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Effects of Si_3N_4 addition on formation of aluminum nitride by self-propagating combustion synthesis

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Abstract

An experimental study on the preparation of aluminum nitride (AlN) by self-propagating high-temperature synthesis (SHS) was conducted with powder compacts under nitrogen pressures of 0.79–4.24 MPa. Reactant compacts were diluted by 30–50 wt% of AlN to avoid the melting of aluminum during combustion. In addition, silicon nitride (Si_3N_4) was adopted as a solid source of nitrogen in the reactant compacts and its contribution to the improvement of nitride formation was explored. For the AlN-diluted compacts with no Si_3N_4 addition, a preheating temperature of 200 °C is shown to be required to achieve the self-propagating reaction in nitrogen and a large content (i.e., 50 wt%) of AlN dilution is needed to obtain a high degree of nitridation about 90%. The self-sustaining reaction proceeds with a distinct combustion front traversing the entire sample in a steady mode. The flame-front propagation velocity was found to increase with nitrogen pressure, but to decrease with diluent content. After the passage of the flame front, further nitridation caused by continuous infiltration of nitrogen gas leads to the emergence of afterburning glows. On the other hand, the addition of Si_3N_4 in the reactant compacts not only activates the self-sustaining reaction under the condition without prior heating, but also brings about a high product yield up to 90% in the compacts with a low content (i.e., 30 wt%) of AlN dilution. The morphology of synthesized products from AlN-diluted samples exhibits formation of AlN particles and AlN whiskers, and the former dominates in the case of diluting with 50 wt% AlN. The addition of Si_3N_4 was also shown to favor the production of AlN with a particulate structure.

Keywords: Aluminum nitride; Si_3N_4; Diluent; Preheating; AlN whiskers

1. Introduction

Aluminum nitride (AlN) is one of the most promising materials for use as a substrate and a packaging material in the electronic devices, because of its high thermal conductivity, high electrical resistivity, relatively low dielectric constant, and appropriate thermal expansion coefficient close to that of silicon [1,2]. AlN also shows potential in refractory applications. For example, AlN has been used as crucibles for the manufacture of high-purity metals, grinding materials, and ballistic armors [3]. Commercial AlN powders are usually produced via either carbothermal reduction of alumina (Al_2O_3) in N_2 [4], or direct nitridation of aluminum metal in N_2 or NH_3 atmosphere [5]. However, the high production cost of AlN has been the major disadvantage of conventional synthesis methods. With the merits of time and energy savings, combustion synthesis in a mode of self-propagating high-temperature synthesis (SHS) represents an alternative route having the potential of cost reduction for the production of AlN [6–8].

Combustion synthesis of AlN is based upon the exothermic reaction between compacted aluminum powders and nitrogen gas. A major problem encountered in this SHS process involving solid and gaseous reagents is that the reaction temperature is considerably higher than the melting point (660 °C) of aluminum, which results in the reduction of sample porosity because of the melting of Al and consequently hinders the infiltration of nitrogen gas. Ways to overcome this barrier of solid–gas SHS reactions include performing the reaction under high pressures of nitrogen [9], diluting the sample compact with the product AlN [10–13], or utilizing additives like ammonium chloride (NH_4Cl) [14–17]. Costantino and Firpo [9] showed that a high nitrogen pressure of 100 MPa or more was required to obtain a high product yield of 80–95 wt% AlN. On the other hand, the addition of product AlN powders to the reactant compact was

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confirmed to be effective for the synthesis of fine and pure AlN powders [10]. Shin et al. [11] performed SHS reactions under low nitrogen pressures using the sample compacts diluted with 30–70 wt% of AlN and obtained an optimum conversion about 90 wt% from a reactant containing 50 wt% of diluents in nitrogen of 0.8 MPa. According to the reaction mechanism proposed by Jiang et al. [12], combustion of Al powders with an appropriate amount of diluent AlN in nitrogen is dominated by the gas-phase reaction between Al vapor and gaseous nitrogen. They observed AlN whiskers and AlN rod crystals, which are typical morphology for products growing through the vapor–liquid–solid (VLS) or vapor–solid (VS) mechanism. To improve the conversion limitation at atmospheric pressure, Bradshaw and Spicer [13] conducted combustion synthesis of AlN with a forced flow of nitrogen through a loosely packed bed of Al powders contained in a graphite reactor and obtained almost-complete conversion yielding AlN products with a predominantly whisker morphology. However, reactant powder mixtures with a solid-phase dilution of 50% AlN were found to favor the formation of particle-shaped products [13].

To achieve a high degree of conversion under low nitrogen pressures, the introduction of additives containing halogens was shown to have a catalytic effect on combustion synthesis of AlN without increasing the reaction temperature [14–17]. Chung et al. [14] obtained high product yields (about 90%) from the combustion reaction of Al powder compacts added with a small amount of NH_4Cl under nitrogen pressures of around 0.5 MPa. Rosenband and Gany [17] found a remarkable increase in the extent of aluminum nitridation when the reactant compact contained a low content of NH_4Cl about 2.5 wt%. They also indicated a maximum degree of nitridation at the NH_4Cl content in the range of 5–10 wt% [17]. Although the addition of NH_4Cl enhances the nitridation of aluminum, it increases the concentration of water vapor in the reaction system and then leads to the increase of oxygen contents in the product AlN [18]. The presence of oxygen in aluminum nitride was shown to significantly degrade the thermal conductivity and to easily cause hydrolysis and oxidation of AlN [1,19]. Recently, Sakurai et al. [20] adopted NH_4F (up to 15 wt%) as an additive in combustion synthesis of AlN under a gas mixture of nitrogen and hydrogen (up to 20 vol%). It was found that the addition of NH_4F and H_2 lowered the reaction temperature and reduced the oxygen content in the final product [20]. Furthermore, the specific surface area of synthesized AlN powders was increased by 80% [20].

In spite of the extensive studies on the preparation of AlN by combustion synthesis, it is still a great challenge to accomplish a high degree of conversion. The specific objective of this study was to investigate the role of silicon nitride (Si_3N_4) as a solid source of nitrogen in combustion synthesis of AlN from aluminum powder compacts. Effects of the processing variables including nitrogen pressure, sample compaction density, AlN diluent content, and initial sample temperature on combustion characteristics and the extent of nitridation were studied. In additional, phase composition and morphology of synthesized products were examined.

2. Experimental procedure

Aluminum (Al) powder (Showa Chemical Co.) with a particle size of −350 mesh and a purity of 99% was used as the reactant material. To avoid excessive melting of aluminum in the powder compact during nitridation, reactant compacts were diluted by aluminum nitride particles (Strem Chemicals, 99% purity) with average sizes of 2.5–4.0 μm. In addition to Al and AlN, silicon nitride (Si_3N_4) powders (Adrich, −325 mesh, 99% purity) were adopted as the solid source of nitrogen to improve the nitridation of reactants.

For the sample compacts without the addition of Si_3N_4, the content of AlN dilution ranged from 30 to 50 wt%. Al and AlN powders were mixed in a ball mill and then were cold-pressed into cylindrical compacts with a diameter of 7 mm and a height of 12 mm. Moreover, powder compacts were formed with two compaction densities equal to 45 and 55% of the theoretical maximum density (TMD) of the powder mixture. In the case of test specimens containing Si_3N_4, Al powders were mixed with 30 wt% AlN and 15 wt% Si_3N_4 to prepare the reactant compacts with a green density of 45% TMD.

The SHS experiments were conducted in a stainless-steel windowed combustion chamber under a nitrogen pressure ranging from 0.79 to 4.24 MPa. The nitrogen gas used in this study had a purity of 99.999%. The sample holder was equipped with a 600 W cartridge heater used to raise the initial temperature of test samples prior to ignition. Moreover, a compacted pellet (2 mm in height and 7 mm in diameter) made up of a powder blend of titanium (Ti) and carbon black (C) (with a molar ratio Ti:C = 1:1) was placed on the top of the test specimens to serve as an ignition enhancer which was triggered by a heated tungsten coil. The amount of nitrogen uptake was calculated from the measurement of weight change of the sample compact after combustion. Details of the experimental setup and measurement approach were reported elsewhere [21–23]. It is important to note that a preheating temperature of 200 °C is found to be a prerequisite for the samples without Si_3N_4 addition to achieve self-sustaining combustion, whereas it is not required by the Si_3N_4-containing compacts.

3. Results and discussion

3.1. Observation of combustion characteristics

Typical combustion sequences of AlN-diluted powder compacts under nitrogen pressures are illustrated in Figs. 1 and 2, respectively, for the conditions without and with the addition of Si_3N_4. As shown in Figs. 1 and 2, upon ignition nitridation of the sample compact proceeds in a wave of self-sustaining combustion. The propagation of the reaction front transforms the cold reactant into an incandescent product. Furthermore, it was found that after the passage of the flame front, the combustion luminosity on the compact starts to decrease, but instead of constant losing of the luster an afterburning glow appears and lasts for a short period of time about 1–2 s. The afterburning reaction is typical of the combustion synthesis involving gaseous reagents [6,7]. It is believed that complete conversion of aluminum to nitride at the reaction front is difficult to achieve, because mainly of insufficient nitrogen. As a result, continuous infiltration of nitrogen gas into the porous compact to react with the solid reactant led to the appearance of afterburning glows on the burned sample. It is important to note that Fig. 2 presents the combustion process of a Si_3N_4-added reactant compact (containing 15 wt% Si_3N_4 and 30 wt% AlN) with no prior heating, in contrast to that a preheating temperature of 200 °C or higher is required for the Si_3N_4-free samples with 30–50 wt% AlN dilution to achieve self-propagating combustion, such as that shown in Fig. 1.