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The growth of AlN dendritic crystals with uniform morphology by an aluminum microdroplet localization approach

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ABSTRACT

We developed an attractive combustion approach for synthesizing uniformly shaped AlN dendritic crystals by combustion of $Al + 0.1AlF_3 + kAl_2O_3$ powder mixtures in a nitrogen atmosphere. The combustion temperature measured for various k values was between 1650 and 1750 °C and the micro-droplets of Al formed in the beginning stages of the process were enveloped by the solid layers of Al_2O_3, and the subsequent multipoint nucleation and crystallization produced morphologically and size uniform dendritic crystals. We proposed a theoretical model for calculating the thickness and the number of Al_2O_3 layers around of Al microdroplets at known concentration of Al_2O_3. Depending on the concentration of Al_2O_3, these structures were simple stars with six points and stellar dendrites with multiple petals.

1. Introduction

Fabrication of nano- to microscopic-scale inorganic one-, two- and three-dimensional structures are of great interest for materials chemistry due to their importance in basic scientific research and potential technological applications [1,2]. In the past few decades, there has been an increasing number of reports on the synthesis of inorganic structures, such as wires [3–5], tubs [6,7], plates [8,9], cubs [10,11], and dendrites [12–14]. Among the inorganic materials, group III metal nitrides (AlN, GaN, InN) have been extensively studied for their outstanding properties and potential to be used in future devices [15–18]. As an important member of the group III nitrides, hexagonal AlN is well known for its unique properties, such as a direct wide band gap (6.2 eV), high thermal conductivity, superior mechanical strength, a high piezoelectric response, small or even negative electron affinity, and it can be used in field electron emitters [19,20], flexible pulse-wave sensors [21], and nanoscale mechanical resonators [22]. Among the variety of AlN dendritic structures, feathers [23,24], urchins [25], and six-fold symmetry crystals (stellar and fernlike dendrites) [16,26] are known. These structures are attracting much attention stimulated by their practical importance related to the crystal symmetry and thermal-electrical characteristics. Therefore, studies on the shape control of AlN dendritic structures will provide insights into the crystallization behavior at a nano- or micro-sized scale owing to the traditional lack of understanding of the growth history and shape evolution process. Moreover, the shape control of AlN dendritic structures can gradually improve the characteristics of micro- and nanocrystals and extend their potential to be used in modern industry.

Recently, we succeeded in synthesizing new dendritic structures of AlN, namely, 6-fold and multi-fold symmetry dendrites [1,16,26]. We showed that in a burnt specimen, the AlN dendrites located in a single site display individual size and morphological patterns, like snow crystals [27]. Therefore, the possibility of achieving some degree of control over the symmetry of AlN crystals is an important scientific task to be solved.

In this article, we demonstrate the successful growth of uniformly shaped AlN dendritic crystals by the combustion of an $Al + 0.1AlF_3$ mixture blended with 0–0.5 moles of Al_2O_3. In the growth process, Al_2O_3 particles acted as a localization agent for the Al microdroplets. Each Al microdroplet formed in the combustion process was surrounded by submicrometer size particles of Al_2O_3, which minimized the coagulation of Al droplets and promoted the formation of AlN dendritic crystals with uniform morphological patterns. The AlN crystal possessed a dendritic structure with six or multiple branches radiating outward in an equatorial plane. In a similar fashion, secondary dendrites were found to grow above and below the equatorial plane, resulting in a 3D radiating structure.

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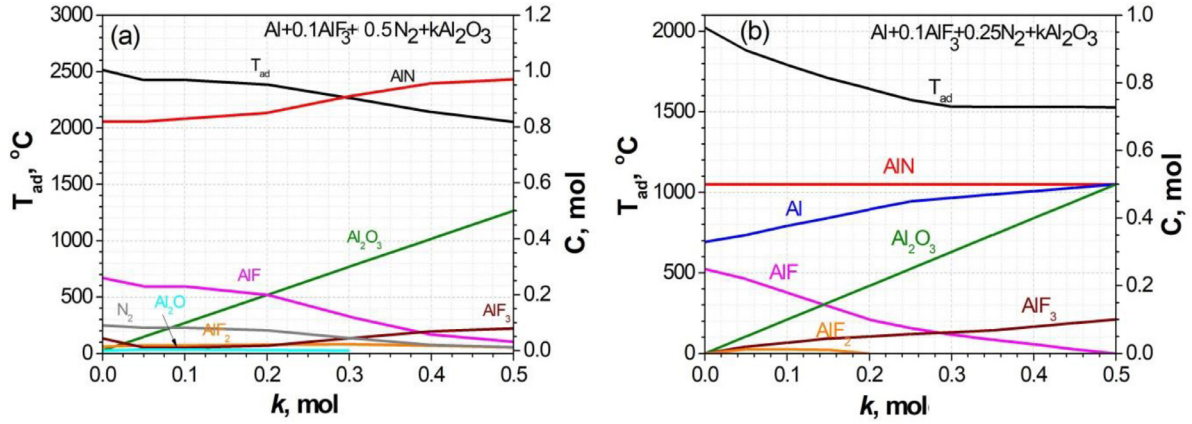

Fig. 1. Adiabatic combustion temperatures and equilibrium reaction phases in the $Al + 0.1AlF_3 + kAl_2O_3$ system upon Al_2O_3 (k): (a) 0. 5 N_2; (b) 0.25 N_2.

2. Experimental

2.1. Chemicals and reagents

Al powder (purity 99%, particle size ≤ 50 μm) was obtained from Samchun Chemicals (Korea). Al_2O_3 powder (purity 99.9%, particle size 0.1–0.3 μm) was obtained from Terio Corporation (China). The reagent–grade AlF_3 was purchased from Junsei Chemicals Co. Ltd. (Japan).

2.2. Combustion experiments

In a typical experiment, 54 g of Al was hand mixed with 16.8 g of AlF_3 powder and 10.2–51 g of Al_2O_3 using a ceramic mortar and pestle. The reaction mixture was compacted by hand into a paper cup (diameter: 4.0 cm, height: 5–7 cm). During compaction, two Λ-shaped tungsten–rhenium thermocouples (WR-26/WR-5), 200 μm in diameter, were placed inside the pellet near the center. The 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 1–2 g of Ti powder was placed on top of the reaction pellet as an ignition agent. The cup containing the reaction mixture and thermocouples was subsequently placed under a nickel – chromium coil installed in the combustion chamber. The reactor was tightly closed, and the air was pumped out with a vacuum pump, after which the reactor was filled with nitrogen to a pressure of 4.0 MPa. Local ignition of the reaction pellet 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 and temporal history of the process at a frequency of 10 Hz.

2.3. Analysis methods

Thermodynamic analysis of the adiabatic combustion temperature and the equilibrium composition of reaction species were performed using the "THERMO" software package [28]. 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. Thus, it can only approximate the actual system. Nevertheless, the results enable the rapid screening of the appropriate scope of reaction conditions that should be studied through an experiment, thereby minimizing expensive trial-and-error chemistry. The crystal structures and morphology of the final powders were characterized using an X-ray diffractometer with Cu $K\alpha$ radiation (PANalytical X'Pert PRO XRPD, Netherlands). A field-emission scanning electron microscope (JEOL JSM-6700F, Japan) was used for the morphological characterization of the burned pellets.

3. Experimental results and discussion

3.1. Combustion thermodynamics and experiments

Our recent publication [26] reported the growth of sixfold symmetry crystals of AlN from an $Al + 0.1AlF_3$ mixture. AlN 3D crystals grown in the combustion wave displayed different morphological patterns and were randomly dispersed within the sample. In the current study, several inorganic materials (Al_2O_3, SiO_2, NaCl, etc.) were tested to make the AlN crystal growth process controllable. Among these substances, the best control over the combustion parameters and the shape uniformity of AlN dendritic crystals were reached with fine Al_2O_3 powder. For that reason, we chose the mixture of $Al + 0.1AlF_3 + kAl_2O_3$ (k is moles of Al_2O_3) composition for a combined theoretical and experimental study.

Preliminary thermodynamic analysis to determine the adiabatic combustion temperature (T_{ad}) and the equilibrium reaction phases (C) in the $Al + 0.1AlF_3 + kAl_2O_3$ system was conducted. In calculation the starting temperature was set 25 °C and the gas pressure 4.0 MPa. The calculation was performed upon the moles of Al_2O_3 for two concentrations of nitrogen: 0.5 (stoichiometric amount) and 0.25 mol (lack of nitrogen). As shown in Fig. 1a and b, in both calculations the adiabatic temperature exhibited a decreasing tendency. At a high nitrogen concentration (Fig. 1a), the temperature decrease was from 2515 to 2053 °C, while at a low nitrogen concentration (Fig. 1b) it was from 2023 to 1527 °C. As would be expected, at $k = 0.5$, the amount of AlN was twice as large as at $k = 0.25$, and therefore the adiabatic temperatures were comparably high. In both systems, with AlN, AlF_3 and Al_2O_3 phases, the calculation also predicted the formation of aluminum low fluorides (AlF_2 and AlF) and Al_2O in the gas phase. In both calculations, the combustion temperatures were sufficiently high to allow rapid nitriding of the aluminum.

The combustion experiments were conducted on the $Al + 0.1AlF_3 + kAl_2O_3$ mixture under a 4.0 MPa nitrogen pressure for the $k = 0$–0.5 mol range. The photo images of the burning process ($k = 0.05$) captured from the window of the pressure vessel are shown in Fig. 2a. The combustion wave (indicated by dashed lines) moves from the top to bottom of the sample and shows an oscillation character, which is manifested in the form of flares and flat zones. The number of flares is 5 to 7 in the 6 cm long sample, i.e. the distance between the flares is about 1 cm (frequency is