Rapid preparation of aluminum nitride powders by using microwave plasma

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Abstract

Traditionally, syntheses of aluminum nitride (AlN) powders by thermal nitridation approaches are carried out at high temperature for several hours. In this study, high-density hexagonal AlN powders have been synthesized from aluminum powders at a relatively low temperature and short reaction time by the microwave plasma-induced nitridation approach at atmospheric-pressure. The effects of reaction time (15–45 min), temperature (660–850 °C), content of NH4Cl (0–50%) in Al powders, applied power (800–1200 W), and inlet hydrogen concentration (0–1%) on the characteristics of the synthesized AlN powders are discussed. The results show that the active N-containing species produced from the NH4Cl and N2 accelerated the nitridation process, the addition of NH4Cl inhibited the aggregation of powders, and inlet hydrogen reduced the residual oxygen, resulting in wurtzite AlN powders with fine particles and nanowires within porous microstructures after a relatively short time (15 min), at low temperature (800 °C), and with the content of NH4Cl = 50%, and H2 = 1%.

1. Introduction

Aluminum nitride (AlN) has been acknowledged as an important ceramic material for use as packaging materials and electrical substrates [1]. AlN is attractive due to its high thermal conductivity, low dielectric constant, low dielectric loss, high electrical resistivity, good mechanical strength, non-toxicity, low thermal expansion coefficient (4 x 10^-6 K^-1) that is similar to silicon, and high band gap (6.2 eV) [2].

There are several thermal methods for producing AlN powders, such as gas phase synthesis by reacting AlCl3 with NH3 and N2 [3], solvent thermal synthesis by reacting AlCl3 with Na3N in solvent (xylene) [4,5], self-propagating high-temperature synthesis by igniting the Al and NH4X (X = F, Cl, Br) compact in N2 [6], direct nitridation of Al/LiOH powders [7], and carbothermal reduction of Al2O3 [8,9]. However, the traditional thermal synthesis methods for producing AlN powders usually require a long reaction time (over several hours), high temperature (>1000 °C), or post-calcination treatment because of the slow N2 diffusion rate or reaction rate.

The production of AlN powders has also been proposed via various plasma processes, such as arc plasma [10–16], DC pulsed wire discharge [11,17], and radio frequency (RF) plasma [18,19]. These have some advantages, such as short reaction time, high conversion rate, and high energy efficiency for the production of AlN powders. Moreover, in the plasma environment, active and energetic species, such as excited nitrogen molecules or atoms, and nitrogen ions, could rapidly react with the Al atoms that cover the powder’s surface to form AlN films, preventing the coalescence of Al powders. By using a microwave plasma, the advantage is without the problem of electrode deterioration because the microwave plasma belongs to non-electrode discharge. Moreover, the microwave plasma with a high plasma density can be operated at a relative low temperature (<1000 °C) than the other plasma approaches for producing AlN powders, such as at 1700–2100 °C by using transferred arc plasmas [10,11].

To achieve AlN with high thermal conductivity, impurities such as excess carbon and residual oxygen in the AlN structure should to be removed in all the synthesis methods. This removal is not easily controlled by the conventional thermal approaches, due to the slow reaction rate. However, they can be rapidly removed under plasma processes.

Therefore, in this study, a N2 atmospheric-pressure microwave plasma was used to synthesize AlN powders from the Al/NH4Cl in order to avoid the coalescence of Al powders at a short reaction time and relatively low temperature. In addition, H2 was added in the N2 gas to remove residual oxygen.

2. Experiment

The continuous microwave plasma system (Fig. 1) was assembled with a commercially available magnetron (National Electronics YJ-1600, 2.45 GHz) with a maximum stationary power of 5 kW in continuous-wave mode. The microwave passed through a circulator and a waveguide with a three stub tuner, then reached the cavity with an arc to ignite the plasma. A quartz tube intersected the waveguide (ASTEX WR340), while the resonator was placed perpendicular to it.

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The flow rate of gas was regulated by a mass flow controller. The gases supplied in the axial gas were N\textsubscript{2} and H\textsubscript{2} with flow rates of 3 slm (standard liter min\textsuperscript{-1}) and 0–120 sccm (standard cm\textsuperscript{3} min\textsuperscript{-1}), respectively. The flow rate of the swirl N\textsubscript{2} gas was 9 slm. Before the reaction, the chamber was flushed by high-purity N\textsubscript{2} to remove the residual oxygen and steam. Various contents of NH\textsubscript{4}Cl (0–50%) were added to the aluminum powders with particles sizes of 1–3.8 \mu m and pressed into ingots with a 13 mm of diameter to be used as the feedstock. Then the ingots were placed into the sample holder which is a stainless steel container. Without additional temperature supply was used in this study, and the Al/NH\textsubscript{4}Cl ingots in the sample holder were located at the position of 800 °C in the discharge zone. The effects of the operating parameters, including reaction temperature (660–850 °C), content of NH\textsubscript{4}Cl (0–50%), inlet hydrogen concentration (0–1%), reaction time (15–45 min), and applied power (800–1200 W) on the characteristics of synthesized aluminum nitride powders were examined, and these are discussed later in this paper.

The crystal structure of the aluminum nitride powders was determined using an X-ray diffraction spectrometer (XRD, Rigaku RINT-2000) with CuK\textsubscript{α} radiation that scanned from 15° to 85° (2θ). The contents of O and C elements were analyzed by elemental analyzers (HORIBA EMGA-620 W). The powders were also examined using a scanning electron microscope (SEM, Hitachi S3000N) to determine their sizes and morphologies. The thermal characteristics of the powders were determined with a thermogravimetric analyzer (TGA, SDTQ600) by heating raw Al powders (purity > 99.5%, 1–3.8 \mu m) or commercial AlN powders (purity > 98.5%, 8–12 \mu m) from room temperature to 1200 °C at a heating rate of 10 °C/min in nitrogen gas (for Al) or air (for AlN) with a flow rate of 100 ml/min. The microstructures of the AlN nanowires were studied by high-resolution transmission electron microscopy (HRTEM, JEOL TEM-3010, 200 kV). The surface analyses and the determination of the chemical composition were performed by X-ray photoelectron spectroscopy (XPS, Fison ESCA210). The function groups of the powders mixed in a KBr disk were scanned from 1500 to 4000 cm\textsuperscript{-1}. The dielectric property was measured by an LCR meter (Agilent 4294A). The Raman spectroscopy was measured using an excitation wavelength of 488 nm (Argon ion laser). An optical emission spectrometer (OES, Ocean Optics, HR 4000GC) was also used to measure the active species involved in the formation of AlN in the discharge zone.

3. Results and discussion

3.1. Thermal analyses of raw Al and commercial AlN powders

The morphology of the raw Al powders that were used as the feedstock for synthesizing AlN powders was nearly spherical, with the particle sizes being in the range of 1–3.8 \mu m. Moreover, the element analysis data indicated that amounts of the impurities, including O, C, and Fe elements were 2.4%, 0.1%, and 0.06 ppm, respectively.

The chemical equilibrium compositions calculated in Al–N\textsubscript{2} system indicated a complete conversion of gaseous Al and the formation of thermodynamically stable h-AlN being favorable at about 2000–2650 K [11,20]. Such a high temperature can be achieved by using a thermal plasma, which needs more power to be applied as well as safer construction of the experimental equipment. Hence, at a moderate temperature, for example, above the melting point of bulk aluminum (660 °C), this can be easily carried out in a plasma reactor by melting the aluminum from the surface, which then reacts with the active N-containing species to form AlN. In order to set the range of synthesis temperature in the microwave discharge zone, thermal analyses of raw Al powders in N\textsubscript{2} and commercial AlN powders in air were then carried out (Fig. 2).

The results show that there was no variation of weight below 800 °C (Fig. 2A), while the weight of powders increased significantly above 800 °C due to the formation of AlN. In addition, Fig. 2B shows that the weight of the commercial AlN powders fell a little below 850 °C, while the weight increased significantly above 850 °C due to the formation of Al\textsubscript{2}O\textsubscript{3} [21]. Hence, in this study, the reaction temperature of the sample was set in the range of 660–850 °C and in the discharge zone.

3.2. Effects of reaction temperature on the synthesized AlN powders

The nitridation of Al to AlN is usually carried out at a high temperature of 1150–1500 °C. In this work, AlN powders were synthesized in the microwave plasma for 45 min at various temperatures (660–800 °C) and with an applied power of 1200 W without the addition of NH\textsubscript{4}Cl, the XRD patterns show that the conversion of Al into AlN increased along with the reaction temperature from 660 to 800 °C (Fig. 3). The reaction temperature greatly promoted the AlN formation. However, even at 800 °C, it is difficult for Al to convert completely into AlN. Moreover, only a crystallite size of 35 nm, as calculated by the Debye–Scherrer equation, was found in AlN powders. This is because when the temperature is above the melting point of Al (660 °C), Al melts and the initial oxide film on the surface of the powders is broken by the significant tensile stress arising due to increased volume of the particles, then the liquid Al agglomerates to larger particles. Hence, when AlN was formed on the shell, a low diffusion rate for the N-containing species passing through the hard AlN layer and the initial oxide film would be found, resulting in slowing down the nitridation rate [22].

The morphology and shape of the Al powders (Fig. 4A) are nearly spherical, with particle sizes in the range of 1–3.8 \mu m. At 800 °C, agglomerated AlN/Al powders with a larger particle sizes of 3–6 \mu m (Fig. 4B) were produced, because Al powders were melted, resulting in the liquid Al forming larger clusters and the agglomeration of AlN particles.

3.3. Effects of NH\textsubscript{4}Cl on the characteristics of AlN powders

The molten Al powders agglomerated into large clusters, resulting in the inhibition of N\textsubscript{2} gas diffusing into the unreacted Al core during the nitridation process. Therefore, different contents of NH\textsubscript{4}Cl powders were dispersed in the Al powders and were compressed as ingots at high-pressure.

Fig. 5 shows the XRD patterns of the as-synthesized AlN powders from as-prepared ingots reacting for 45 min at 800 °C and 1200 W. The results show that the conversion of Al into AlN rose significantly from 70.8% to about 100% as the NH\textsubscript{4}Cl content increased from 0 to 50 wt.\%.

The results show that by rapidly sublimating and decomposing NH\textsubscript{4}Cl within the ingot, numerous porous structures (Fig. 6A) were formed, and commercial AlN powders were produced. This structure can prevent the aggregation or coalescence of molten Al by means of rapidly dissociating NH\textsubscript{4}Cl and carrier gas (N\textsubscript{2}) to produce energetic N- and Cl-containing species that react with Al on the surface to further form a hard, thin film of nitrides. Subsequently, N-containing species can thus diffuse more easily into the Al particles and promote the nitridation rate, resulting in a greater AlN yield [22,23].

In addition, the sublimation of NH\textsubscript{4}Cl occurs around 400 °C, and this then decomposed to HCl and NH\textsubscript{3}. HCl can further react with...
In this study, high purity AlN powders were synthesized using an atmospheric-pressure microwave plasma at a short reaction time of 15 min and a relatively low temperature of 800 °C, with conventional thermal methods usually requiring a long reaction time (over several hours) and high temperature (>1000 °C) due to the slow diffusion rate or reaction rate between Al metal and N2 gas.

The results show that while operating at a higher reaction temperature the conversion of Al, the Al powders agglomerate due to the molten Al, making the diffusion of N-containing species into the core of the aggregated particles more difficult, even a reaction time of 45 min. When NH4Cl powders were mixed with Al powders and pressed into a compact ingot, the yield of AlN rose significantly with increasing NH4Cl content, and reached almost 100% at the NH4Cl content of 50%, 800 °C, 1200 W, H2 = 1% for only reacting 15 min. This is because the sublimation and decomposition of NH4Cl rapidly produces AlN film to form porous microstructures, avoid the coalescence of molten Al, and synthesize fine particles and nanowires. In addition, NH4Cl and inlet H2 in the discharge zone generate more active N-containing species, not only enhancing the nitridation rate and shortening the synthesis time (15 min), but also removing and reducing the residual O atoms in the structure, especially at a higher applied power (1200 W) by generating a higher electron density with a higher concentration of N-containing compounds.

Acknowledgments

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