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Carbothermal synthesis of spherical AlN granules: Effects of synthesis parameters and Y_2O_3 additive

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Abstract

In this study, micron-sized spherical AlN granules were delicately synthesized by carbothermal reduction–nitridation (CRN) route with the aid of Y_2O_3 additive. The effects of synthesis parameters and Y_2O_3 content on the nitridation rate, particle size and especially on the surface morphology were systematically investigated. The results showed that the reduction and nitridation of intermediate Y-aluminates were extremely significant to promote the formation of micro-sized spherical AlN granules by improving the nitridation rate, increasing the grain size, providing the spherical morphology and promoting the uniform growth of AlN granules. Furthermore, the elevated N_2 gas pressure, high reaction temperature also made contribution to the formation of spherical morphology and large particle size. Based on the experimental results, the underlying reaction mechanism in the carbothermal synthesis of spherical AlN granules with Y_2O_3 was attentively proposed.

Keywords: A. Powders: chemical preparation; B. Grain size; D. Y_2O_3; Spherical AlN granules

1. Introduction

In recent years, Aluminum Nitride (AlN) has attracted increasing attention in the electronic industry because of its excellent thermal and electrical properties such as high thermal conductivity, good electrical resistivity, low dielectric constant, and low thermal expansion coefficient close to that of silicon [1–3]. AlN granules are regarded as one of the best candidate fillers for polymers to improve heat-dissipating capability of electronic packaging [4]. As the heat dissipation requirements increase, the filler loading needs to be raised as high as possible, and meanwhile the powder/polymer composite mixtures need to keep good fluidity at that high filler loading [5]. Hence, the synthesis of spherical AlN granules which satisfy such conflicting requirements becomes increasingly important.

Despite the potentially commercial importance, the large-scale synthesis of spherical AlN remains a challenge to date because AlN tends to decompose at high temperature and cannot be transformed to spherical morphology just by the traditional surface tension method [6]. To our best knowledge, only a few related preparation methods have been reported so far [7–10]. However, the existing methods usually involve either low sphericity of particles, or undesired impurities due to incomplete conversions. In addition, special equipment and complex process control are also required in most cases, which will increase the cost and limit the applications. From this point of view, it is highly desirable to further exploit some much simpler and more efficient synthetic routs to prepare AlN granules with high sphericity and enhanced properties.

Generally, commercial AlN powders have been synthesized mainly by two methods: direct nitridation (DN) of aluminum powders ($2Al+N_2 \rightarrow 2AlN$); and carbothermal reduction–nitridation (CRN) of alumina powders ($Al_2O_3+3C+N_2 \rightarrow 2AlN+3CO$) [11]. Comparatively, the CRN process is a better choice for industry production, since it results in AlN powders with better properties such as high purity, facile sinterability and resistance against humidity [12]. To date, a lot of researchers have devoted themselves to improving the quality of the AlN powders synthesized by the CRN method [13–18]. Unfortunately, most of them just aimed at preparing fine or ultrafine AlN powders in order to meet the requirements of

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sintering AlN ceramics. However, the obtained powders with nano or submicron size are too small to be used as fillers. Up to now, the carbothermal synthesis of coarser AlN particles, particularly spherical AlN granules has received limited attention.

In our previous study [19], we reported an efficient carbothermal strategy to directly synthesize micron-sized spherical AlN granules, where the particle size and morphologies of the synthesized AlN products were synergistically controlled by the addition of additives and the use of elevated N_2 pressure in the nitridation process. In particular, additives are significant to promote the nucleation and growth of AlN in the liquid aluminates phase, resulting in the formation of smooth spherical appearance. However, the effects of additives content on the particle size and surface morphology have not been investigated. In addition, the elegant selection for the optimum synthesis parameters also should be considered.

Additives have been wildly used for sintering high-quality AlN ceramic. Among them, Y_2O_3 is one of the most commonly used additives since it can react with Al_2O_3 to form liquid-phase yttrium aluminates to promote the densification of AlN ceramics [20]. Also, it purifies the AlN lattices by forming YAP and YAM with low activity of Al_2O_3 in them, which favors for oxygen removal and thus improves the thermal conductivity of AlN ceramics [21–23]. Furthermore, the efficiency of Y_2O_3 additive on the carbothermal synthesis of AlN powders has also been demonstrated by several researchers [24–27]. It was expected that Y_2O_3 was beneficial for enhancing the reactivity of Al_2O_3 powders and thus decreasing the synthesis temperature of CRN process. However, most of them just aimed at obtaining AlN powders via a low-temperature synthesis so as to reduce the production cost. Therefore, they put the emphasis on the effects of Y_2O_3 on the nitridation rate instead of the surface morphology. To our knowledge, only Komeya et al. [26,27] ever mentioned Y_2O_3 was likely to affect the morphology of AlN granules in the CRN process, providing spherical or rod-like shapes, but it is regrettable that no further investigation was reported.

Accordingly, in this study, we made an attempt to prepare spherical AlN granules directly by the CRN process, using Y_2O_3 as the promoting additive. The effects of synthesis parameters and Y_2O_3 content on the nitridation rate, surface morphology and particle size were systematically investigated. In addition, a speculation for the growth mechanism of carbothermal synthesis of spherical AlN granules was also proposed.

2. Material and methods

The Al_2O_3 powders (Admatechs Co., Aichi, Japan; average particles size, 0.7 μm; specific surface area, 7.5 m^2/g), carbon black (Delong Carbon Co., Henan, China; average particles size, 20 nm; specific surface area, 260 m^2/g), and Y_2O_3 powders (Beijing Chemical Co., Being, China) were used as the starting materials. The content of Y_2O_3 additive varied within the range of 0–10 wt% relative to the mass of Al_2O_3, and the weight ratio of carbon black to alumina was constant at 0.5.

The raw materials, Al_2O_3, C and Y_2O_3, were firstly mixed in deionized water medium for 24 h using a planetary mill with alumina balls. After dried, ~1 g mixed powders was put into a graphite crucible, and then heat treated in a graphite furnace (High-Multi 5000, Fujidempa Kogyo Co., Tokyo, Japan) at a temperature ranging from 1400 to 1800 °C for 2 h. For each run, a constant nitrogen gas pressure within the range of 0.1–1 MPa (0.1, 0.5 and 1 MPa) was maintained in the furnace. Subsequently, residual carbon in each converted powders were removed by heat treatment in air at 650 °C for 2 h.

The phase identification of the products was investigated by X-ray diffraction (XRD, D8 Advance A25, Bruker Co., Karlsruhe, Germany) with Cu Kα radiation and a scan speed of 0.1°/s. The AlN conversion fraction was determined using a calibration curve based on XRD peak intensities of AlN–Al_2O_3 mixture. The microstructures were observed using scanning electron microscopy (SEM, Hitachi, S-3400N, Tokyo, Japan) attached with an energy dispersive X-ray microanalyzer (EDX).

3. Results and discussions

3.1. Effect of N_2 gas pressure on the nitridation rate

To investigate the effects of N_2 gas pressure on the nitridation rate, a typical mixture of Al_2O_3/C with 5 wt% Y_2O_3 was heated at 1400–1800 °C for 2 h under different N_2 gas pressures (0.1 MPa, 0.5 MPa and 1 MPa). Fig. 1 shows the AlN conversion fraction variation for products after heating under three different N_2 gas pressure as a function of synthesis temperature. As shown, at 1400 °C, AlN conversion fraction reach as high as 84% under the normal N_2 gas pressure of 0.1 MPa, but when the N_2 gas pressure increases to 0.5 MPa and 1 MPa, the fraction sharply decrease to 43% and 11%, respectively. The similar decreasing trend of AlN fraction with the N_2 gas pressure also can be observed at 1500 °C. It can be easily conclude that the N_2 gas pressure plays an important role in the CRN process, and the elevated N_2 gas pressure hampers the nitridation rate. This conclusion is in agreement with the reports of Forslund et al. [28,29], who found that an increased CO level in the system was the main reason for the

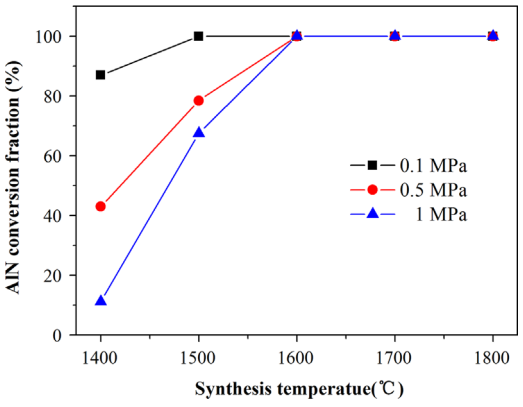

Fig. 1. Effect of N_2 gas pressure on the AlN conversion fraction after firing a typical mixture of Al_2O_3/C with 5 wt% Y_2O_3 at various temperatures for 2 h.