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Large-scale synthesis of AlN nanofibers by direct nitridation of aluminum

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Abstract

AlN nanopowders and nanofibers were synthesized by direct nitridation of Al and rice bran mixture compacts in a tube furnace up to 1300 °C in a nitrogen flow without addition of extra catalyst. The effect of the compaction pressure applied onto the green bodies on the morphology of the final AlN products was investigated. A green body compacting pressure in between 320 MPa and 480 MPa was found to be favorable for the synthesis of AlN fibers with aspect ratio up to 400, diameter in the range of 50–500 nm, and length up to tens of micrometers; for a lower pressure of 160 MPa and a higher pressure of 640 MPa, nano-sized AlN powders were the primary morphology in the final product. The AlN products were characterized by several techniques and the VLS growth mechanism was proposed as the main reason for the AlN fibers formation.

Keywords: A. Pressing; D. Nitride; Nanofibers

1. Introduction

Aluminum nitride (AlN) is an important member of the group III nitrides with the highest bandgap of around 6.2 eV [1]. It is a promising advanced ceramic material with many excellent properties, such as high electrical resistivity ($10^{13}\ \Omega$ cm), small dielectric constant (8.8 at 1 MHz), high thermal conductivity (320 W/(m K)), and low thermal expansion coefficient (which closely matches that of silicon, $4.7 \times 10^{-6}\ \mathrm{K}^{-1}$) [2,3]. Therefore, aluminum nitride is a potential candidate for many applications, such as microelectronics packaging where rapid heat dissipation for high-density, high-power, and high-speed integrate circuits is required [4]. It is desirable to form AlN nanofibers, nanotubes and nanowires because of the one-dimensional (1D) quantum confinement geometries [5], which may dramatically improve the desired properties and make AlN a promising candidate for making novel nano-devices such as field effect transistors, light-emitting diodes [5], and field emission devices (since AlN has a very small value of electron affinity ranging from negative to 0.6 eV) [6], as well as for understanding fundamental concepts underlying the observed electronic, optical and mechanical properties of materials [5]. As a result, an overwhelming volume of research is directed towards obtaining high quality 1D AlN nano-materials, including combustion synthesis [3], vapor–solid (VS) process [6,7], anodic porous alumina template [5,8], directly nitriding aluminum powders under ammonia/nitrogen with or without a catalyst [9–13], carbothermal reduction and nitridation of electrospun precursor fibers or solid solution precursors [1,14], direct sublimation method [15], and so on. In this study, AlN nanopowders and AlN nanofibers were synthesized by direct nitridation of Al, and the morphologies of AlN were found to be a strong function of the compaction pressure of the green body. The products were characterized by using several techniques and the AlN formation mechanism was discussed.

2. Materials and experimental procedure

To assist the direct nitridation of aluminum (−325 mesh aluminum powders from Alfa Aesar, 99.5% purity), raw rice bran (from a local farm in Louisiana, average particle size less than 1 mm) was selected to act as dispersant/catalyst donor. The as-received rice bran was rinsed with distilled water and dried up at 120 °C in a furnace to remove mechanical residuals and moisture. Initial powder mixtures (aluminum + raw rice bran) were prepared by milling aluminum powder and raw rice bran of same weight. The milling process was carried out in a Spex 8000 high energy ball mill using 5-mm diameter stainless steel

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balls and a customer-designed stainless steel vial with an inert atmosphere at very low temperature provided by liquid nitrogen cooling; the weight ratio of the mixture and the milling balls was 1:20 and a milling time of 15 min gave well dispersed fine powders. In an inert atmosphere, the milled powders were used to form a series of compact disc samples (12.7 mm in diameter and ∼3 mm in thickness) under different compression pressures: 160 MPa, 320 MPa, 480 MPa and 640 MPa. Then the nitridation of the disc-shaped samples was performed in a conventional electric tube furnace (a horizontal alumina tube, *L*: 1000 mm; *D*: 80 mm) in a flowing nitrogen atmosphere (30 mL/min). All the samples prepared under different compression pressures underwent the same temperature program: from room temperature to 1300 °C at a ramp of 10 °C/min; and then immediately cool down at 20 °C/min to room temperature. The nitride disc samples were collected from the furnace and heated up to 650 °C in air for 2 h to deplete the carbon. The disc samples' color turned from dark black to gray white in this process due to the loss of carbon. A parallel comparative experiment was conducted by replacing the rice bran with commercial carbon black while all the other conditions remained the same. Finally, the products were characterized by XRD (MiniFlex XRD, Rigaku Corporation, Japan; Ni-filtered Cu K_α radiation $\lambda = 1.54178$ Å, 2°/min with a step width of 0.02°) and FE-SEM (Quanta 3D FEG, FEI Company, USA).

3. Results and discussion

Cryo-milling of ductile materials, such as aluminum powders, has been proven to be a useful method for making materials with ultrafine microstructures. In this experiment, the cryo-milling process split the original particle into much smaller pieces as well as formed a thoroughly dispersed system. Fig. 1 shows FE-SEM micrograph of the as-milled Al and rice bran powder mixture that was employed to synthesize AlN. The powder consists of irregular particles and possesses a size range of 1–20 μm, which is much smaller than the original size of Al and rice bran powders. The density of the green bodies was obtained by measuring the weight and thickness of the compact discs, which were 1.640 g/cm^3, 1.650 g/cm^3, 1.664 g/cm^3 and 1.709 g/cm^3 for the discs under the compression pressure of 160 MPa, 320 MPa, 480 MPa and 640 MPa, respectively. The density revealed the porosity difference in the samples, which, we believe, would affect the nitrogen diffusion, in consequence, the AlN formation and their morphology.

Fig. 2 shows the XRD patterns for the initial powders and the AlN products. Fig. 2(a) is for the initial powders and has only peaks for aluminum phase, indicating that the initial aluminum powders are well preserved by the inert atmosphere from oxidization during the milling process. The nitridation products were confirmed to be hexagonal AlN by the XRD results. Regardless of the different compaction pressure levels used to form those green bodies, the final products share the same AlN XRD patterns, and Fig. 2(b) shows a typical XRD pattern for the products. According to the XRD data, the obtained product is hexagonal AlN with lattice parameters of $a = 3.129$ Å and $c = 4.992$ Å, which are in good agreement with JCPDS card: No. 25-1133. The XRD pattern is apparently broadened, which means the AlN crystals are much smaller than those in bulk AlN. Although the compaction pressures in forming the green bodies did not significantly affect the XRD pattern of the AlN products, the compaction pressure was found to affect significantly the morphologies of the products.

FE-SEM images for AlN products are shown in Fig. 3. All the images were collected from the cross-section of those disc-shaped samples. The compaction pressures under which the green bodies were formed are as following: 160 MPa in Fig. 3(a), 320 MPa in Fig. 3(b), 480 MPa in Fig. 3(c) and 640 MPa in Fig. 3(d). It is obvious that the morphologies of the primary products are strongly dependent on the compaction pressure: appropriate pressures (320–480 MPa) lead to a high yield of fibers; the products for lower or higher pressure levels primarily consist of agglomerated AlN particles, seen in Fig. 3(a) and (d). The AlN fibers were found to have an aspect ratio up to 400, diameter in the range of 50–600 nm, and tens of

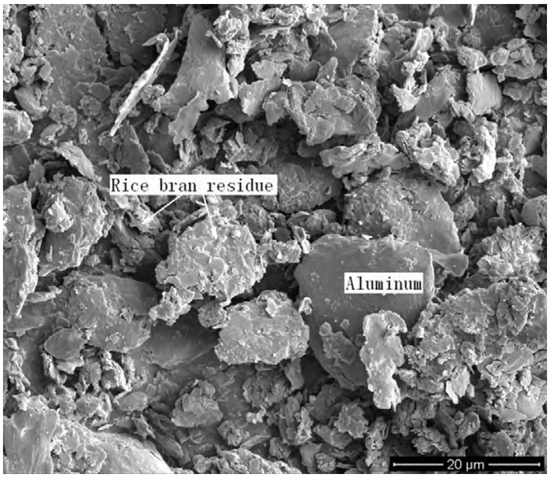

Fig. 1. FE-SEM image of the raw Al-rice bran powder mixture.

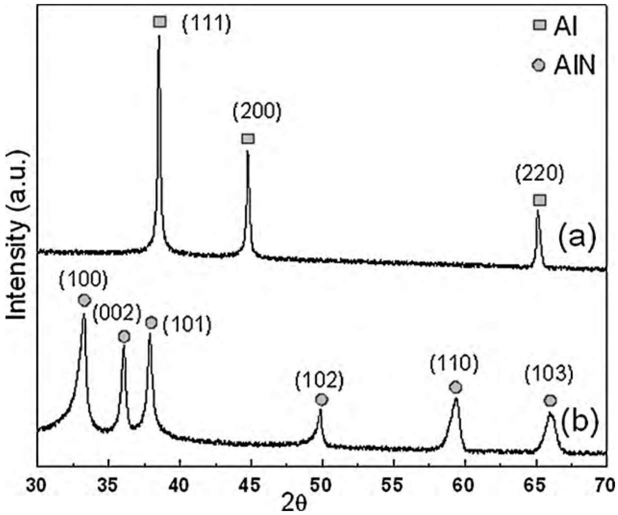

Fig. 2. XRD pattern for initial Al-rice bran powder (a) and a typical AlN product (b).

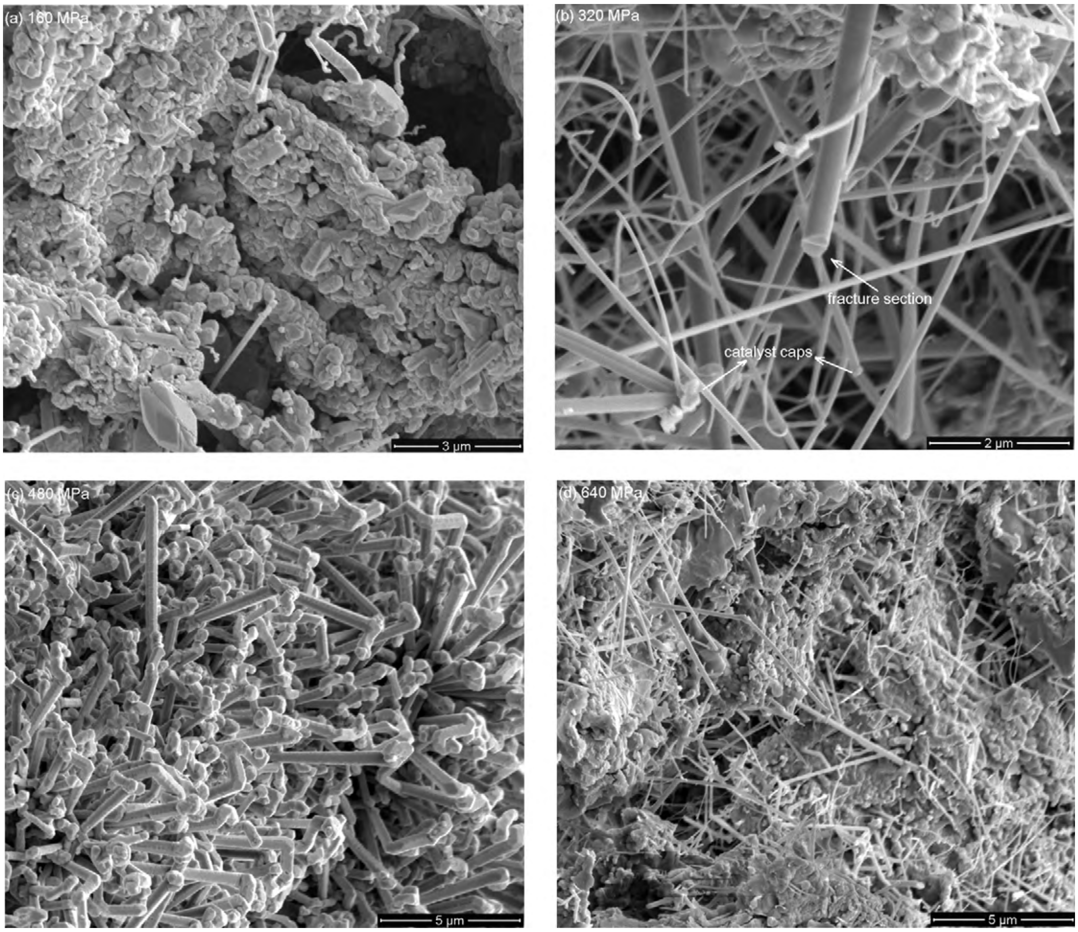

Fig. 3. FE-SEM images (sample cross-section) for the AlN product under different pre-compression pressure levels (160 MPa, 320 MPa, 480 MPa and 640 MPa).

micrometers in length. The AlN fiber diameter is more uniform in the samples prepared under 480 MPa of compression, in comparison to those samples at 320 MPa. In both cases, caps on the tip of the fibers are apparent, which evolved from the liquid catalyst drops involved in the VLS mechanism by which AlN fibers grew [3] (more pronounced in Fig. 3(c)).

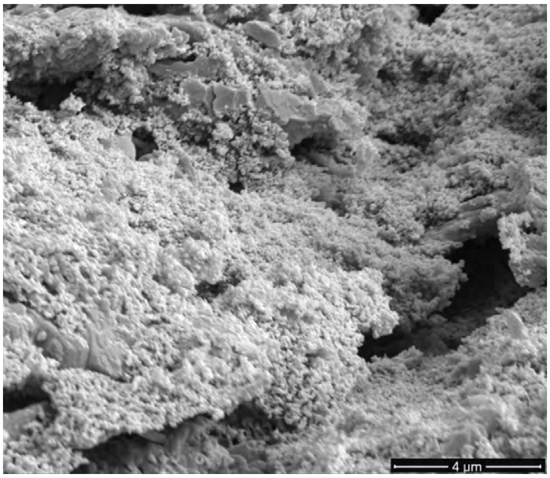

Fig. 4. A typical FE-SEM image of the AlN powder from nitridation of Al–carbon black powder (pre-compression pressure of 320 MPa).

The XRD results and FE-SEM (Fig. 4) for the control experiment, using pure carbon black instead of rice bran, were also obtained in the same way. The peaks in XRD patterns for all the samples were originated from AlN and all the products gave nearly the same morphologies, only AlN nanoparticles and no AlN fibers. The comparative tests using carbon black and aluminum powder testify the importance of both feedstock compositions and the compression pressure of the green body to the formation of AlN nanofibers. The trace metal elements in rice bran may vary based on the locations where the rice bran was grown, it was reported that the trace elements in rice bran may include K, Ca, Mg, Mn, Cr and others (several to hundreds μg/g in dry weight) [16]. The rice bran used in this study was examined by XPS (X-ray photoelectron spectroscopy) to investigate the trace metals. After heated the rice bran to 600 °C in air for 2 h, the ash was analyzed, and the results are shown in Table 1. It has 6% CaO, 5% MgO, and about 1% of Fe,Co,Ni. In this experiment, the pre-compression pressures on the green bodies are believed to alter the volumetric density of the AlN nuclei formed in the initial phase of the reaction (low temperature), since the porosities are different, which affected the nitrogen diffusion into the compact samples; and the formation of the AlN fibers was followed when temperature went higher by VLS (vapor–liquid–solid) mechanism [3,17]. The catalyst-assisted VLS growth is mediated by a liquid–solid

Table 1
Concentration of species in rice bran ash.

Elements (in rice bran ash)	wt%
C	80.0
SiO_2	8.0
CaO	6.0
MgO	5.0
Fe, Cr, Ni (oxide)	1.0

interface: a liquid droplet, which is saturated by vapor species and located at the growth front of the fibers, acted as the catalytic active site. In the present study, it is reasonable to believe that only a proper population of AlN nuclei formed under relatively low temperature (<660 °C) would eventually lead to the growth of fibers by the VLS mechanism.

At a temperature as low as 550 °C, the nitridation of the Al and N_2 began [18]. The N_2 diffused into the compacts where reaction between solid Al and nitrogen happened to form AlN on the outside of the aluminum particles. As the temperature went higher, the trace metals in the rice bran agglomerated onto AlN nucleus to form alloy liquid droplets; on the other hand, the tiny aluminum particles trapped by AlN shell melt and this changed the contact opportunity between nitrogen and aluminum. Herein, the amount of AlN formed on the outside of the aluminum particle could make big difference since it remained solid and could control the contact window of the aluminum and the nitrogen. For the samples with plural AlN fibers, it is believed that the population of the AlN seeds formed at lower temperature is desirable to protect the aluminum inside from sufficiently contacting the nitrogen in the gas phase; whereas, the aluminum inside the AlN shell evaporated to escape into gas phase since the vapor pressure of aluminum is increased due to a big curvature (vapor pressure for small particle size, given by Kelvin equation $\ln(p/p_o) = (2\gamma V_m)/(rRT)$) and the high temperature. The evaporation of the aluminum improved the mass transportation for aluminum, and it could move farther than liquid aluminum. The aluminum gas is easy to condense into the alloy liquid droplets adhering to the AlN nucleus formed when the temperature was high. In the liquid droplets saturated by aluminum and nitrogen, the reaction between aluminum and nitrogen happened inside forming AlN as the same time the AlN solidified out from the drops because of a higher melting point and grew on the AlN seeds. In this process AlN grew out of the liquid matrix and elongated continually. When the aluminum element was depleted, the reaction between aluminum and nitrogen ended and the liquid drops remained at the tips of fibers; it finally solidified there as the temperature dropped, which had been confirmed by experimental observation, SEM images in Fig. 3(b) and (c).

The samples formed at 320 MPa and 480 MPa should induce a proper population of AlN seeds when the temperature was low and just right amount of nitrogen diffused into the disc samples due to the perfect porosity, and the chemical reaction in these samples could be described using the discussions above and finally, AlN fibers were produced. However, under a lower compaction pressure of 160 MPa, more nitrogen diffused into the loosely compacted samples because there were more pores in the compacts. The abundant nitrogen reacted with aluminum to form AlN, which almost depleted the aluminum elements at the lower temperature stage; as a result, when the temperature went high and the growth mechanism was favorable to grow fiber, there was no enough aluminum supply. So the sample produced mainly AlN particles, shown in Fig. 3(a). Under the higher compression pressure of 640 MPa, however, less nitrogen could diffuse into the denser samples at lower temperature stage because there were less pores in the compacts which resulted in less AlN formed on the outside of aluminum particles in the denser samples. Once the temperature went high and the aluminum melted, since there was few AlN shell barrier outside the aluminum droplets, the nitrogen could easily contact liquid aluminum, which resulted into many AlN crystals formed over a very short time; consequently, there was not much Al left for each crystal seed to grow up. So the tiny AlN particles eventually agglomerated other than growing fibers by VLS mechanism, Fig. 3(d). Although the primary product in the sample formed under 640 MPa was nano-sized AlN powder, there were still some nano-sized fibers located near the cracks, which means it formed proper population of AlN crystal seeds in those locations (just like the cases discussed above for the samples formed under 320 MPa and 480 MPa) at a low temperature, and followed the same mechanism the fibers grew.

4. Conclusion

AlN nanoparticle and nanofibers were synthesized by directly nitridation of cryogenic milled rice bran, an abundantly available agricultural byproduct, and commercial aluminum powder mixture. The dependence of the morphologies of the product, AlN, on the compaction pressure levels was investigated and discussed in details. A green body compression pressure range, from 320 MPa to 480 MPa, was identified to promote the AlN fiber yield. The VLS growth mechanism and the importance of rice bran as dispersant/catalyst donor were suggested and discussed for the formation of AlN fiber. This pressure controlled morphology method could be employed to synthesize AlN nanofibers at large scale and low cost.

Acknowledgements

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