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Effects of Al particle size and nitrogen pressure on AlN combustion synthesis

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ABSTRACT

This study investigates the combustion synthesis of AlN fibers using an NH_4Cl additive and reports the effects of Al particle size (3, 30, and 180 μm) and N_2 pressure (0.10, 0.25, and 0.50 MPa) on the purity and morphology of AlN fibers. The combustion temperature was directly measured during the synthesis to elucidate the formation mechanism of the AlN fibers. The phase purity and morphology of the products were studied using X-ray diffraction and scanning electron microscopy, respectively. When the particle size of Al was reduced from 180 to 3 μm, the purity of the AlN product increased significantly owing to the large reaction area, which increased the combustion temperature. Furthermore, lower N_2 pressures enhanced the formation of AlN nanofibers due to the accelerated gasification of Al. The optimum values of the particle size of Al and the N_2 pressure for the formation of high-purity AlN nanofibers were found to be 3 μm and 0.10 MPa, respectively.

1. Introduction

Among the III-V semiconductors, AlN has attracted a great deal of attention because of its wide band gap (6.2 eV) [1]. Other salient properties of AlN include a high thermal conductivity (~320 W/m·K) [2], low thermal expansion coefficient (4.5×10^{-6}/K, which is close to that of silicon) [3], and high electrical resistivity (4.0×10^{9} Ω·m) [4]. These properties make AlN suitable for electronic applications, such as packaging materials for large-scale integration devices and substrates for the fabrication of light emitting diodes. The packaging materials are usually made of plastic because of its formability, but the low thermal conductivity of plastic (~1 W/m·K) is a major disadvantage. The use of AlN fillers in heat dissipation substrates can effectively enhance heat transfer [5]. One-dimensional AlN fibers dissipate heat faster than AlN particles because fibers can easily connect with each other to create paths for heat dissipation and to reduce thermal resistance in polymer composites [6]. However, conventional methods used for the preparation of AlN fibers, such as physical vapor deposition [7,8] and chemical vapor deposition [9–11], are time consuming and uneconomical.

Combustion synthesis (CS), established by Merzhanov et al., is an efficient method for the synthesis of a wide variety of materials (alloys, oxides, nitrides, hydrides, etc.) [12]. The CS method uses the heat released in an exothermic reaction to propagate the reaction through all the reactants, resulting in the formation of high-purity products within a short time using little external energy. However, the reaction between aluminum and nitrogen (Al (s)+N_2 (g)=AlN (s), ΔH=−318 kJ/mol at room temperature; calculated using HSC Chemistry (Ver. 5. 11 Outokumpu, Finland)) is highly exothermic, and up to 70 mass% of the reactants must be AlN. AlN is added to prevent the decomposition and agglomeration of AlN, because agglomeration prevents the infiltration of nitrogen into Al particles [13]. Moreover, adding a small amount of an inorganic halide, such as $MgCl_2$, NaCl, NH_4Cl, or NH_4F promotes the formation of AlN fibers [14–17]. The CS method has also been used to prepare Si_3N_4 [18] and SiAlON [19–21]. Niu et al. investigated the effects of various metal chlorides on the formation of AlN particles and whiskers [16]. However, studies on the effects of the particle size of the Al starting material and the N_2 pressure on the morphology of AlN fibers are lacking.

In the present work, we synthesized AlN by CS using an NH_4Cl additive to promote the formation of AlN fibers and investigated the effects of Al particle size and N_2 pressure on the purity and morphology of AlN fibers prepared by CS. Based on the obtained results, we proposed a mechanism for the formation of AlN fibers.

2. Experimental procedure

Aluminum powder (99.9%, Kojundo Chemical Laboratory Co., Ltd.; 3, 30, and 180 μm), AlN powder (99.9%, Kojundo Chemical Laboratory Co., Ltd.; 2 μm), and NH_4Cl powder (99.5%, Kanto Chemical Co., Inc.) were used as the starting materials. These powders were mixed in air in

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Table 1
Al particle sizes and N_2 pressures used for CS in the present study.

Particle size of Al powder (μm)	N_2 pressure (MPa)
3	0.1
30	
180	
3	0.25
30	
180	
3	0.5
30	
180	

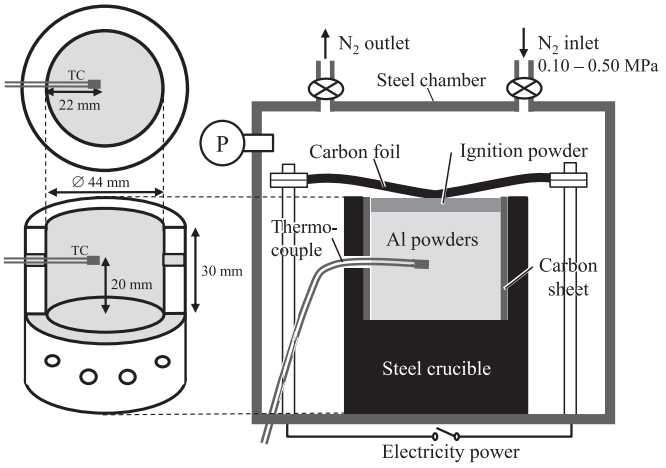

Fig. 1. Schematic of the CS reactor system, in which the ignition was started on top of the reactants. The inset shows the schematic of the cross section of the carbon crucible.

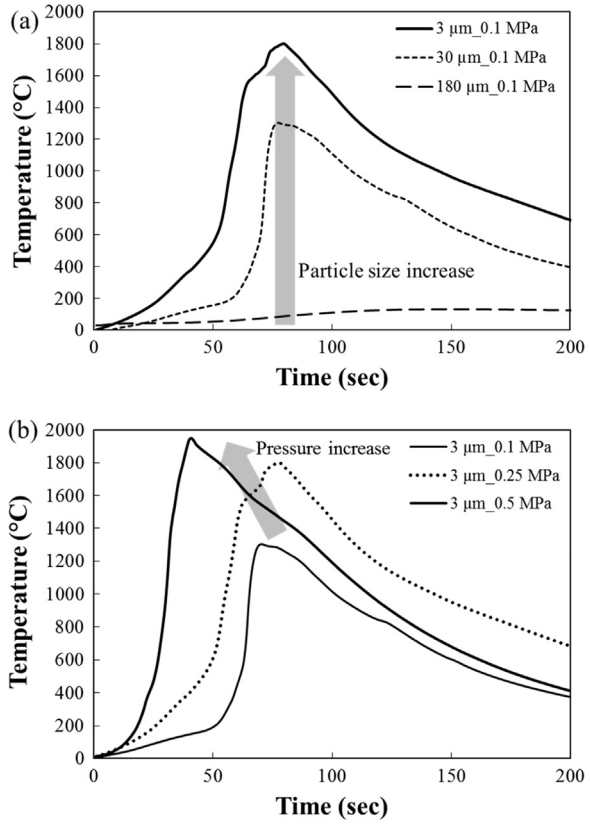

Fig. 2. Temperature-time histories of CS under different conditions: (a) different particle sizes of Al at N_2 pressure of 0.1 MPa and (b) different N_2 pressures at Al particle size of 3 μm.

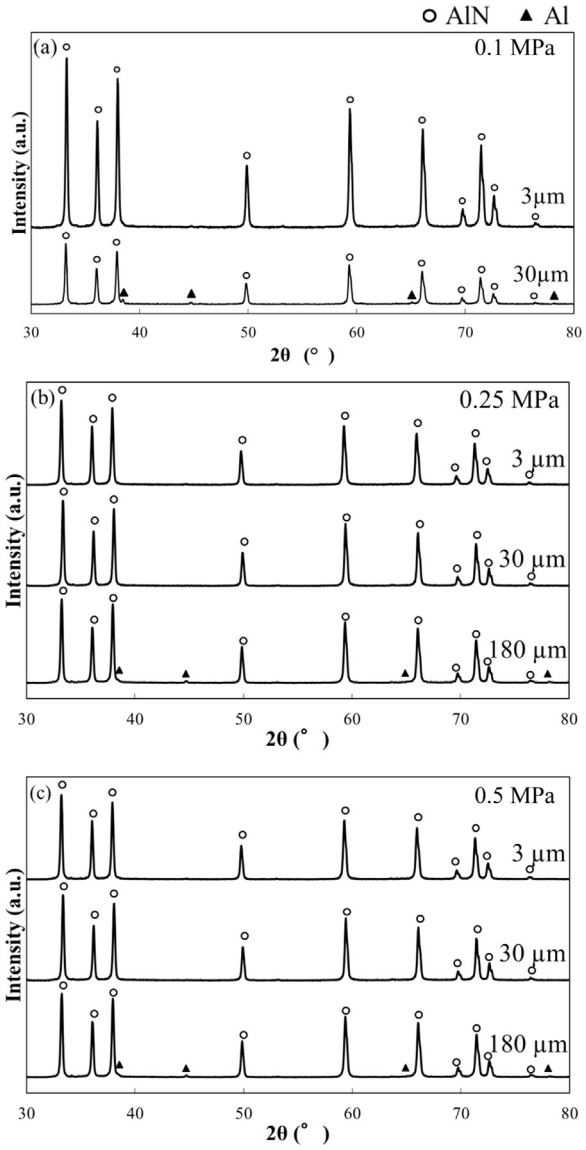

Fig. 3. XRD patterns of the products obtained by CS using different particle sizes of Al at N_2 pressures of (a) 0.10, (b) 0.25, and (c) 0.50 MPa. Note that, unreacted Al was not observed in the product when Al particle size of 3 μm was used as the raw material.

the mass ratio of Al: AlN:NH_4Cl=50:45:5 by ball milling (Fritsch P-6) for 15 min. The mixture was packed in a porous carbon crucible, and 2.0 g of ignition powder (Al: AlN=1:1) was placed on top of the mixture. The crucible was placed in a CS reactor filled with N_2 up to the experimental pressure. The different Al particle sizes and N_2 pressures used in the present study are listed in Table 1. Fig. 1shows the schematic of the CS reactor system. The combustion reaction was carried out by passing a current of 60 A through a carbon foil for 10 s. The reaction temperature was measured during CS using a W-Re thermocouple. After the completion of the combustion reaction (within 5 min), the sample was cooled in the reactor for 30 min.

The combustion product obtained was slightly ground using a mortar and pestle before characterization. The phase purity and the morphology of the product were studied using X-ray diffraction (XRD; Rigaku MiniFlex diffractometer) and scanning electron microscopy (SEM; JSM-7001FA, JEOL Ltd.), respectively. The adiabatic temperature was calculated using HSC Chemistry (Ver. 5. 11 Outokumpu, Finland).