Materials Research Bulletin 61 (2015) 152–158

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Synthesis of aluminum nitride powders from a plasma-assisted ball milled precursor through carbothermal reaction

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ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form 30 September 2014
Accepted 4 October 2014
Available online 8 October 2014

Keywords:
Aluminum nitride
Plasma
High energy ball milling
Carbothermal reaction
Alumina

ABSTRACT

In this paper, aluminum nitride (AlN) powers have been produced with a novel and high efficiency method by thermal annealing at 1100–1600 °C of alumina (Al_2O_3) powders which were previously ball milled for various time up to 40 h with and without the assistant of dielectric barrier discharge plasma (DBDP). The ball milled Al_2O_3 powders with DBDP and without DBDP and the corresponding synthesized AlN powers are characterized by X-ray diffraction, scanning electron microscope, and transmission electron microscopy. From the characteristics of the ball milled Al_2O_3 powders with DBDP and without DBDP, it can be seen that the ball milled Al_2O_3 powders with DBDP have small spherical structure morphology with very fine particles size and high specific surface area, which result in a higher chemical efficiency and a higher AlN conversion rate at lower thermal temperature. Meanwhile, the synthesized AlN powders can be known as hexagonal AlN with fine crystal morphology and irregular lump-like structure, and have uniform distribution with the average particle size of about between 500 nm and 1000 nm. This provides an important method for fabricating ultra fine powders and synthesizing nitrogen compounds.

1. Introduction

In recent years, AlN as an advanced materials with a very wide band gap of 6.2 eV, high thermal conductivity and melting point, low and Si-compatible coefficient of thermal expansion, etc [1–3], has been applied in light-emitting diodes, surface acoustic wave sensors, reinforcement of functional composites, dielectric layers in optical storage media, etc [4,5]. Generally, there are two primary methods to synthesize AlN powders commercially: (i) direct nitridation of Al with N_2 or NH_3; and (ii) carbon thermal reduction of Al_2O_3 with carbon black in the presence of N_2. Compared with the direct nitridation method, the carbon thermal reduction method has some unique advantages such as, higher purity, better sinterability, and more stability against humidity [6,7]. Before the carbon thermal reduction of Al_2O_3, the Al_2O_3 powders would be refined by the high energy ball milling, which is a kind of simple and effective technology to reduce the thermal temperature and soaking time, and attracts many researches' attentions in recent years [8–11]. However, all these depend on the milling systems and milling conditions, and during ball milling process, long milling time is required to refine the powder, microstructure and to form compound phases, which result in the low efficiency of materials synthesis and induces contamination from milling media and atmosphere [10–13]. Therefore, they are unsatisfactory for practical engineering applications.

Due to the long milling time and low production efficiency, there are many approaches that are proposed to increase the milling efficiency by introducing other external fields, such as magnetic field, electric field [10]. Dielectric barrier discharge plasma (DBDP), as one of non-thermal plasmas, is an important method to improve the efficiency of the AlN synthesis, which exhibits many unique advantages, such as high electron energy, high electron density, and high concentration of active species of OH, N, O_3, N_2 (C), N_2^+ (B), N_2 (A) [14–17], which can effectively refine Al_2O_3 powders during the high-energy ball milling process to produce the smaller crystallite size of Al_2O_3 powders with larger lattice distortion. Zhu et al. reported that the pure Al, Fe and W metals powders were treated by the milling method combining ball milling and DBDP [11]. Zhu et al. developed a new synthesizing method of WC–Co nano-composite powder by DBDP milling and

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http://dx.doi.org/10.1016/j.materresbull.2014.10.015

carburization, starting from the W, Co, and graphite powder mixture [18]. Huang et al. reported a simple, single-step, catalyst-free, plasma-assisted growth of dense patterns of size-uniform single-crystalline AlN nanorods at a low substrate temperature without any catalyst or hazardous precursors [19]. In this paper, a high efficiency mechanical alloying method with the combination of high-energy ball milling and DBDP has been presented. The pure Al_2O_3 powders are ball milled with DBDP and without DBDP in N_2 at atmospheric pressure. The ball milled Al_2O_3 powders with and without DBDP and the corresponding synthesizing AlN powers are characterized by X-ray diffraction, scanning electron microscope, and transmission electron microscopy.

2. Experimental details

In this experiment, the ball mill is a vibratory type and the milling cylinder vibrated with a double amplitude of 10 mm and a frequency of 25 Hz. The experimental setup of ball mill is illustrated schematically in Fig. 1. In the milling process, the stainless steel balls are used as milling medium, the powders are sealed in a stainless steel mill vial with a hard metal lining and are milled with DBDP and without DBDP in a pure N_2 at atmospheric pressure. When a sine alternating current power is supplied to the electrode of the mill vial, the DBDP is produced on the surface of PTFE, which covered the electrode bar inside mill vial. The applied voltage and discharge current was measured with a 1:1000 high-voltage probe (Tektronix P6015A 1000 × 3.0 pF 100 MΩ) and a current probe (Tektronix TCP312 Bandwidth 100 MHz). Both the waveforms were recorded and displayed in an oscilloscope (Tektronix TDS5054B 500 MHz). The raw materials used in this experiment are commercial Al_2O_3 powders, the purity of Al_2O_3 powders were 99.99%. The weight ratio of ball to powder is 30:1 and the speed of the drive shaft is 1400 rpm. The cylinder of mill is cooled using circulation of water during milling. After predetermined milling time, the carbothermal reaction of the ball milled Al_2O_3 powders mixed with excess carbon is performed in a vertical graphite furnace. The precursor mixture is held in a graphite crucible. Before heating, the furnace was vacuumed and then flushed with nitrogen repeatedly to eliminate oxygen before the reaction. The precursor mixture was in a flowing N_2 (1 L/min) at various thermal temperatures in the range of 1100–1600 °C for 2 h. Finally, the superfluous carbon was removed in a muffle furnace. The ball milled Al_2O_3 powders and the synthesizing AlN powders are characterized by the X-ray diffraction (XRD Bruker D8 Focus Germany) with Cu K radiation (λ = 0.15406 nm) in a continuous scan mode from 20° to 80° at a scan rate of 7°/min. The particle morphology is determined using field scanning electron microscope (SEM Hitachi model S-4800 Chiyoda Tokyo Japan), and transmission electron microscopy (TEM Tecnai G220 S-Twin JEM-100CX USA) operated at 200 kV with line resolution of 0.144 nm and point resolution of 0.248 nm is used to thoroughly characterize the microstructure.

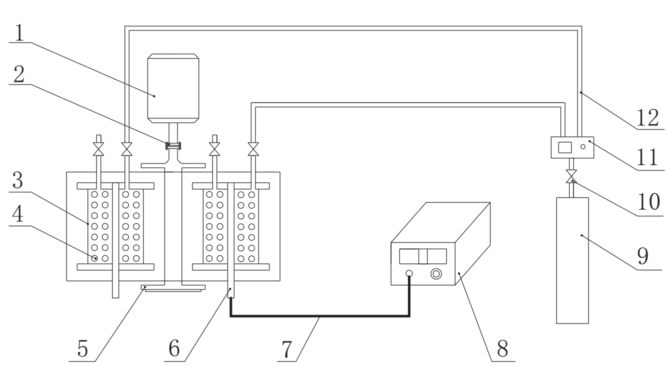

Fig. 1. Schematic illustration of the structure and principle of vibratory mill assisted by DBDP.

3. Result and discussion

A filamentary DBDP can be acquired in N_2 at atmospheric pressure and the discharge image of the DBDP with an exposure time of 500 ms is shown in Fig. 2(a) at 40 kV and 8 kHz. The typical waveforms of applied voltage and discharge current are recorded in Fig. 2(b). To understand the physical mechanisms of the actual discharge process, the displacement current should be subtracted from the total current to obtain the discharge current. The displacement current is measured without discharge occurring. The waveform of the discharge developed at the surface of the PTFE consists of current pulses with a half-width of tens of nanoseconds, which is the typical characteristic of filamentary DBDP [20]. The current directions (positive or negative) and magnitudes of the current pulses are different in the voltage-rising and voltage-falling half cycles. The intensity of pulsed currents is typically in the range of 0–15 A. The discharge current peaks are asymmetric for the positive half cycle and the negative half cycle, which maybe comes from the asymmetric configurations of high voltage and grounded electrodes. In this dielectric barrier discharge (DBD), the two electrodes have been bridged by the plasma with high electric conductivity, electrons and ions behave differently in the velocity and the movement direction. Therefore, electric charges move toward the two electrode and accumulate on the dielectric layer. The charges accumulated on the dielectric layer play an important role in DBD [21].

Fig. 3 shows the XRD patterns of the ball milled Al_2O_3 powders with DBDP and without DBDP at different milling times. It can be clearly seen that there is only Al_2O_3 peaks in the XRD patterns and no other phase can be observed. However, the intensity and FWMH of diffraction peaks of ball milled Al_2O_3 powders become much lower and much broader with increase of the milling time from 0 h to 40 h, suggesting that the ball milling resulted in grain refining Al_2O_3 powders. Therefore, the ball milling process strongly influenced the grain size of the Al_2O_3 powders, although no

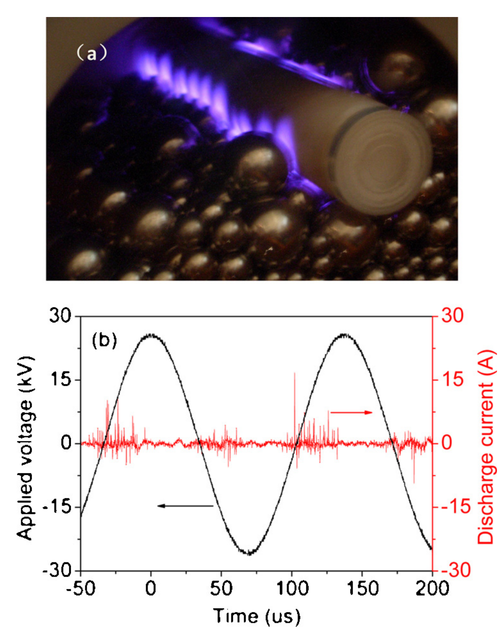

Fig. 2. (a) The discharge image of DBDP with an exposure time of 500 ms at applied voltage of 40 kV and driving frequency of 8 kHz. (b) The corresponding typical waveforms of applied voltage and discharge current of DBDP.