Original Research Paper

Preparation of aluminum nitride granules by a two-step heat treatment method

Kuan-Ting Lai [a],*, Cheng-Hung Shih [a], Chung-Te Wu [a], Min-Yu Yang [b], Chi-Shiung Hsi [b]

[a] Chemical Systems Research Division, National Chung-Shan Institute of Science and Technology, Taoyuan 325, Taiwan
[b] Department of Materials Science and Engineering, National United University, Miaoli 360, Taiwan

ABSTRACT

The sintered aluminum nitride granules were prepared in a continuous process through a two-step heat treatment at 1600 °C for 5 h and 1850 °C for 5 h using the spherical γ-alumina/phenol-resin precursor obtained by spray granulation as the starting material. In the first step of heat treatment, the alumina powders were nitrided to form porous aluminum nitride granules via a carbothermal reduction reaction and then were continuously heated in the second step of heat treatment to produce dense spherical aluminum nitride granules without using sintering aids. The obtained porous and sintered aluminum nitride granules were characterized by XRD, SEM and BET measurements and exhibited an average grain size of about 1 and 3 μm, respectively. Furthermore, the specific surface area of the obtained porous and sintered aluminum nitride granules dramatically decreased from 2.49 to 0.16 m^2/g showing that the low-porosity, dense, polycrystalline aluminum nitride granules were successfully prepared.

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1. Introduction

Polymer/ceramic composites with high thermal conductivity ceramic fillers play an important role in heat dissipations of the electronic devices such as electronic packaging. Spherical alumina and silica granules have been used as fillers to increase the thermal conductivity of polymers. The high thermal conductivity ($\kappa \approx 320$ W/mK), high electrical resistivity, low dielectric constant, and thermal expansion coefficient close to that of silicon displayed by aluminum nitride (AlN) have attracted much attention in the electronic industry [1,2]. Spherical aluminum nitride granules with a particle diameter of 10–100 μm exhibit high fluidity and high mechanical strength, which are suitable for serving as a heat-dissipating filler to replace the alumina and silica for high thermal conductivity composites to improve heat-dissipating capability of electronic packaging [3].

Two synthetic processes of AlN powders have been well-developed, that is, nitridation of aluminum powders and carbothermal reduction of alumina powders in the nitrogen atmosphere [4,5]. Aluminum nitride powders synthesized from the CRN (carbothermal reduction and nitridation) process are favorable for industry production by reason of its high purity and facile sinter-ability. Nevertheless, the CRN process proceeds under higher reaction temperature (>1700 °C) and longer reaction time due to heterogeneous mixing of carbon black and alumina powders. In addition, excess carbon black (the molar ratio of carbon black/alumina $> 4/1$) is required for full conversion of alumina to AlN in this process, which results in taking longer time to complete the decarbonization and increasing the cost [6,7].

Many efforts have been devoted to synthesize the nano or sub-micro size of AlN powders by improving the mixing of starting materials via the CRN process such as sol-gel and hydrothermal method [8–14]. Both methods can improve the CRN process with lower temperature. However, there are some drawbacks in these methods. The sol-gel method is complicated and hydrothermal method needs long reaction time. Additionally, the nano or submicro size of AlN powders are too small to be used as fillers. It is important to fabricate micro-sized spherical AlN granules as fillers to increase the filler loading and good fluidity of polymer/ceramic composites exhibiting higher thermal conductivity. However, the synthesis of AlN granules with spherical morphology and particle size within 10–100 μm is still a challenge [15–20]. To our best knowledge, there have been a few reports about preparing micro-sized spherical AlN granules. Suehiro et al. synthesized spherical AlN from spherical Al_2O_3 by the gas reduction-nitridation without mixing carbon using $NH_3-C_3H_8$ gas and some Al_2O_3 impurities residue due to incomplete reduction [16]. Chowd-

* Corresponding author.
   E-mail address: s9823824@m98.nthu.edu.tw (K.-T. Lai).

hury et al. investigated the nitridation of core-shell structured C@Al_2O_3 composites particles synthesized by encapsulation of C-nanoparticles [17]. Wang et al. synthesized the sintered spherical AlN granules produced from aqueous suspension using the surface-treated AlN powders via freezing granulation and sintering process [18]. However, the disadvantage of preparing a spherical AlN granule using AlN powder as a starting material is high production cost. Wang et al. also made an attempt to synthesize micro-sized spherical AlN granules using alumina and carbon black as raw materials and Y_2O_3 as additive by the CRN process. However, this method is difficult to obtain AlN granules larger than 10 μm as a result of the limitation of conversion rate [19].

In this study, we provide an inexpensive and promising process to produce the dense spherical aluminum nitride granules by using the γ-alumina and phenol-resin as the aluminum and carbon source, respectively. The dense spherical aluminum nitride granules with high sphericity, low porosity and an average particle size of 29 μm suitable for serving as a heat-dissipating filler were prepared via combining spray granulation and two-step heat treatment method. The homogeneously spherical γ-alumina/phenol-resin precursor was prepared by spray drying. In the first step, precursor was nitrided to produce spherical aluminum nitride granules that later to be sintered in the second step to form dense aluminum nitride granules.

2. Material and methods

Commercial γ-Al_2O_3 powders with specific surface area 130 m^2/g, spec. gravity 3.2g/cm^3 and particle size ~10 nm (Alu130, Evonik) and Novolac type of phenolic resin (Hsu I Enterprises Co., Ltd., Tainan, Taiwan) were used as the raw materials. Phenolic resin was mixed with γ-Al_2O_3 with weight ratio of 0.7:1, and the mixture was blended with ethanol and became homogeneously milky slurry. The slurry was granulated (spray dryer CL-8, Ohkawara Kakohki Co., Ltd., Japan) in a 110 °C nitrogen atmosphere with an atomizer at a rotation speed of 10,000 rpm to form spherical γ-alumina/phenol-resin precursor with yellow-white color. The precursor was placed in a BN crucible. The carbonization and nitriding of the precursor was carried out continuously in a graphite furnace under nitrogen atmosphere. The spherical γ-alumina/phenol-resin precursor was converted to the intermediate of spherical γ-alumina/carbon composite at 700 °C via carbonization and then nitridation of the spherical γ-alumina/carbon composite at temperature of 1600 °C for 5 h in N_2 atmosphere to yield spherical aluminum nitride granules. The spherical aluminum nitride granules were continuously heat-treated at temperature of 1850 °C for 5 h in N_2 to produce dense spherical aluminum nitride granules. Subsequently, residual carbon of obtained sintered granules was removed by heat treatment at 650 °C in air for 5 h. The crystalline phases of the raw powders, γ-alumina/phenol-resin precursor and aluminum nitride granules were characterized by an X-ray diffractometer (XRD; Rigaku-Ultima, Japan) with Cu Kα radiation. The microstructures of powders were observed by Field Emission Scanning Electron Microscopy (FESEM, Nova NanoSEM 450, FEI, USA) equipped with an Energy Dispersive X-Ray Spectrometer (EDS) system (X-MAX, OXFORD, UK). Infrared spectra of the raw powders and the γ-alumina/phenol-resin precursor were recorded on a spectrophotometer (Perkin-Elmer model Spectrum One B) with KBr tablets. The pyrolysis weight loss of the γ-alumina/phenol-resin precursor in N_2 was monitored by thermogravimetric analyzer (TGA 7, Perkin Elmer, USA). The specific surface area of powders were measured using BET surface analyzer (ASAP 2010, Micromeritics, USA). The particle size distributions of the sintered AlN granules were measured by a laser diffraction particle size analyzer (LS 13 320, Beckman Coulter, USA). Analyses of carbon,

hydrogen, and nitrogen were obtained with a CHN analyzer (Vario EL III, elementar Analysensysteme GmbH, Germany).

3. Results and discussion

3.1. Characterization of the precursor

The γ-alumina/phenol-resin/ethanol slurry was spray to dry, leading to γ-alumina/phenol-resin precursor. Fig. 1a presents SEM micrograph of spraying drying γ-alumina/phenol-resin precursor, which shows spherical morphology with the granular size of 20–40 μm. The EDS elemental mapping images show that the uniform distribution of Al, O, and C elements in the γ-alumina/phenol-resin precursor (Fig. 1b–e). The uniform distribution of Al, O and C implies that γ-alumina is very well-mixed with the phenolic resin. The specific surface area of the spherical γ-alumina/phenol-resin precursor evaluated by gas adsorption technique was 64 m^2/g, which was about half surface area of the γ-alumina (130 m^2/g). The spherical precursors were agglomerate of γ-alumina/phenol-resin with porous microstructure. The XRD pattern of γ-alumina/phenol-resin precursor is presented in Fig. 2. Gamma-Alumina (JCPDS No. 29-0063) was the only phase detected from the diffraction pattern of γ-alumina/phenol-resin precursor, which suggests the precursor consists of crystalline γ-Al_2O_3 and amorphous phase derived from phenolic resin. Phenolic resin was dissolved in ethanol and further covered on the surface of the γ-alumina powder forming amorphous layers during spray drying.

Fig. 3 exhibits the infrared spectra (KBr) of the γ-alumina/phenol-resin precursor obtained by spray granulation and raw materials derived from commercial phenolic resin and γ-alumina. The IR spectrum of the γ-alumina/phenol-resin precursor displays the characteristic peaks of Novolac type of phenolic resin at 3434, 3018, 2917, 1613, 1510, 1439, and 1364 cm^{-1}. The absorption bands at 3434 and 1364 cm^{-1} correspond to the O—H stretching and O—H in plane bending from the phenol. The IR bands at 3018 and 2917 cm^{-1} correspond to the aromatic C—H stretching and the aliphatic C—H stretching, respectively. In addition, the IR peaks at 1613 and 1510 cm^{-1} are assigned to C=C stretching vibration in aromatic rings and the peak at 1439 cm^{-1} is assigned to C—H bending vibration of methylene bridge. According to IR spectra in Fig. 3, the phenolic resin does not decompose and maintain its structure after spray drying. Further confirmation presented the IR absorption bands at 819, 755, 610, and 575 cm^{-1}, which were assigned to the AlO_4 and AlO_6 stretching in γ-Al_2O_3 [21,22]. The IR spectrum of the γ-alumina/phenol-resin precursor in Fig. 3(c) discloses that the superimposition of the Infrared spectra of phenolic resin and γ-alumina, indicating that γ-alumina/phenol-resin precursor obtained from spray drying is a physical mixture without interaction between γ-alumina and phenol-resin.

Fig. 4 shows the thermogravimetry (TG) and differential thermogravimetry (DTG) measuring results of the γ-alumina/phenol-resin precursor in nitrogen atmosphere. There were four weight loss behaviors observed from the differential curve; 40, 100, 270, and 510 °C. The weight loss of 3.3 wt% in a range of 25–150 °C was attributed to the evaporation of the ethanol and water. The weight loss of 11.3 wt% in a range of 150–370 °C was caused by the decomposition of methylene group from phenolic resin to produce phenol and cresol. Also, the condensation reaction between methylene group and hydroxyl group yielded water. Further weight loss of 9.1 wt% in a range of 370–700 °C was attributed to the decomposition and carbonization of phenolic resin and release of H_2、CO 、CH_4 and H_2O [23].