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A thermochemical pathway for controlled synthesis of AlN nanoparticles in non-isothermal conditions

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ABSTRACT

The synthesis of AlN nanoparticles in non-isothermal high-temperature conditions was developed. The process involved Al_2O_3–Mg–NH_4Cl mixtures preparation and combustion in nitrogen atmosphere. Temperature profiles in the combustion waves were recorded by thermocouples, and the values of combustion temperature and wave velocity were determined from the recorded profiles. The existence of two independed combustion regimes with maximum temperatures of about 850 °C and 1400–1600 °C were revealed based on concentrations of NH_4Cl. AlN nanocrystals were obtained and investigated by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, and Brunauer–Emmett–Teller surface area. AlN nanocrystals prepared under non-isothermal combustion process were comprised well distributed multi-faceted particles with an average size of 50–200 nm. The chemical reactions in the combustion wave were discussed and a possible thermochemical pathway for the synthesis of AlN nanoparticles was proposed.

1. Introduction

The industrial use of inorganic nanoparticles (oxides, carbides, nitrides, etc.) in a wide variety of applications has rapidly expanded in the last decade. Ubiquitous applications have increased the interest in the development of new inexpensive production technologies. Among inorganic nanoparticles, metal nitrides (AlN, BN, Si_3N_4, TiN, etc.) have drawn significant attention owing to their attractive structural, optical, electronic, and magnetic properties [1–3]. During the past ten years, there has been considerable technological interest in AlN because it possesses an excellent combination of material properties for electronic substrate applications, including high thermal conductivity (typically 170–200 W/m-K), an excellent thermal expansion match to silicon, good mechanical strength, and nontoxicity (when compared to BeO as a competing material) [4]. Moreover, AlN is a wide band gap semiconductor (6.05 eV) and currently there is much research into developing light-emitting diodes using the alloy of aluminum gallium nitride [5,6].

There are two basic isothermal processes to prepare AlN powders commercially: direct nitridation [7,8], and carbothermal reduction [9–11]. In the direct nitridation method, Al metal powder is reacted with N_2 or NH_3 at high temperatures to produce AlN powders. In the carbothermal method the precursor Al_2O_3 or Al $(OH)_3$) powders are reduced by C in N_2 flow at high temperatures. Both processes are a batch type and occur at 1400–1800 °C temperature intervals. The direct nitridation and carbothermal reduction methods usually yield AlN powders with particle diameters between 0.5 and 3.0 μm [12,13].

Recently carbothermal reduction method was modified to produce AlN nanoparticles [14–16]. In modified carbothermal process aluminum nitrate ($Al(NO_3)_3$), urea ($CO(NH_2)_2$, glucose ($C_6H_{12}O_6$) and NH_4NO_3 were used as a raw materials to prepare AlN nanopowders [14,15]. The raw materials were dissolved in water, which was then dried in an air oven, and then heated in the furnace at 400–450 °C to generate a foamy mixture of Al_2O_3 + C composition. Then the as-prepared foamy mixture was heat-treated in N_2 flow at 1200–1500 °C to produce AlN nanopartiles. Jung et al. [16] reported the modified carbothermal reduction process in which aluminum nitride (AlN) particles and whiskers were synthesized by heat treatment of aluminum gluterate complex under nitrogen flow in the temperature range 1200–1500 °C and then burning out the residual carbon. Novel synthesis methods such as pulsed laser

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ablation [17–20], electrochemical methods [21], low-temperature nitridation of metallic aluminum [22], the use of organometallic precursors, and vapor synthesis have been also reported for the preparation of nanocrystalline AlN [23–27].

The synthesis of AlN powders under non-isothermal high-temperature conditions were reported in [28–36]. Direct nitridation of aluminum powder in a combustion regime was conducted under nitrogen pressure using additives such as AlN, NH_4Cl and NaN_3. The additives were used to increase the N_2 concentration in the combustion wave to enhance the nitridation process of Al particles. Various efforts to obtain phase-pure AlN fine powders under non-isothermal combustion process have been done, but a sufficient solution has not been yet obtained.

The present work aims to overcome the limitations of the previously reported combustion technique to ultrafine AlN powder synthesis. Towards this end, the mixtures of $Al_2O_3 + (3.5 + 0.5\,k)$ $Mg + kNH_4Cl$ (k is the mole number of NH_4Cl) were utilized in the combustion experiment. The temperature change in the combustion wave was monitored by thermocouples and a thermochemical pathway for controlled synthesis of AlN nanoparticles is proposed.

2. Experimental

α-Al_2O_3 (purity: 99.9%, particle size: 0.2–0.3 μm, Terio Corporation, China) and Mg (purity: 99% purity, particle size: 50–200 μm, Samchun Chemicals and Metals Co., Ltd. Korea) were used as precursor materials for the synthesis of AlN nanoparticles. NH_4Cl (purity: 99%, Samchun Chemicals and Metals Co., Ltd. Korea) was used as a solid nitrogen source to increase the concentration of nitrogen inside the reaction pellet and to control the combustion temperature. For this purpose, $Al_2O_3 + (3.5 + 0.5k)Mg + kNH_4Cl$ (where k is the mole number of NH_4Cl) composition was used in the combustion experiment; k was added to the main mixture in the range 2–6 mol.

In a typical experiment, ~80 g of the reaction sample was prepared by mixing the raw materials in an ceramic mortar for 30 min, and soft compacting by hand into a paper cup (diameter: 4.0 cm, height: 8–9 cm). During compaction, two Λ-shaped tungsten-rhenium thermocouples (WR-26/WR-5), 100 μm in diameter, were placed inside the sample near the center. Individual thermocouples were coated with a thin layer of Al_2O_3 (~5–10 μm) to increase their resistance to oxidation and to avoid possible interactions between the thermocouples and the powder bed at elevated temperatures. Approximately 2–3 g of Ti powder was placed on top of the reaction sample as an ignition agent, because it freely burn in nitrogen at 800 °C and above. The cup, containing the reaction mixture and thermocouples, was placed under a nickel/chromium coil in a combustion chamber (the details of experimental setup was reported in our earlier work [37]). The chamber was filled with 2.5 MPa of nitrogen to maintain a stable combustion environment for reduction–nitridation process. Local ignition of the reaction sample was achieved within 1–2 s using a nickel-chromium filament electrically heated to 900–1000 °C. A computer-assisted data logger (GL100A, Graphtec Co., Japan) continuously recorded the temperature–time history of the process at a rate of 10 Hz.

After the combustion was complete, the burnt sample was cooled to room temperature. The surface layer (1–2 mm) was mechanically removed, and the main sample was transferred to a 500-mL beaker for further purification. The beaker was then placed on a combined magnetic stirrer hot plate equipped with a stir bar. The leaching was proceeded under continuous agitation at the temperature 50 °C for 10 min. After 10 min, the beaker was removed from the hot plate and allowed to cool at ambient temperature. The white suspension was vacuum-filtered and washed several times by water and ethanol. Then, the sediment was oven-dried for 5 h at 50 °C and stored in container prior to further analysis.

Thermochemical calculations of the equilibrium concentrations of all reaction species were performed using commercially available software package, "THERMO" which is specially designed for combustion processes [38]. The amount of each phase was calculated as a function of temperature based on the minimization of the Gibbs free energy. "THERMO" does not account for the kinetics of the chemical reactions. Therefore, it can only approximate the actual system. However, the results enable the rapid screening of the appropriate range of reaction conditions that should be studied experimentally, thereby minimizing expensive trial-and-error chemistry.

A thermogravimetric analyzer (TGA/DSC-1, Mettler Toledo, USA) was used to determine the ignition temperature of the initial mixture and the heat flow rate. The crystal structures and morphologies of the final powders were characterized using an X-ray diffractometer with Cu Kα radiation (Siemens D5000, Germany), a field-emission scanning electron microscope (JEOL JSM-6700F) and a transmission electron microscopy (TEM, JEOL JEM-1400, Japan). The specific surface area of the samples was determined using a SA-9600 Brunauer–Emmett–Teller (BET) surface area analyzer (Horiba, USA). The Oxygen/Nitrogen Analyzer ON-900 (Eltra GmbH, Germany) was used to determine O and N content in AlN samples via inert gas fusion.

3. Results and discussion

3.1. Thermochemical analysis

The adiabatic combustion temperature (T_{ad}) and equilibrium concentration of the reaction species for $Al_2O_3 + (3.5 + 0.5k)Mg + kNH_4Cl + N_2$ mixtures with k 2–6 mol are shown in Fig. 1. The starting temperature and reaction pressure were 25 °C and 2.5 MPa, respectively. Note that the total amount of Mg was also increased in accordance with NH_4Cl concentration (0.5 mol Mg for each mol NH_4Cl) in order to convert Cl^- ions into $MgCl_2$ phase. As shown in Fig. 1 a linear decrease of the temperature from 1410 (k = 2) to 836 °C (k = 6) occurred upon increasing the NH_4Cl concentration. The equilibrium solid phases predicted by the thermochemical analysis are AlN, MgO and $MgCl_2$; however, a small amount of Mg and Mg_3N_2 (k = 2–6) is also predicted. The gas phase is mainly consisted of H_2 and N_2 components. Notably, the average decrease rate of the temperature estimated from the slope was 150–200 °C per mol of NH_4Cl. Such a drastic temperature

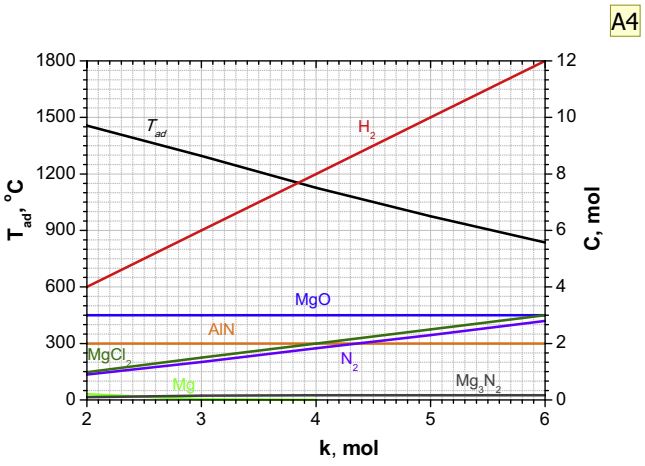

Fig. 1. Thermochemical analysis of equilibrium compositions (C) and adiabatic combustion temperature (T_{ad}) for $Al_2O_3 + (3.5 + 0.5k)Mg + kNH_4Cl + N_2$.