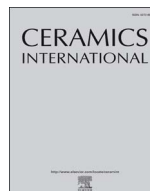




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# Spherical AlN particles synthesized by the carbothermal method: Effects of reaction parameters and growth mechanism

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## ARTICLE INFO

### Keywords:

Spherical AlN particles  
Carbothermal method  
Reaction parameters  
Growth mechanism

## ABSTRACT

In this work, AlN particles with spherical morphology, smooth appearance and controllable particle size were purposely synthesized through an efficient carbothermal strategy at 1800 °C aiding with the CaF<sub>2</sub> additive. The influences of typical synthesis parameters, such as carbon content, CaF<sub>2</sub> particle size and reaction time on the formation rate, particles size and surface morphology of AlN particles were deeply and comprehensively studied. It was indicated that the intermediate Ca-aluminates was extremely essential to enhance the nitridation rate, promote the AlN growth and form the spherical morphology. More importantly, based on the systematic investigations and intensive analyses, the underlying growth mechanism of spherical AlN particles in the carbothermal process was rationally proposed and elaborated herein.

## 1. Introduction

Recently, aluminum nitride (AlN) has received extensive attention in the heat-dissipation applications, benefiting from its remarkable physicochemical properties, including high thermal conductivity (~320 W/mK), low dielectric loss, high electrical resistivity, as well as suitable thermal expansion coefficient matched with that of silicon [1–3]. AlN particles have been widely used as thermal conductive fillers combined with polymers to fabricate the thermal interface materials [4–6]. With the increasing demand for heat dissipation of integrated circuits, the thermal interface materials with higher thermal conductivity are highly desirable, which requires the filling fraction of AlN particles to be raised as high as possible. Nevertheless, most of commercially available AlN powders presents the angular morphology, which is difficult to achieve high filling fraction due to their weak dispersity and low fluidity in the polymers [7]. Therefore, it is of great urgency and significance to synthesize spherical AlN particles with good fluidity for the fabrication of thermal interface materials with high performance.

Although spherical AlN powders presented great commercial potential, their large-scale preparation still exists big obstacles: AlN is easy to decompose rather than melt under ultra-high temperature [8], so it is difficult to achieve spheroidization by the conventional high-temperature fusion technique. Up to now, only limited literatures on the synthesis of spherical AlN can be retrieved [9–13]. Our group have long been engaged in the preparation of spherical AlN particles, and two

facile and efficient synthesis strategies have been developed: one is a two-step approach, including preparation of AlN granulations and the following sintering process for their densification [14,15]; the other is one-step process, in which spherical AlN particles could be directly synthesized via carbothermal reduction and nitridation (CRN) of Al<sub>2</sub>O<sub>3</sub>, aiding with elevated N<sub>2</sub> pressure and appropriate additives [16–18]. The first method can successfully fabricate spherical AlN particles with large particle size (~50 μm), but commercial AlN powders were still applied as raw materials, resulting in the relatively high production cost. In comparison, the CRN method is more suitable for the large-scale production because the resultant spherical AlN particles present many outstanding performances, such as high sphericity, good dispersity, low synthesis cost and simple preparation process [19–21]. Hence, the carbothermal synthesis of spherical AlN particles have exhibited high commercial value and broad application prospects.

Although spherical AlN particles have been successfully synthesized by the carbothermal method in our previous work, the growth mechanism of spherical AlN particles are still unclear. Additionally, the influence of synthetic parameters on the reaction rate and the final AlN morphology still need to be further investigated as well.

On the basis of above consideration, in this study, the reaction process in the carbothermal synthesis of spherical AlN particles were comprehensively and deeply studied. Effects of typical synthesis parameters, including carbon content, additives particle size and reaction time on the nitridation rate, particles size and surface morphology were elaborately studied. According to the research results, the formation

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<https://doi.org/10.1016/j.ceramint.2017.12.071>

Received 28 November 2017; Received in revised form 7 December 2017; Accepted 11 December 2017  
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mechanism of spherical morphology and growth process of AlN particles were attentively proposed.

## 2. Experimental

Commercial Al<sub>2</sub>O<sub>3</sub> powders (0.7 μm, Admatechs, Japan), carbon black (10 nm, Delong Carbon, China) were used as raw materials, CaF<sub>2</sub> (≥ 99.99%, Sinopharm Chemical Reagent, China) was applied as additive to accelerate the carbothermal process, inspired by our previous studies [22]. In this study, the mole ratio of C to Al<sub>2</sub>O<sub>3</sub> was varied from 2.5 to 3.0, 4.0 and 4.5. The CaF<sub>2</sub> content was kept at 5 wt% relative to the mass of Al<sub>2</sub>O<sub>3</sub>.

In a typical synthesis procedure, the raw Al<sub>2</sub>O<sub>3</sub>, carbon black and CaF<sub>2</sub> additive were milled to mix uniformly and dried completely in air. After that, ~ 1 g of the mixture powders were placed into a graphite crucible, and further heating in a High-Multi 5000 furnace (Fujidempa, Japan) under an elevated N<sub>2</sub> pressure of 1 MPa [18]. The selected reaction temperature was 1500 °C and 1800 °C, while the reaction time was varied in the range of 0.5–4 h. After the heating process, the obtained powders was transferred to a muffle oven and heated in air for 2 h at 650 °C to remove excess carbon.

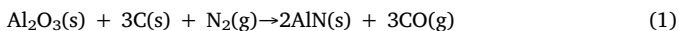
In addition, considering the long milling time could change the particle size of CaF<sub>2</sub>, CaF<sub>2</sub> granulations were adopted to accurately evaluate the effects of CaF<sub>2</sub> particles size on the nitridation rate and the morphology of AlN particles. The specific procedure were as follows: The C/Al<sub>2</sub>O<sub>3</sub> mixtures with a mole ratio of 4.0 were firstly prepared following the above method. CaF<sub>2</sub> granulations were prepared by grinding methods [23], and further sieved and graded to three kinds of particles (< 75 μm, 75–150 μm, > 150 μm) by the 100 and 200 meshes. After that, 5 wt% of CaF<sub>2</sub> granulations were weighed and added to the Al<sub>2</sub>O<sub>3</sub>/C mixtures, then the obtained powder mixtures were fully mixed in a vibrating manner. According to the particle size of CaF<sub>2</sub> granulations changing from small to large, the obtained powders mixtures were briefly named as ACF-S, ACF-M, ACF-L.

The crystalline structures of products were detected by X-ray diffraction analysis by Cu Kα and scanning speed of 0.1°/s (D8 Advance A25, Bruker, Germany). The AlN conversion fraction was calculated according to the XRD peak intensities of (104) of Al<sub>2</sub>O<sub>3</sub> and (100) of AlN. The microstructures of the spherical AlN granules were evaluated by the scanning electron microscope (JSM-7001F, JEOL, Japan).

## 3. Results and discussion

### 3.1. Effects of carbon content

As established, the formation of AlN via the traditional CRN process is mainly realized by the following equation [24]:



In order to evaluate the effects of carbon content on the CRN process, precursors with the same 5 wt% CaF<sub>2</sub> but different C/Al<sub>2</sub>O<sub>3</sub> mole ratio (2.5, 3.0, 4.0, and 5.0) were prepared, respectively. The CRN reaction was conducted at 1500 °C and 1800 °C for 2 h. Based on the XRD analysis, the relation between AlN conversion fraction and C/Al<sub>2</sub>O<sub>3</sub> mole ratio at different temperatures were presented in Fig. 1.

As observed, no samples achieved full conversion at 1500 °C. When the mole ratio of C to Al<sub>2</sub>O<sub>3</sub> was 3.0, namely, the theoretical value of CRN reaction according to Eq. (1), the sample presented a highest AlN conversion fraction of ~ 79%, indicating the highest nitration rate was achieved. However, when the molar ratio of C to Al<sub>2</sub>O<sub>3</sub> was lower or higher than the theoretical value, that was excessive carbon or insufficient carbon was used, the conversion fraction of AlN significantly decreased.

In our previous studies, we have demonstrated the additive of CaF<sub>2</sub> could react with alumina to produce low melting Ca-aluminates, which

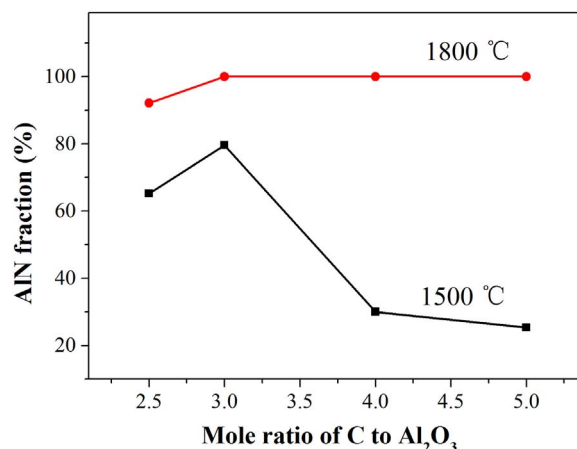
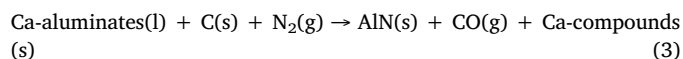


Fig. 1. The relation between AlN conversion fraction and mole ratio of C to Al<sub>2</sub>O<sub>3</sub> at different temperature.

could be further reduced and nitrided to transform into AlN [22]. The whole procedure can be described by the following equations:



In addition, when the reaction temperature was high enough, the Ca-compounds tended to be further nitrided and completely reduced to Ca gas, which were finally vaporized in the atmosphere. Obviously, the formation and nitration of liquid Ca-aluminates had an important influence on the production rate of AlN. For a clearer explanation, the XRD patterns of different samples prepared at 1500 °C were concretely shown in Fig. 2.

As observed, the CaAl<sub>12</sub>O<sub>19</sub> were detected in all samples, suggesting the reaction between Al<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub>. When the ratio of C to Al<sub>2</sub>O<sub>3</sub> was

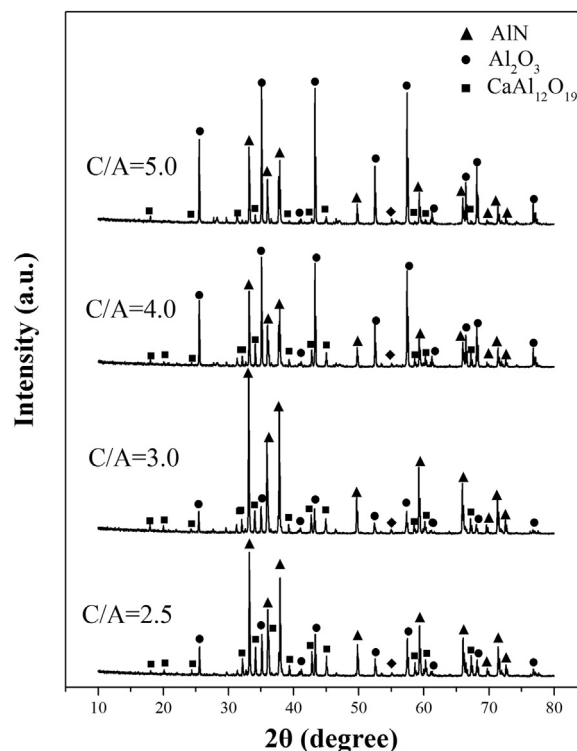


Fig. 2. XRD patterns of the products after heating various samples with different C/Al<sub>2</sub>O<sub>3</sub> mole ratio (2.5, 3.0, 4.0 and 5.0) at 1500 °C.

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