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Self-Propagating High-Temperature Synthesis of AlN Nanostructures and Their Sintering Properties †

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Abstract

This investigation describes novel growth of quasi-aligned aluminum nitride (AlN) nanofibers by the self-propagating high-temperature synthesis (SHS) under low nitrogen pressure. The starting charge consists of Al and AlN diluent (40/60 mole%) with a mixture of Y_2O_3 *and* NH_4Cl *additives (5 wt% each). The combustion reaction was performed under 0.25 MPa* N_2 *pressure. The microstructure of as-synthesized AlN powder consists of two major types; aggregates of irregular particles (~0.5 μm, the same as the original AlN diluent) and balls-like grains (same size and shape as original Al particles) consisting of a thin crust (≤150 nm) covering unique quasi-aligned AlN nanofibers grown in the interior. This powder can be easily consolidated to near theoretical density without sintering additives in a period of 5 min at 1600 ℃ using the spark plasma sintering (SPS) process. The microstructure of sintered AlN was homogeneous with dual morphologies of many ultrafine sub-grains (fibers, nanometer size in diameter) aggregated in large grains. The thermal conductivity was 91 W/m-K.*

KEY WORDS: (SHS), (AlN), (Nanofibers), (Morphology Control)

1. Introduction

Aluminum nitride (AlN) has attracted increasing attention in manufacturing of substrates and packaging materials for high-density microelectronics because it possesses a unique combination of physical properties such as high thermal conductivity, high electrical resistivity, low dielectric constant, wide band gap and the thermal expansion coefficient matches that of silicon [1-3]. AlN powder is usually produced by the carbothermic reduction and nitridation of alumina or direct nitridation of aluminum in nitrogen gas based atmosphere [1]. The self-propagating high-temperature synthesis or SHS (also called combustion synthesis) represents a cost-effective alternative for the production of pure AlN powder [4, 5]. However, the process control to yield AlN powder with uniform morphology (shape and size) has not been established yet [6-11] although its importance to engineer the properties of AlN-based materials and devices. Our study reports new oriented growth of AlN nanofibers under low N_2 gas pressure by SHS. In addition, since sintering is a necessary process in fabrication of many AlN components, the sintering properties of the resultant powder using spark plasma sintering is also reported.

2. Experimental

The combustion experiments were carried out in a conventional SHS autoclave. About 50 g of loosely packed aluminium and aluminium nitride (as diluent) powder mixture (40:60 mole ratio) containing a mixture of yttrium oxide and ammonium chloride powders (5 wt% each, as promoting additives) was ignited in a porous graphite container under a low nitrogen pressure of 0.25 MPa. The average particle size of the original Al and AlN powders is 23 and 0.5 μm, respectively. The nitridation was initiated from the bottom, using a 2 g ignition pellet placed beneath the charge, and by passing ~60 A current for 10 s through a carbon ribbon heater under the pellet. The morphology of AlN powder was observed by the field emission scanning electron microscope (FE-SEM; ERA-8800, ELIONIX, Japan) for representative samples from various locations of the product cake. For the sintering experiments, the as-synthesized AlN powder was ultrasonically agitated for 60 min in acetone. Then, one gram of dry powder was sintered without additives using SPS apparatus (Dr. Sinter® Model 1050, Sumitomo Coal Mining Company, Ltd., Japan). The sintering was performed at 1600 °C for 5 min under 30 MPa pressure. The heating and cooling rates were 100 °C/min.

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3. Results

The combusted cake was very fragile with a homogeneous white color. **Figure 1** shows the XRD pattern of the nitride product. The diffraction lines are assigned to hexagonal AlN structure similar to reported bulk AlN powder (JCPDS-file 25-1133). No residual metallic Al has been detected. The typical temperature-time history of the combustion reaction is given in **Fig. 2**. The temperature was measured at the middle center of the charge. The pattern shows the occurrence of mild combustion with relatively low T_{max} (1620 °C) and slow speed (0.26 mm/s).

The grain morphologies of as-synthesized AlN particles are shown in **Fig. 3**. The microstructure consists of two major types; aggregates of irregular particles (~0.5 μm, the same as the original AlN diluent) and balls-like grains (same size and shape as original Al particles) consisting of the thin crust (≤150 nm) which covers unique quasi-aligned AlN nanofibers grown in the interior. From the SEM observations, one can conclude that: (1) there was no grain growth or sintering for both the formed and original AlN diluent particles, and (2) the quasi-aligned AlN nanofibers were formed inside the reacting Al particles.

Formation of this new morphology is believed to happen through a two-stage process. The first one occurs at a preliminary stage of the combustion outside Al particles. After the ignition, the evolved heat causes the sublimation and dissociation of ammonium chloride which are endothermic reactions and effectively reduce the combustion temperature and speed. This gives enough time for an yttria interaction with the thin oxide layer naturally present on the surface of Al particles with the formation of a stable Al–N–Y–O surface layer or crust. The second stage occurs inside the Al particles which now consist of crusts covering molten Al cores. It begins by the infiltration of various gaseous species such as $HCl_{(g)}$, $NH_{3(g)}$, $N_{2(g)}$ through the crust into the molten cores. At this moment, these "crust–core" systems function as individual "micro-reactors" where the nitridation and growth processes continue inside. The molten Al cores are spontaneously halogenated to $AlCl_3$ vapor and the nitridation proceeds by the gas-gas reaction of $AlCl_3$ and NH_3/N_2 vapors. The AlN nanofibers are deposited from the vapor-phase quasi-aligned on the inner surface of the crusts (acting as substrates) toward the center of the micro-reactors probably by both VLS (vapor-liquid-solid) and VS (vapor-solid) mechanisms [12]. A possible reactions sequence can be described as follows:

(1) Dissociation of NH_4Cl:

$$NH_4Cl_{(s,\,v)} \rightarrow HCl_{(g)} + NH_{3(g)}$$

(2) Formation of thin crust:

$$Y_2O_{3(s)} + Al_2O_{3(s)} + N_{2(g)} \rightarrow Al\text{–}Y\text{–}N\text{–}O_{(s)}$$

(3) Chlorination of Al core:

$$Al_{(l)} + 3HCl_{(g)} \rightarrow AlCl_{3(v)} + 3/2H_{2(g)}$$

(4) Gas-gas nitridation:

$$AlCl_{3(v)} + 1/2N_{2(g)} + 3/2H_{2(g)} \rightarrow AlN_{(s)} + 3HCl_{(g)}$$

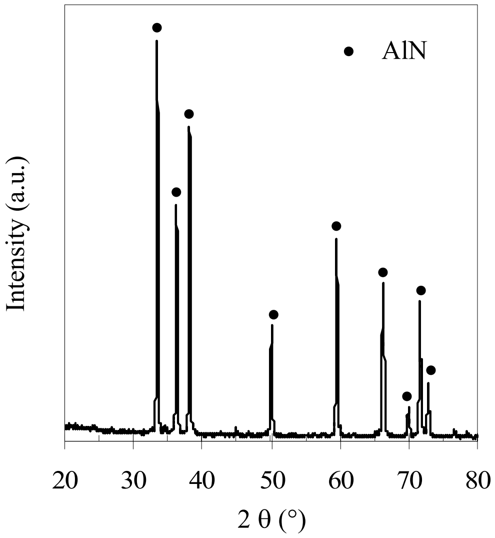


Fig. 1 X-ray diffraction pattern of as-synthesized AlN powder.

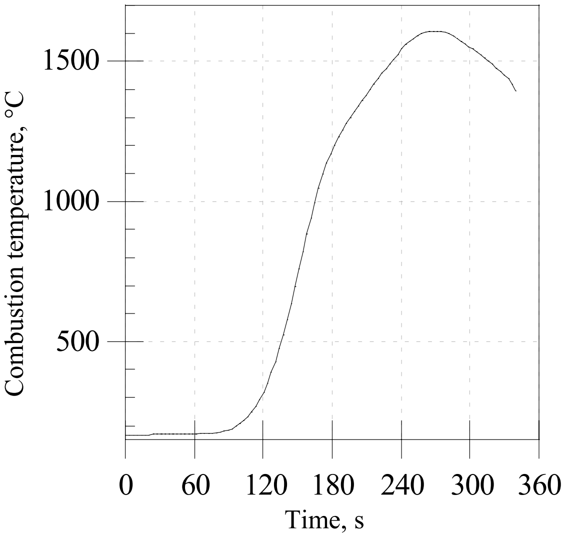


Fig. 2 The temperature-time history of the combustion reaction.

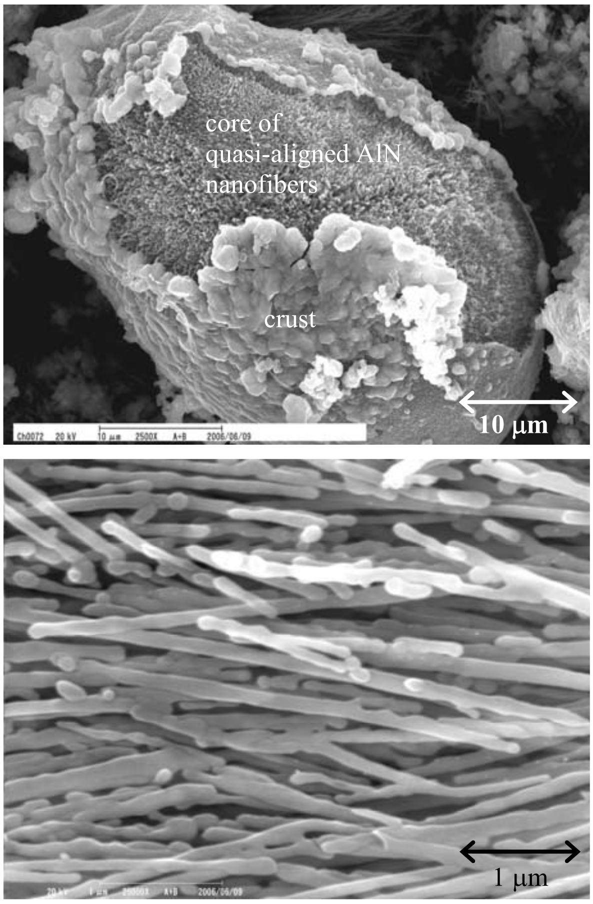


Fig. 3 FE-SEM images of as-synthesized quasi-aligned AlN nanofibers.

This SHS-derived AlN powder was then sintered using Dr. Sinter® Model 1050 SPS apparatus. The sintering was performed at 1600 °C for 5 min under 30 MPa pressure. A commercial AlN powder was also sintered under the same condition for comparison. **Figure 4** shows the results of density and thermal conductivity measurements of the two specimens. The density of sintered commercial AlN was low (~ 90%) while the SHS-derived AlN powder could be fully densified (~ 99 %) without the use of any sintering aids. The thermal conductivity, as measured by the laser flash method, of both specimens was 69.7 and 91 W/m-K, respectively.

Figure 5 gives the XRD pattern of SHS-derived sintered AlN sample. The crystalline phase is h-AlN with minor amounts of $Al_5Y_3O_{12}$. The formation of the minor $Al_5Y_3O_{12}$ phase is due to the addition of yttria during the SHS reaction. Its presence seems useful to attain the full densification at such moderate sintering condition.

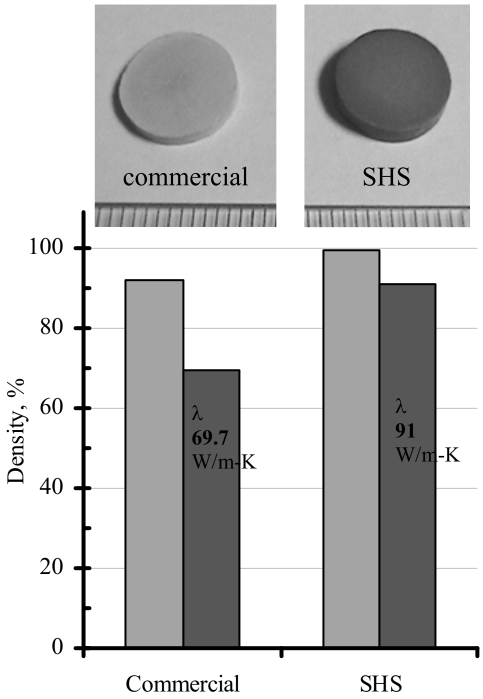


Fig. 4 Density and thermal conductivity of sintered AlN specimens.

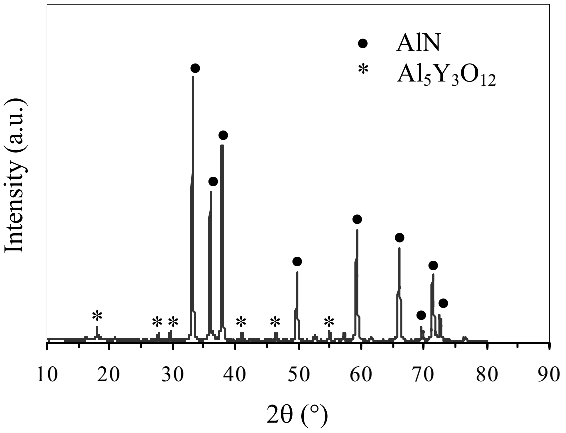
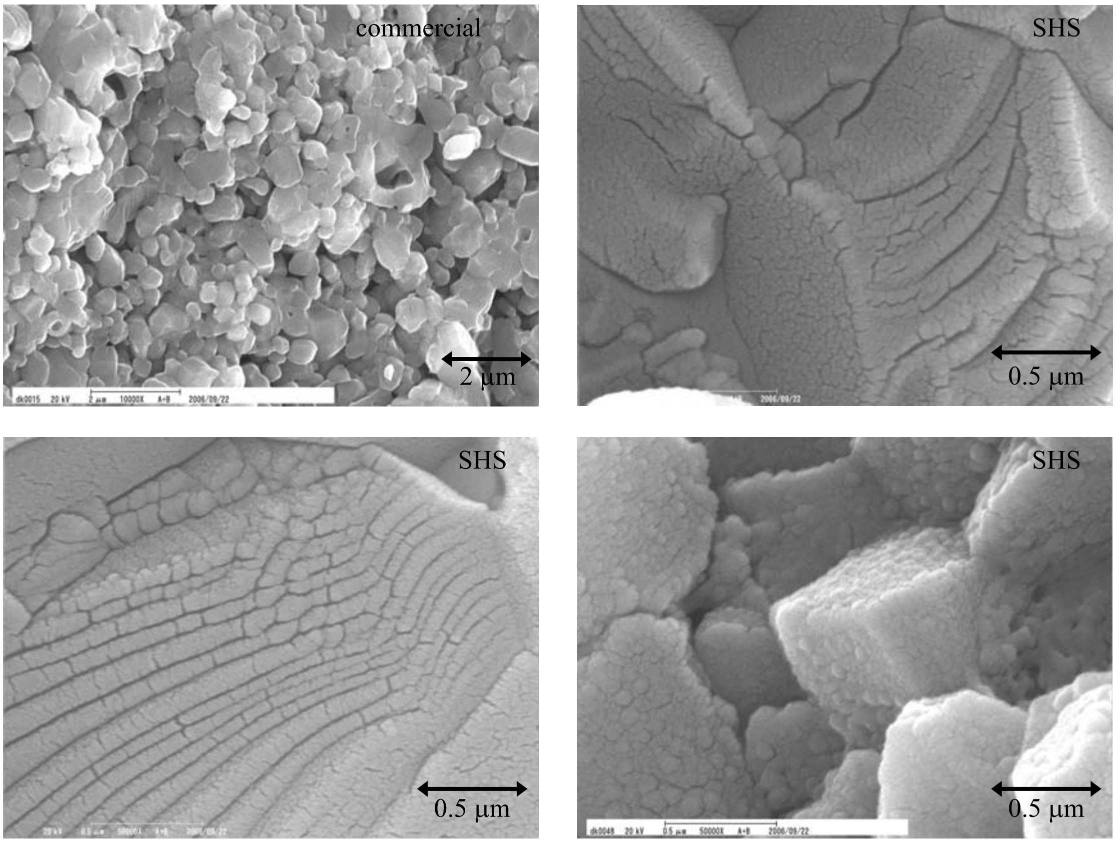


Fig. 5 An XRD pattern of sintered AlN specimen (from SHS-derived powder).

Figure 6 shows the microstructure of sintered AlN specimens. The sintered AlN sample (SHS-derived) has a homogeneous microstructure. It has dual morphologies of submicrostructures (many ultrafine grains or fibers, nanometer size in diameter) aggregated in large grains-like.



4. Conclusions

Novel quasi-aligned AlN nanofibers can be formed by the self-propagating high-temperature synthesis (SHS) under low nitrogen pressure. Yttria-ammonia additives are effective in the promotion of unidirectional growth at the interior of reacting coarse Al particles. The as-synthesized AlN powder can be easily sintered to near full densification by SPS at relatively low sintering temperature and short time. This produces the microstructure of dual morphology consisting of many ultrafine sub-grains (< 30 nm) aggregated in larger grains (like blocks).

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