JOURNAL OF MATERIALS SCIENCE **39** (2004) 3167–3169

Synthesis and characterization of nanocrystalline aluminum nitride from a low temperature combustion precursor

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In recent years, a lot of interest has been shown in aluminum nitride nanopowder. This is because that AlN has high thermal conductivity, high thermal stability, high electrical resistivity, low dielectric constant, and a thermal expansion coefficient matched with silicon [1]. AlN is a promising material for hybrid substrates in circuits, heat sinks, and high power/high frequency electronic devices [2], and is also important for infrared and ultraviolet optoelectronic parts and surface acoustic wave devices [3, 4]. In addition, AlN can be used for melting crucibles, cutting tools, and fillers for polymer. Although AlN powders have been synthesized by many methods [5], the commercially available AlN powders have been mainly produced by carbothermal reduction process. However, a high calcining temperature (more than 1600 °C) and long mixing times of the alumina and carbon source is still required to obtain high-quality AlN powder [6].

The present work is concerned with the synthesis of AlN nanocrystalline powder from a new carbothermal reduction process with a low temperature combustion precursor. The method was adopted due to the possibility of obtaining a uniform mixture of nano-sized alumina and carbon from a low temperature combustion reaction of a solution of aluminum nitrate, urea, and cane sugar.

Stoichiometric amounts of aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) and urea were first dissolved in double distilled water and then mixed with aqueous cane sugar solution in a beaker. The amount of urea as fuel, which can react completely with aluminum nitride, was calculated using the method of Jain and Adiga [7], while the amount of cane sugar was calculated according to the molecular ratio of aluminum and carbon ($n_{Al}/n_c = 1.8$–2.5). The resultant solution was heated at 200–300 °C in a muffle furnace to produce loose and brown-black precursor powders containing amorphous alumina and carbon. The precursor powder was placed in graphite crucible, and calcined in a graphite furnace at 1500 °C for 2 h with a flowing nitrogen atmosphere. After the carbon was removed at 700 °C for 2 h in air, the resultant nanocrystalline powder was uniaxially pressed at ∼100 MPa into cylindrical compacts 10 mm in diameter and 8 mm in height, which were then pressurelessly sintered in N_2 at 1800 (5 °C/min) for 2 h, in a graphite furnace. The bulk density was measured by the Archimedes method. The thermal conductivity of the AlN pellets was measured by laser flash method. The crystalline phases were identified by X-ray diffraction with Cu K_α radiation. The morphology of AlN and the particle size of nanocrystalline powder were characterized by Transmission Electron Microscopy. The Brunner–Emmett–Teller (BET) method was used to measure the specific surface area. The nitrogen and oxygen content of the resultant powders were found using LECO nitrogen–oxygen apparatus.

Urea and aluminum nitrate can react to form a complex of $Al(NO_3)_3{\cdot}CO(NO_2)_2{\cdot}H_2O$ or $Al(NO_3)_3){\cdot}CO(NO_2)_n$ ($n = 2$–6) in the as-prepared solution. On heating, the complex decomposes to $Al(NO_3)_3{\cdot}CO(NO_2)$ and urea or water. On further heating the complex can decompose to Al_2O_3 and other unidentified products with a flame containing NH_3, CO_2, NO_2, and O_2. Therefore, aluminum nitrate and urea can combust and form aluminum urinates with the reaction of NH_3 and NO_2, following the evolution of N_2, O_2, and H_2O. Carbon can be formed from sugar cane by pyrolysis at high combustion temperature or dehydration in strong nitric acid [8]. The detailed procedure for synthesising nanocrystalline AlN powder is shown in Fig. 1. During nitridation reaction of the precursor, the amorphous alumina and carbon could be crystallized and amorphous alumina transformed into γ-Al_2O_3 without the formation of α-Al_2O_3 phase. Thus nanosize AlN was obtained via carbothermal reduction reaction as represented in the following:

$$2Al_2O_{3(C)} + 3C_{(C)} + N_{2(g)} \rightarrow 2AlN_{(C)} + 3CO_{2(g)} \quad (1)$$

Table I lists the characteristics of nanocrystalline AlN powder as synthesized.

Fig. 2 shows the X-ray diffraction patterns of the AlN powders synthesized by carbothermal reduction at 1500 °C for 2 h. All of the peaks indicate that the powders are hexagonal AlN with a wurtzite structure. All reflections are broadened due to the size effect, which indicates that the grain size of the samples is on a nanometer scale. The average size of the obtained AlN particles is estimated to be approximately 50 nm by the Scherrer formula.

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TABLE I The properties of AlN nanocrystalline power and sintering body

Chemical composition (wt%)				Mean particle size (d_{ITEM}/nm)	Particle surface area (m^2/g)	Density (g/cm^3)	Thermal conductivity (W/m·K)
N	O	C	Si				
32.5	1.8	0.1	0.003	50–80	21.91	3.21	70.6

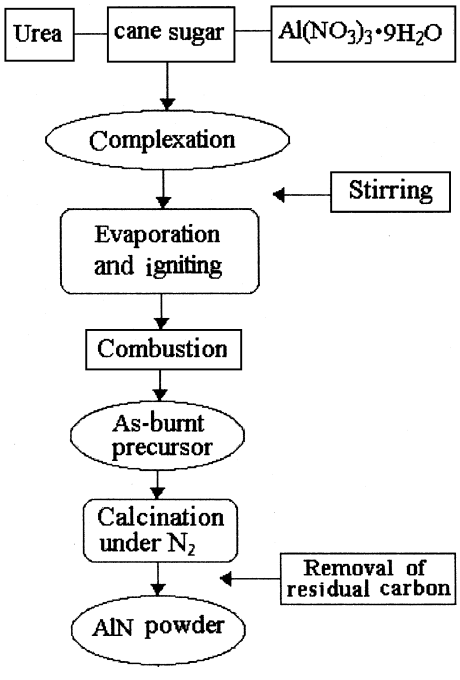

Figure 1 Schematic illustration of the preparation procedure of nano-size AlN powder.

The morphology of the AlN nanocrystalline was observed by TEM. Fig. 3 shows the TEM image of AlN nanocrystalline powder. It is clearly seen that the particles are in nearly spherical in shape, and the average particle size of the sample is about 50–80 nm. This agrees very well with the results of XRD measurements. Fig. 3b is a selective area electron diffraction pattern, from which all the diffraction rings can be indexed to the hexagonal AlN. Density and thermal conductivity values of AlN specimens sintered without sintering aids at 1850 °C for 2 h are showed in Table I.

Fig. 4 is the SEM micrograph of a fractured, sintered AlN specimens. It can be seen that full densification

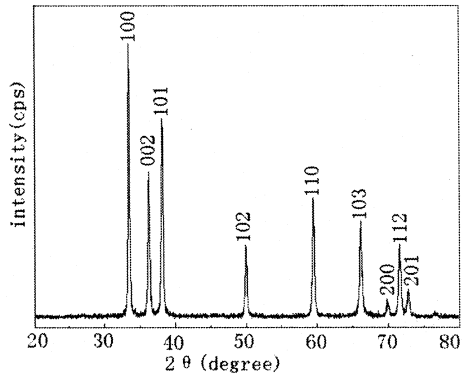

Figure 2 XRD pattern of AlN powder as synthesized at 1500 °C in nitrogen for 2 h.

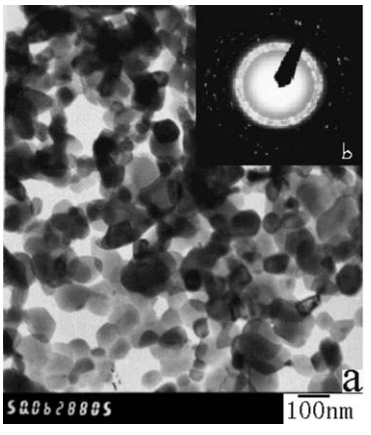

Figure 3 (a) TEM image of the AlN nanocrystalline powder and (b) selective area electron diffraction pattern.

was achieved by sintering at 1850 °C for 2 h without sintering aids. The grain growth of the nanocrystalline AlN was quite rapid so that when 98.5% of the theoretical density (3.21 g/cm^3) was obtained, the grain size was of the order of 2–4 micrometrs. The final grains were over 25 times larger than the initial grain size.

AlN nanocrystalline powder has been synthesized through carbothermal reduction of a low temperature combustion precursor containing homogeneous alumina and carbon at 1500 °C for 2 h. The prepared AlN powders have an average size of about 50–80 nm and are approximate spherical in shape. Nanocrystalline AlN specimens can achieve 98.5% of the theoretical density by pressureless sintering without sintering aids, showing that nano-sized AlN powders possess excellent sintering properties.

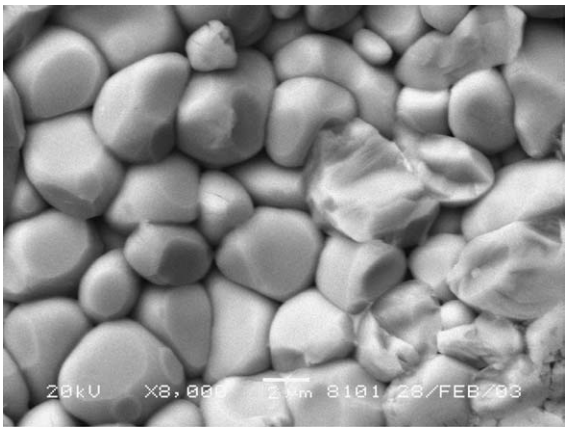

Figure 4 SEM micrograph of sintered AlN specimens at 1800 °C for 2 h without sintering aids.

Acknowledgment

This work was supported by the National Defense Preliminary Research Foundation of China.

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Received 16 April
and accepted 3 December 2003