Effects of carbon source type and dosage on the synthesis of Al$_2$O$_3$–AlN composite powders by the carbothermal reduction–nitridation method

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Al$_2$O$_3$–AlN composite powders were synthesised in N$_2$ by the carbothermal reduction–nitridation method with Al(OH)$_3$ and different carbon sources (i.e. carbon black, graphite and starch) as starting materials. The effects of the carbon source type, carbon source dosage and reaction temperature on the synthesis performance of the Al$_2$O$_3$–AlN composite powders were investigated. The dried precursors and their synthesised products were characterised by X-ray diffractometer, comprehensive thermal analysis instrument and scanning electron microscope. The results showed that when the denoted mass ratio of Al$_2$O$_3$/AlN is 7:3, the optimum conditions for the synthesis of Al$_2$O$_3$–AlN composite powders with carbon black and starch as carbon sources are 1500°C for 2 h and 1600°C for 2 h, respectively. In addition to generating elemental carbon and gaseous H$_2$O, the single-phase starch raw material produces gaseous C$_2$H$_2$ during heating. The actual mass loss rate generated in the system is consequently significantly higher than the theoretical mass loss rate. The Al$_2$O$_3$–AlN composite powder samples synthesised at 1500°C with carbon black as the carbon source are mainly composed of approximately hedgehog-shaped aggregates, which consist of a mixture of flakes and nearly spherical particles (100–300 nm). The powder samples synthesised at 1500°C with graphite as the carbon source form diverse microstructures composed of spherical, flaky and rod-like particles. When starch is used as the carbon source, the encapsulated structure particles formed at 1500°C tend to increase gradually with decreases in the Al$_2$O$_3$/AlN mass ratio.

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1. Introduction

Alumina (Al$_2$O$_3$) presents the advantages of high strength, high hardness, high-temperature insulation resistance, corrosion resistance, other excellent physical and chemical properties, a wide range of raw materials and relatively low cost; furthermore, the processing and manufacturing technologies for this material are mature, with a history of extensive use in electronics, electrical appliances, chemical manufacturing, environmental protection, machinery, automobiles, textiles, metallurgy, aerospace and other fields.$^{1,2}$ Aluminium nitride (AlN) has exhibits a considerably wide range of applications in the electronics industry because of its high thermal conductivity, reliable electrical insulation, low dielectric constant and dielectric loss, nontoxicity, and high-temperature and corrosion resistance.$^{3-5}$ The mechanical strength of single AlN ceramics is low, however, and the production cost is high. When AlN and Al$_2$O$_3$ are combined to prepare Al$_2$O$_3$–AlN composite ceramics, their superior performances can be combined to realise complementary advantages.

To date, many studies have reported on the preparation of Al$_2$O$_3$–AlN composite ceramics, their related properties and the phase stability of the system. Kim et al.$^6$ prepared a AlON–AlN composite ceramics with a mole fraction of 1–25% AlN by reactive sintering under a nitrogen atmosphere. They also investigated the stability and microstructure of AlON-AlN composite ceramics. The formation temperature of AlON decreases from 1700 to 1600°C with increases in the AlN content and sintering temperature. Tsyganenko et al.$^7$ investigated the properties of AlN-based materials with additives of 5–50 mass % Al$_2$O$_3$. Adding Al$_2$O$_3$ to AlN increases the oxidation resistance and mechanical strength of the materials. Boey et al.$^8$ investigated the phase reaction and sintering behaviour of a ternary Al$_2$O$_3$–AlN–Y$_2$O$_3$ system near the critical temperature range of 1600–1700°C in a pure nitrogen environment. AlN shows complete densification (>98%) without the formation of AlON by sintering an initial Al$_2$O$_3$-rich ternary system (Al$_2$O$_3$–20 wt% AlN–5 wt% Y$_2$O$_3$) at a
relatively low temperature (1680°C). AlON formation is delayed until 1700°C. Maghsoudipour et al.9) investigated the sintering behaviour of three different compositions in the AlN/Al2O3 system using Y2O3 as a sintering aid. The AlN/Al2O3 ratio and sintering temperature exert a considerable influence on the microstructure and crystalline phases present in the samples. Recently, Li et al.10) prepared AlON ceramics by spark plasma sintering (SPS) using Al2O3, AlN and different Y2O3 contents as raw materials. High-density single-phase AlON ceramics were obtained at 1600°C, and their related properties and reaction mechanism were investigated. Li et al.11) prepared Al2O3–AIN composite ceramics by hot pressing at 1600°C with high-purity Al2O3 and AlN as the main raw materials; they also added a certain amount of nano-Al2O3 powders, and studied the mechanical strength, fracture toughness, density and other properties in depth.

In summary, many scholars have achieved remarkable research results concerning Al2O3–AIN system composite ceramics. Nevertheless, most of the research work to date was carried out by direct mechanical mixing of Al2O3 and AlN powder and preparing Al2O3–AIN composite ceramics by hot-pressing sintering, SPS or other sintering methods. Preparation of homogeneous and less agglomerated ultrafine Al2O3–AIN composite powders is essential for preparing Al2O3–AIN composite ceramics with excellent performance. The particle size, mixed-state and composition uniformity of Al2O3–AIN composite powders all affect the properties of Al2O3–AIN composite ceramics significantly. Mechanical mixing is inefficient for preparing homogeneous powder as raw material; this method adversely affects microstructures of composite ceramics and their related performance. The synthesis of Al2O3–AIN composite powders with a fine particle size and mixed homogeneity consequently exerts a significant effect on the preparation of high-performance Al2O3–AIN composite ceramics. At present, only a few studies have reported on the synthesis of Al2O3–AIN composite powders.12–14) In the present study, Al(OH)3 was used as the aluminium source to further improve the composite effect of Al2O3 and AlN. Different carbon sources (i.e. carbon black, graphite and starch) were also introduced into the system. The Al2O3–AIN composite powders were synthesised by the carbothermal reduction–nitridation method in a tubular atmosphere under a nitrogen atmosphere. The effects of different carbon source types, carbon source dosages and reaction temperatures on the phase composition and microstructure of Al2O3–AIN composite powders were analysed. The reaction mechanism of Al2O3–AIN composite powders is also discussed.

2. Experimental procedures

Aluminium hydroxide [Al(OH)₃, ≥99.0%, 8.8μm], carbon black (C, ≥99.9%, 20nm), graphite (C, ≥99.0%, 5.6μm) and starch [(C₆H₁₀O₅)n, ≥99.0%] were used as the raw materials. The preparation process for Al2O3–AIN composite powders is shown in Fig. 1. First, two raw materials, Al(OH)₃ and carbon black, were weighed by electronic analytical balance according to the Al2O3/AIN mass ratio of 7:3 in the synthesised product according to Eq. (1). The raw material was subsequently placed in a ball mill jar and mixed for 4 h in a planetary fast ball mill using ethanol (C₂H₅OH, ≥99.5%) as the liquid medium; the solid–liquid ratio was 1:2. The slurry was dried, sieved and placed in a tubular furnace. The temperature in the tubular furnace was increased to 500°C at a rate of 10°C·min⁻¹ and maintained for 20 min under a flow of N₂ atmosphere. The temperature was increased from 500 to 1300, 1400, 1500 and 1600°C at the same heating rate and incubated for 2 h. At the end of the incubation period, the temperature was lowered to approximately 250°C at a cooling rate of 10°C·min⁻¹ and cooled naturally to room temperature to obtain a carbon-containing Al2O3–AIN powder. The synthesised carbon-containing Al2O3–AIN composite powders were decarburised at 650°C for 3 h under an air atmosphere in a box-type resistance furnace and subsequently cooled naturally to room temperature to obtain a decarburised Al2O3–AIN composite powder. Graphite and starch raw materials were used as the carbon sources, instead of the above-mentioned carbon black raw material, to investigate the effect of different carbon source types on the synthesis properties of Al2O3–AIN composite powders. The Al2O3–AIN composite powders were prepared according to the above experimental procedure. In addition, the Al2O3/AIN mass ratio was denoted as 10:0, 5:5, 3:7 and 0:10 to investigate the effect of the amount of organic starch on the synthesis of Al2O3–AIN composite powders. Afterward, composite powders with different Al2O3/AIN mass ratios were prepared according to the experimental procedure.

The phase compositions of the precursors and the samples obtained at different calcination temperatures were

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**Fig. 1.** Preparation process of Al2O3–AIN composite powders.
analysed by X-ray diffractometer (XRD, Tongda TD-3500). The mass of the powder samples before and after the high-temperature synthesis reaction was weighed with an electronic analytical balance (accurate to approximately 0.1 mg). The weight loss rate of the synthesis reaction was also calculated. The changes in the single-phase starch raw material and the starch-containing precursor powder during heating were analysed by comprehensive thermal analyser (TG–DTA, Shimadzu DTA-50). The powder sample microstructure was analysed by scanning electron microscopy (SEM, FEI Quanta 250).

3. Results and discussion

3.1 Phase compositions

The XRD patterns of dried precursor powder samples with a denoted Al₂O₃/AlN mass ratio of 7:3 using different carbon sources are shown in Fig. 2. It can be seen from Fig. 2(a) and 2(c) that strong Al(OH)₃ diffraction peaks appeared in the XRD patterns, and no other phase diffraction peaks existed. Strong Al(OH)₃ and graphite diffraction peaks occurred, however in the XRD pattern in Fig. 2(b). Figure 3 shows the XRD patterns of composite powders obtained at different temperatures with an Al₂O₃/AlN mass ratio of 7:3 using carbon black as the carbon source. The reaction temperature exerted a considerable influence on the phase composition of the synthesised powder samples. When the reaction temperature was 1300°C, the diffraction peak of Al(OH)₃ disappeared from the precursor material. Strong Al₂O₃ and weak AlN diffraction peaks were observed, moreover, indicating that the Al(OH)₃ in the raw materials was completely decomposed to produce Al₂O₃ products at this temperature. In addition, the amount of AlN formed by further nitridation of Al₂O₃ remained small. When the reaction temperature was increased to 1400°C, the characteristic diffraction peaks of Al₂O₃ and AlN in the XRD pattern showed no significant change. At 1500°C, a strong AlN diffraction peak appeared in the XRD pattern. This peak indicated that a large amount of AlN powder was produced in the system. When the reaction temperature was increased further to 1600°C, the XRD pattern displayed no significant change. These observations, combined with the subsequent weight loss analysis, showed that the carbothermal reduction–nitridation reaction of the AlN powder produced by the mixed precursor was completed at 1500°C with carbon black as the carbon source. The XRD patterns of composite powders obtained at different temperatures with a denoted Al₂O₃/AlN mass ratio of 7:3 using graphite as the carbon source are shown in Fig. 4. When the reaction temperatures were 1300 and 1400°C, the XRD pattern of the powder sample showed strong Al₂O₃ and weak AlN diffraction peaks. The characteristic diffraction peaks were also observed with graphite as the raw material. At 1500°C, strong AlN, Al₂O₃ and graphite diffraction peaks were observed, indicating that a large amount of AlN powder was formed in the system. This result indicated...
that, when the treatment was carried out at 650°C for 3 h, a small amount of graphite remaining in the composite powders was not successfully removed. When the reaction temperature was further increased to 1600°C, the XRD pattern exhibited no significant change. Analysis showed that the carbothermal reduction–nitridation of AlN powder in the mixed precursor materials at 1600°C was still not completed with graphite as the carbon source. The XRD patterns of composite powders obtained at different temperatures with a denoted Al₂O₃/AlN mass ratio of 7:3 using starch as the carbon source are shown in Fig. 5. When the reaction temperature increased to 1400°C, a weak AlN diffraction peak appeared in the XRD pattern. At 1600°C, strong AlN and Al₂O₃ diffraction peaks appeared in the XRD pattern. Combined with the subsequent weight loss analysis of the synthesis reaction, these observations indicated that the carbothermal reduction–nitridation of the AlN powder was completed at 1600°C using starch as the carbon source and a denoted Al₂O₃/AlN mass ratio of 7:3.

In this experiment, organic starch was selected as the carbon source to investigate the influence of the amount of the carbon source on the phase composition of the synthesized powder samples. The phase composition of the powder samples synthesized at 1500°C with different Al₂O₃/AlN mass ratios was analyzed, and the results are shown in Fig. 6. The diffraction peak of AlN gradually increased and the Al₂O₃ diffraction peak gradually decreased with increases in the AlN content in Al₂O₃/AlN composite powders. This result indicated that at 1500°C, when starch was used as a carbon source, the system produced a large amount of elemental carbon with increased starch content in the raw materials; this carbon reacted with Al₂O₃ and N₂ to generate more AlN products. Notably, when the denoted Al₂O₃/AlN mass ratio was 0:10, the Al₂O₃ formed by Al(OH)₃ decomposition was theoretically all nitrided to form an AlN product. Al₂O₃ diffraction peaks were, however, still observed in the XRD pattern (Fig. 6).

Possible reasons for this observation were as follows: (1) under the experimental conditions, the synthesis reaction in the system was a solid (Al₂O₃)–gas (N₂)–solid (elemental carbon) reaction, and such reactions are difficult to carry out thoroughly. (2) In the actual heating process, in addition to decomposition of the formed elemental carbon and gaseous H₂O, the starch may also generate a certain amount of C₆H₁₂ gaseous compounds, which escape with the gas flow. The system may consequently have lacked carbon, thus preventing part of the Al₂O₃ from being nitrided to produce AlN products.¹⁵,¹⁶

3.2 Thermal decomposition behaviour of the precursors

In addition to the thermal effect, the synthesis of Al₂O₃–AlN composite powders by carbothermal reduction–nitridation with starch as the carbon source was accompanied by a change in mass. TG–DTA analysis was carried out on a single starch raw material and starch-containing dry precursor powders with an Al₂O₃/AlN mass ratio of 7:3 to investigate the thermal decomposition behaviour of mixed precursor materials. The results are shown in Figs. 7 and 8. Figure 7 shows that the DTA curve of a single starch exhibited an endothermic peak at 271°C, the corresponding TG curve dropped remarkably, and the mass change was 78.21%. This phenomenon was mainly attributed to the fact that the starch also generated a certain amount of C₆H₁₂ gaseous substances at high temperatures, in addition to contributing to formation of gaseous H₂O. Consequently, the system produced a large quality loss. As shown in Fig. 8, the system resulted in a mass loss of 29.90% from room temperature to about 325°C. A wide endothermic peak occurred at a temperature of about 305°C in the DTA curve, mainly due to decomposition of starch and Al(OH)₃.

3.3 Synthesis reaction weight loss rate

In this experiment, the total reaction formula during the
The total reaction formula during the synthesis of Al2O3 composite powders with starch as the carbon source can be expressed as follows:

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2\times \text{Al(OH)}_3 + 3\text{C} + \text{N}_2 = (x - 1)\text{Al}_2\text{O}_3 + 2\text{AlN} + 3x\text{H}_2\text{O} + 3x\text{CO} \quad (1)
\]

Equations (1) and (2) show that Al2O3–AlN composite powders with different Al2O3/AlN mass proportions can be synthesised by adjusting the different proportions of Al(OH)$_3$ to C or C$_6$H$_{10}$O$_5$ in the mixed raw materials. When three kinds of carbon sources were used to produce Al2O3–AlN composite powders by carbothermal reduction–nitridation, CO gas and H$_2$O gaseous matter were generated. The resulting gases escaped with the gas flow, resulting in a mass loss of the powder sample. The synthesis progression of AlN–Al2O3 composite powders can be evaluated on the basis of the weight loss rate calculated by the mass change before and after calcination of the powder samples. Table 1 shows the weight loss rate of the precursors from different carbon sources with a denoted Al2O3/AlN mass ratio of 7:3 at different calcination temperatures. The weight loss rate of the synthesis reaction in the precursor powder samples tended to increase gradually with increases in the calcination temperature. This increase indicated that the reaction process was enhanced further by increases in the calcination temperature. When carbon black was the carbon source, the weight loss rate of the powder sample increased with increases in the calcination temperature. When the reaction temperature was 1300°C, the mass loss rate of the sample was only 35.28%. When the reaction temperature reached 1400°C, the mass loss rate of the sample increased to 37.04%. At 1500°C, the weight loss rate of the sample increased to 45.72%, which exceeded the theoretical weight loss rate (40.12%) for the sample. When the reaction temperature reached 1600°C, the weight loss rate of the sample reached 46.41%, which was only 0.69% higher than that of the sample at 1500°C. The actual weight loss rate over the theoretical weight loss rate at 1500°C was attributed mainly to the fact that gaseous Al2O3 intermediate products were generated during the Al2O3 carbothermal reduction–nitridation reaction at high temperatures. The partial escape of gaseous Al2O3 escaped from the system, along with the nitrogen gas stream, contributed further to the measured weight loss rate over the theoretical weight loss rate. Analysis results showed that when carbon black was used as the carbon source, the synthesis reaction of the powder samples was completed at 1500°C, which was consistent with previous XRD analysis results. When graphite was the carbon source, the optimum reaction temperature for synthesising AlN–Al2O3 composite powders was 1500°C. When the denoted mass ratio of Al2O3/AlN was 7:3, the suitable reaction temperature with starch as the carbon source was 1600°C.

Table 2 presents the weight loss rate of composite powders obtained at 1500°C with different denoted Al2O3/AlN mass ratios using starch as the carbon source. The mass loss rate of the sample increased with increases in the AlN mass fraction in the composite powders (corresponding to the decrease in the Al2O3 mass fraction). When the denoted Al2O3/AlN mass ratio was 10:0, the mass loss rate of the sample was only 36.49%. When the denoted Al2O3/AlN mass ratio was reduced by 5:5, the mass loss rate of the sample was 41.93%, and when the denoted Al2O3/AlN mass ratio was further reduced to 5:5, the mass loss rate of the sample was 45.68%.

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**Table 1.** Weight loss rate of the precursors from different carbon sources with a denoted Al2O3/AlN mass ratio of 7:3 at different calcination temperatures

| Calcination temperature/°C | Mass fraction/% |
|-----------------------------|-----------------|
|                             | Carbon black | Graphite | Starch |
| 1300                        | 35.28        | 33.20    | 43.71  |
| 1400                        | 37.04        | 37.64    | 44.59  |
| 1500                        | 45.72        | 41.93    | 45.68  |
| 1600                        | 46.41        | 42.15    | 46.18  |

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**Table 2.** Weight loss rate of composite powders obtained at 1500°C with different denoted Al2O3/AlN mass ratios using starch as the carbon source.

| Calcination temperature/°C | Mass fraction/% |
|-----------------------------|-----------------|
|                             | Carbon black | Graphite | Starch |
| 1500                        | 35.28        | 33.20    | 43.71  |
| 1500                        | 37.04        | 37.64    | 44.59  |
| 1500                        | 45.72        | 41.93    | 45.68  |
| 1600                        | 46.41        | 42.15    | 46.18  |
Table 2. Weight loss rate of composite powders obtained at 1500°C with different denoted Al2O3/AlN mass ratios using starch as the carbon source

| No. | Al2O3/AlN mass ratio | Mass fraction/% |
|-----|-----------------------|-----------------|
| 1   | 10:0                  | 36.49           |
| 2   | 7:3                   | 45.68           |
| 3   | 5:5                   | 52.00           |
| 4   | 3:7                   | 55.65           |
| 5   | 0:10                  | 60.52           |

Table 3. Possible chemical reactions during the synthesis of Al2O3–AlN composite powders

| No. | Reaction equation |
|-----|-------------------|
| (3) | $2\text{Al(OH)}_3(s) = \text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{O(g)}$ |
| (4) | $\text{C}_6\text{H}_10\text{O}_5(s) = 6\text{C(s)} + 5\text{H}_2\text{O(g)}$ |
| (5) | $\text{Al}_2\text{O}_3(s) + 3\text{C(s)} = 2\text{Al(g)} + 3\text{CO(g)}$ |
| (6) | $\text{Al}_2\text{O}_3(s) + 2\text{C(s)} = \text{Al}_2\text{O}_3(g) + 2\text{CO(g)}$ |
| (7) | $2\text{Al(g)} + \text{N}_2(g) = 2\text{AlN(s)}$ |
| (8) | $\text{Al}_2\text{O}_3(g) + \text{C(s)} + \text{N}_2(g) = 2\text{AlN(s)} + \text{CO(g)}$ |
| (9) | $\text{Al}_2\text{O}_3(g) + \text{CO(g)} + \text{N}_2(g) = 2\text{AlN(s)} + \text{CO}_2(g)$ |

Fig. 9. SEM images of the powder samples obtained at 1500°C with a denoted Al2O3/AlN mass ratio of 7:3 using carbon black as the carbon source: (a) low magnification; (b) high magnification.

rate of the sample increased to 52.00%. When the denoted Al2O3/AlN mass ratio was reduced to 0:10, the mass loss rate of the sample was 60.52%. The quality loss rate of samples increased gradually with decreases in the Al2O3/AlN mass ratio. This result can be attributed to the fact that the amount of starch raw material increased in the system with decreases in the Al2O3/AlN mass ratio. On one hand, the gaseous material produced by starch decomposition at high temperatures resulted in a large mass loss in the system. On the other hand, elemental carbon reacted markedly with Al2O3 to form AlN, resulting in a large amount of gaseous matter (Table 3) and a large mass loss in the samples.

3.4 Microstructure

SEM images of the powder samples obtained at 1500°C with a denoted Al2O3/AlN mass ratio of 7:3 using carbon black as the carbon source are shown in Fig. 9. The synthesised powder samples were composed essentially of a number of approximately hedgehog-shaped aggregates (stacks) about 1–2 μm in size. The aggregates consisted of flaky or nearly spherical particles with particle sizes of 100–300 nm. A uniform encapsulated structure was formed as a result. Figure 10 shows SEM images of powder samples obtained at 1500°C with a denoted Al2O3/AlN mass ratio of 7:3 using graphite as the carbon source. Comparison of the microstructures in Fig. 9 with those of the powder samples in Fig. 10 showed a variety of microstructures, with spherical, flaky or rod-shaped particles. The particle sizes were relatively large as a whole, and a certain degree of agglomeration was observed. Figure 11 depicts SEM images of powder samples obtained at 1500°C with different denoted Al2O3/AlN mass ratios using starch as the carbon source. When the denoted Al2O3/AlN mass ratio was 10:0, flaky particles and a certain number of irregularly shaped particles were mainly observed in the powder samples. With the increased AlN content in the powder sample, the powder sample microstructure changed remarkably with increases in the AlN content in the powder sample. When the denoted Al2O3/AlN mass ratio was 7:3, the number of large aggregates in the powder sample was significantly reduced, and the number of encapsulated structural particles formed by the small particles in the range of 100–300 nm was significantly increased (Fig. 11(b)). When the Al2O3/AlN mass ratio continued to decrease, the sizes of the flaky and nearly spherical particles in the powder sample showed no significant change (most of the small particle sizes were still between 100 and 300 nm). The sizes of the wrapped aggregates, however, showed a tendency to increase.

3.5 Synthesis reaction mechanism

The chemical reactions that may occur during high-temperature processing of Al2O3–AlN composite powders synthesised by carbothermal reduction–nitridation under the experimental conditions are shown in Table 3. The Al2O3 in the composite powders was mainly formed by the decomposition of Al(OH)3. Given that Al(OH)3 was easily decomposed at a relatively low temperature to produce Al2O3, the synthesis of AlN powder during the preparation of AlN–Al2O3 composite powders was essential. The AlN synthesis process was, moreover, relatively complex; generation involved a multistep reaction.17,18 First, the newly produced Al2O3 reacted with carbon black (graphite or elemental carbon produced by decomposition of starch at a low temperature) to produce metal aluminium vapour...
and Al₂O by carbothermal reduction reaction in accordance with Eqs. (5) and (6). Afterward, the resulting metal aluminium vapour and Al₂O gas were further nitrided in accordance with Eqs. (7)–(9) to form AlN.

The total reaction formula for the synthesis of AlN powder by carbothermal reduction–nitridation was as follows:

$$\text{Al}_2\text{O}_3(s) + 3\text{C}(s) + \text{N}_2(g) = 2\text{AlN}(s) + 3\text{CO}(g).$$

The standard-state reaction temperature (or theoretical reaction temperature) of the reaction Eq. (10) was 1892 K (1619°C). According to previous XRD analysis results, a small amount of AlN was generated at 1300°C, which was lower than the theoretical reaction temperature. On the one hand, this result was attributed mainly to the fact that the thermodynamic theoretical analysis assumed that the pressure in the synthesis system was the standard atmospheric pressure. In the actual experiment, the powder sample synthesis used a flowing N₂ atmosphere. A portion of the reaction gas phase product CO participated in the reaction to form AlN, and the remaining CO gas was removed, along with the CO₂ gas and the continuously flowing N₂. The partial pressure of CO and CO₂ gas was therefore maintained at a low level. Moreover, the low concentration of CO and CO₂ in the system resulted in favourable AlN synthesis. On the other hand, when organic starch and high-activity nanocarbon black raw materials were used as the carbon source in the precursor, the organic starch decomposed at low temperature to produce ultrafine carbon particles with high activity. The contact between the ultrafine carbon particles or the high-activity nanocarbon black raw materials and the amorphous Al₃O₃ particles from the Al(OH)₃ decomposition was sufficient to increase the contact area between the reactant particles. The reactivity of the reactant particles was consequently increased. These two factors contributed to the synthesis of AlN powders at low temperatures.

4. Conclusions

(1) When the denoted Al₂O₃/AlN mass ratio was 7:3, the optimum conditions for synthesis of Al₂O₃–AlN composite powders with carbon black and starch as the carbon source were 1500°C for 2 h and 1600°C for 2 h, respectively.

(2) The Al₂O₃–AlN composite powders synthesised at 1500°C with carbon black as the carbon source were composed mainly of a certain number of approximately hedgehog-shaped aggregates about 1–2 μm in size. The aggregates consisted of flaky or nearly spherical particles with particle sizes of 100–300 nm, they forming a uniform encapsulated structure. The powder samples synthesised at 1500°C with graphite as the carbon source formed a variety of microstructures, such as spherical, flaky and rod-shaped particles.

(3) When the denoted Al₂O₃/AlN mass ratio was 10:0, mainly flaky particles and a certain number of irregularly shaped particles were observed in the powder samples with starch as the carbon source. The encapsulated structure particles formed at 1500°C tended to increase gradually with decreases in the Al₂O₃/AlN mass ratio.

(4) The process of AlN synthesis in the composite powders underwent two steps in their generation. First, the newly generated Al₂O₃ formed metal aluminium vapour and gaseous Al₂O through a carbothermal reduction reaction. Subsequently, the resulting metal aluminium vapour and Al₂O gas were further nitrided to form AlN. The actual temperature of the synthesised powders under these experimental conditions was considerably lower than the calculated theoretical reaction temperature.

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