains with dimensions of 100-300 nm. Moreover, aggregates that were 1-4 µm in size formed between the flake-like particles. As the reaction temperature increased to 1550 °C, the microstructure of the powder samples changed. Furthermore, the agglomeration between the flake-like particles was aggravated and many kinds of spherical wrapping structures were formed. The SEM images of the AlN powders that were synthesized at 1550 °C and 1600 °C with Al(NO₃)₃·9H₂O as the aluminum source at an Al₂O₃/C molar ratio of 1 : 5 are shown in Fig. 10. Compared with that shown in Fig. 9, the agglomeration between the flake-like particles in the powder sample shown in Fig. 10 markedly weakened. In addition, the flake-like particles formed numerous roughly spherical structures with sizes of 0.5-1 µm. Based on the above comparative analysis, the AlN powder samples that were synthesized using $Al(NO_3)_3$. 9H₂O under the experimental conditions have the best quality.



Fig. 9. SEM images of AlN powders that were synthesized at 1550 °C and 1600 °C and with α -Al₂O₃ as the aluminum source at an Al₂O₃/C molar ratio of 1 : 5.

(a)1500 °C, low magnification; (b) 1500 °C, high magnification; (c) 1550 °C, low magnification; (d) 1550 °C, high magnification



Fig. 10. SEM images of AlN powders that were synthesized at 1550 °C and 1600 °C and with $Al(NO_3)_3 \cdot 9H_2O$ as the aluminum source at an Al_2O_3/C molar ratio of 1:5.

(a) 1500 °C, low magnification;
(b) 1500 °C, high magnification;
(c) 1550 °C, low magnification;
(d) 1550 °C, high magnification

Reaction mechanism

The synthesis of AlN powder via CRN at high temperature in a N_2 atmosphere is based on the following total chemical reaction:

$$Al_2O_3(s) + 3C(s) + N_2(g) = 2AlN(s) + 3CO(g)$$
 (1)

Studies [26-27] have shown that reaction formula (1) has two steps. First, the carbothermal reduction between Al_2O_3 and C in the raw material produces metal aluminum vapor (Al) and low-valence gas oxides of aluminum (Al₂O). The reaction formula is:

$$Al_2O_3(s) + 3C(s) = 2Al(g) + 3CO(g)$$
 (2)

$$Al_2O_3(s) + 2C(s) = Al_2O(g) + 2CO(g)$$
 (3)

In the second step, the newly formed metal aluminum vapor and Al₂O gas phase in the system are further nitrided to form AlN. The reaction formula is:

$$2\mathrm{Al}(g) + \mathrm{N}_2(g) = 2\mathrm{AlN}(s) \tag{4}$$

$$Al_2O(g) + C(s) + N_2(g) = 2AlN(s) + CO(g)$$
 (5)

$$Al_2O(g) + CO(g) + N_2(g) = 2AlN(s) + CO_2(g)$$
 (6)

Based on the thermodynamic data in [28], the relationship between the standard Gibbs free energy (ΔG^{θ}_{T}) and the temperature (T) of the reaction formula (1) can be calculated as:

$$\Delta G^{\theta}_{T} = 707690 - 373.29T \tag{7}$$

If the effects of reaction temperature and the partial pressures of CO and N₂ on the formation rate of AlN powder are comprehensively investigated, the free energy change (ΔG) of the reaction formula (1) can be expressed as follows:

$$\Delta G = 707690 - 373.29T + 3RTln(P_{CO}/PN_2)$$
(8)

In formula (7), the theoretical ΔG^{θ}_{T} at 1896 K (1623 °C) becomes negative under standard atmospheric pressure, which is higher than the actual synthesis temperature of AlN powder under experimental conditions. In this experiment, AlN began to appear at 1300 °C (see Fig. 7). The main reason for this deviation is that the theoretical thermodynamic analysis is based on the assumption that the gas pressure is set at the standard atmospheric pressure $(1.01 \times 10^5 \text{ Pa})$. The synthesis experiment for AlN powder, however, was performed under flowing N₂ gas. CO, the reaction gas product, was continuously removed by the flowing N₂; thus, the CO partial pressure was maintained at a low level and the P_{CO}/PN_2 ratio in the experimental system was low, which benefitted the synthesis reaction. Furthermore, the carbon source used for the precursor material was highly active nanocarbon black particles that were approximately 20 nm in size. The carbon black particles and aluminum source were in sufficient contact, thereby increasing the contact area between the reactant particles. These two factors contributed to the initiation of the synthesis reaction in reaction Formula (1) at a lower temperature. In Formula (8), the reaction temperature, CO partial pressure, and N₂ partial pressure all greatly influence the change of reaction free energy (ΔG) . To decrease the temperature of the CRN reaction, the P_{CO}/PN₂ ratio should be decreased. Therefore, decreasing the partial pressure of CO, increasing N_2 flow rate, or increasing N_2 pressure can reduce the formation temperature of AlN and contribute to AlN powder synthesis.

When α -Al₂O₃ was used as the aluminum source, Al_2O_3 and the carbon source were not homogeneously mixed because the Al₂O₃ raw material had coarse particles, stable crystal structure, and poor reactivity. Thus, the synthesis reaction required a higher reaction temperature and a longer time for completion. In the XRD pattern shown in Fig. 6, Al₂O₃ diffraction peaks remained in the powder samples that were synthesized at 1550 °C. This result verifies the above analysis. Compared with the use of α -Al₂O₃ as the aluminum source, the use of Al(OH)₃ did not improve dispersion and bonding between aluminum and carbon in the system. However, the Al(OH)₃ crystals in the precursor powder decomposed into fine, amorphous Al₂O₃ particles with high reactivity during heating. Moreover, the CRN of AlN was accomplished easily (the synthesis reaction temperature is reduced). Therefore, the precursor formulation sample with Al(OH)₃ as the aluminum source can produce a phase-pure AIN powder at 1500 °C, as confirmed by previous experimental results (Fig. 4). When Al(NO₃)₃·9H₂O is used as the aluminum source, Al(NO₃)₃·9H₂O undergoes the following decomposition reaction under certain conditions [29]:

$$Al(NO_3)_3 \cdot 9H_2O(s) = Al_2O_3(s) + 6H_2O(g) + N_2(g) + 2.5O_2(g)$$
(9)

$$Al(NO_3)_3 \cdot 9H_2O(s) = Al_2O_3(s) + 4NO_2(g) + O_2(g) + 9H_2O(g)$$
(10)

$$Al(NO_3)_3 \cdot 9H_2O(s) = Al_2O_3(s) + 6H_2O(g) + N_2O_5(g)$$

(11)

The formation of amorphous Al_2O_3 particles with high activity in the decomposition products is advantageous for the production of AlN powder at a low reaction temperature, which is consistent with the XRD results shown in Fig. 7.

Conclusions

(1) Aluminum source type, raw material ratio, and reaction temperature greatly influence the phase composition of AlN powder samples. Phase-pure AlN powder was synthesized when the precursor powder sample is heated at 1500 °C for 2 hrs with an Al₂O₃/C molar ratio of 1 : 5 and Al(OH)₃ or Al(NO₃)₃·9H₂O as the aluminum source. A weak Al₂O₃ diffraction peak persisted in the AlN powder sample that was synthesized at 1550 °C for 2 hrs with an Al₂O₃/C molar ratio of 1 : 5 and with α -Al₂O₃ as the aluminum source.

(2) The quality of the AlN powder samples that were synthesized with $Al(NO_3)_3 \cdot 9H_2O$ as the aluminum source

is optimal relative to those of the samples that were synthesized with different aluminum sources. The agglomeration between flake-like particles was obviously weakened in the powder sample with the optimal quality. Moreover, numerous roughly spherical structures with sizes of 0.5-1 μ m were formed.

(3) AlN powder was synthesized in two steps via CRN in N_2 atmosphere at high temperature. First, Al_2O_3 and carbon in the system underwent carbothermal reduction to produce metallic aluminum vapor (Al) and low-valence gas oxides of aluminum (Al₂O). Second, the newly formed metal aluminum vapor and Al₂O gas in the system ere further nitrided to form AlN.

(4) Reducing the partial pressure of CO and increasing N_2 flow rate or pressure reduced the formation temperature of AlN and contributed to the synthesis of AlN powder. In this experiment, the formation of AlN powder was initiated at 1300 °C because of the high nitrogen flow rate and high activity of the nanocarbon black particles.

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