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Fabrication of AlN particles and whiskers via salt-assisted combustion synthesis

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Abstract

High-quality AlN ceramic particles and whiskers were synthesized via salt-assisted combustion with the addition of AlN and NaCl, KCl, or $MgCl_2$ to the raw Al powders. The experiments were carried out at nitrogen pressures between 0.2 and 1.0 MPa. The results show that 20–30 mass% salt is required to achieve complete nitridation of Al. The sensible and latent heats of these salts afford effective heat absorption during the reaction, which greatly reduces the amount of diluent AlN required compared with the conventional combustion synthesis of AlN. In addition, AlN particles are obtained when NaCl or KCl is added, whereas irregular whiskers are obtained with $MgCl_2$.

Keywords: Combustion synthesis; AlN; Salt-assisted; Microstructure

1. Introduction

Aluminum nitride (AlN) is considered a promising advanced ceramic owing to its excellent physicochemical properties such as a high thermal conductivity, high electrical resistance, low dielectric constant, low thermal expansion coefficient, and good corrosion resistance. For these reasons, AlN is widely used in electronic devices as a substrate material for semiconductor chips [1–3]. Commercially, AlN powders are synthesized using one of two routes: the direct nitridation of Al powders in a N_2 atmosphere, or the carbothermal reduction nitridation (CRN) of Al_2O_3 with carbon black [4,5]. For direct nitridation, high reaction temperatures and long holding times lead to agglomeration, and the subsequent grinding that is required to obtain fine AlN powders introduces impurities. CRN on the other hand affords fine, high-quality AlN powders but the procedure is expensive, because of the high cost of the raw materials (high purity Al_2O_3 and carbon black) and the additional process required to remove the unreacted carbon.

Combustion synthesis (CS), established by Merzhanov et al., is an inexpensive method for the production of various ceramic materials [6,7]. This process utilizes the heat generated during a strongly exothermic reaction to sustain a self-propagation regime. This method is advantageous because the reaction times are short, the equipment required is simple, and the products are of high purity. However, the combustion synthesis of AlN under nitrogen pressure usually requires a large amount of AlN to be added as a diluent to lower the combustion temperatures [8–11]. Besides, to improve the nitridation conversion rate, ammonium halides such as NH_4Cl or NH_4F have been added to the raw materials. Elsewhere, NH_4Cl mixed with metallic oxide (CaO, MgO) or polytetrafluoroethylene (PTFE, $(C_2F_4)_n$) powders) has been used to fabricate AlN with quasi-aligned nanowhiskers [12–18].

NaCl has been introduced as a novel combustion synthesis diluent for the fabrication of ceramics such as TiC, ZrB_2, and $MoSi_2$ powders [19–21]. In these studies, NaCl was shown to decrease the adiabatic temperature and wave velocity, stabilizing the combustion reaction, and thereby reducing the rate of aggregation and grain growth. Our previous work [22–24] on the combustion synthesis of SiAlON has shown that metal

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chlorides such as NaCl, KCl, and $MgCl_2$ are ideal diluents that absorb the reaction heat effectively via their sensible and latent heats, thereby lowering the combustion temperature. In addition, different morphologies were obtained in the products according to the type and amount of metal chloride used.

To the best of our knowledge however, the use of metal chlorides (NaCl, KCl, and $MgCl_2$) as diluents for the combustion synthesis of AlN has never been investigated. The objective of this study was therefore to fabricate AlN via salt-assisted combustion. The effects on the products of the metal chloride type, nitrogen gas pressure, and aluminum particle size were investigated.

2. Experimental procedure

Al powders (purity 99.9%, particle size: 3, 14, and 30 μm) were used as the raw materials, AlN powder (purity 99.9%, particle size: 2 μm), NaCl (purity 99.9%), KCl (purity 99.9%), and $MgCl_2$ (purity 99.9%) were used as diluents. The effectiveness of AlN combustion synthesis was investigated in terms of diluent type and amount. The reactant powders were mixed and mechanically activated using a planetary ball-mill (Gokin Planetaring Inc., Japan) at a ball-to-sample mass ratio of 10:1. The activated mixture was then loaded into a cylindrical and porous carbon crucible, and placed in a combustion chamber. The nitrogen pressure in the reaction chamber was varied from 0.2 to 1 MPa. A W–Re thermocouple protected by a layer of BN was inserted into the center of the sample to record the combustion temperatures. The combustion reaction was triggered by passing an electric current (60 A, 10 s) through a carbon foil to ignite the Al powder (the ignition agent) placed on top of the mixture. A detailed description of the apparatus for combustion synthesis is provided in a previous report [25].

The phases in the products were identified using X-ray diffraction (XRD, Miniflex, Rigaku, Japan) with Cu *K*α radiation ($\lambda = 1.54056$ nm). The morphology of the samples was characterized by field-emission scanning electron microscopy (FE-SEM, JSM-7400F, JEOL, Japan). The data for calculating the endothermic values were taken from the database provided with the HSC Chemistry software (Ver. 5.11, Outokumpu, Finland).

3. Results and discussion

3.1. Optimization of the amounts of diluent

Combustion synthesis (CS) reaction was not successfully ignited with 5–50 mass% NaCl added by itself to the raw Al powders. This is because the Al particles melt at a lower temperature (660 °C) than NaCl (800 °C), and the large solid NaCl phase in the raw materials inhibits the nitridation of Al. To ignite the combustion reaction successfully, a small amount of AlN was added to the raw materials, to act both as crystal seeds and as a diluent to facilitate the formation of AlN nuclei. Fig. 1 shows the XRD patterns of the AlN powders synthesized with different amounts of NaCl and AlN at a nitrogen pressure of 0.5 MPa. The Al peaks decrease with increasing amounts of diluent, disappearing at

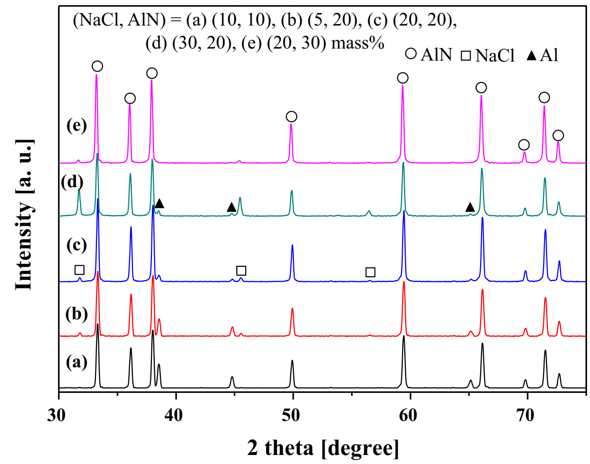

Fig. 1. XRD patterns of the AlN powders combustion-synthesized with the addition of different amounts of NaCl and AlN under a nitrogen pressure of 0.5 MPa with Al particles 30 μm in diameter. The amounts added of (NaCl, AlN) were (a) (10, 10), (b) (5, 20), (c) (20, 20), (d) (30, 20), (e) (20, 30) mass%. Complete nitridation of Al is achieved in (e).

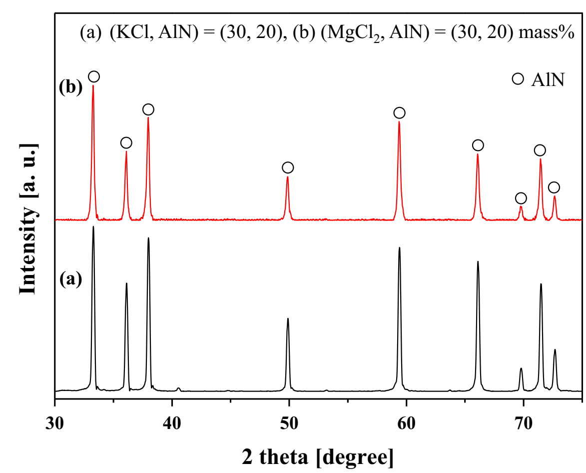

Fig. 2. XRD patterns of the AlN powders synthesized with the optimized amounts of salt and AlN, (a) (KCl, AlN) = (30, 20), and (b) ($MgCl_2$, AlN) = (30, 20) mass% under a nitrogen pressure of 0.5 MPa with Al particles 30 μm in diameter.

20 mass% NaCl and 30 mass% AlN. These are therefore the optimal amounts of diluents required for the nitridation of Al.

A series of similar experiments were performed using KCl and $MgCl_2$ as diluents. The results in Fig. 2 show that to achieve maximal nitridation of Al, 30 mass% salt should be added along with 20 mass% AlN. Fig. 3 shows the AlN particles obtained with the addition of different salts. With NaCl and KCl, the powder is mainly composed of AlN particles with a small number of AlN fibers. However, a very large proportion of irregular AlN whiskers are observed when $MgCl_2$ is used. The different morphologies result from the different supersaturation levels of the AlN vapor and are consistent with a vapor–solid growth mechanism [26].

3.2. Changes in the enthalpy

Fig. 4(a) shows the endothermic values ΔQ (kJ/kg) of the metal chlorides (NaCl, KCl, and $MgCl_2$) and of AlN. The