Powder Technology 287 (2016) 341–345

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

A new method for synthetizing nanocrystalline aluminium nitride via a solid–gas direct reaction

E.S. Caballero [a], J. Cintas [a,*], F.G. Cuevas [b], J.M. Montes [a], J.M. Gallardo [a]

[a] Metallurgy and Materials Engineering Group, Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Camino de los Descubrimientos, s/n, 41092, Sevilla, Spain
[b] Department of Chemistry and Materials Science, Escuela Técnica Superior de Ingeniería, Universidad de Huelva, Campus La Rábida, Carretera Palos s/n, 21819, Palos de la Frontera, Huelva, Spain

ARTICLE INFO

Article history:
Received 28 April 2015
Received in revised form 28 September 2015
Accepted 16 October 2015
Available online 17 October 2015

Keywords:
Nanocrystalline
Mechanosynthesis
Nitriding

ABSTRACT

Herein, we describe a new method for preparing AlN powder by milling aluminium powder at room temperature under a flowing NH_3 gas atmosphere. The initial aluminium powder has a mean particle size of 80.5 μm. During mechanical alloying, NH_3 decomposed at room temperature and N was incorporated into the aluminium crystal lattice. A subsequent heat treatment of the milled powders under vacuum for 1 h resulted in the formation of substantial amounts of AlN. Two different heat treatment temperatures have been tested (650 and 1000 °C). Different milling runs were carried out to evaluate the influence of the milling duration on the amount of AlN formed. Quantification by XRD indicated that the AlN amount that was formed was strongly influenced by the milling time. The heat-treated powders, which were milled for 25 h, led to a significant amount of nanocrystalline AlN (i.e., higher than 97 wt.%).

1. Introduction

Aluminium nitride offers a unique combination of properties that has attracted much interest in the electronics industry in recent years. These properties include high thermal conductivity, good electrical resistivity, high melting temperature, good thermal shock resistance, wide band gap, low dielectric constant, high mechanical strength, and a thermal expansion coefficient similar to that of silicon [1–5]. This combination of properties makes AlN an ideal material for manufacturing integrated circuits in electronic devices.

Two primary commercial processes are employed for the synthesis of AlN powder as follows: (a) *carbothermic reduction and nitridation* (CRN) of alumina or aluminium hydroxide with carbon powder at a high temperature ($Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g)$) [6] and (b) *direct nitriding* (DN) of aluminium metal or aluminium salts under nitrogen ($2Al(l) + N_2(g) \rightarrow 2AlN(s)$) or ammonia. In DN, two reactions are possible depending on whether the ammonia decomposes prior to the nitriding reaction [7], ($Al(l) + (1/2)N_2(g) + (3/2)H_2(g) \rightarrow AlN(s) + (3/2)H_2(g)$) or ($Al(l) + NH_3(g) \rightarrow AlN(s) + (3/2)H_2(g)$).

The DN process is simpler and not very expensive because nitriding results from an exothermic reaction ($\Delta H_0 = -318$ kJ/mol) [8], which results in lower energy consumption even though it is necessary to reach temperatures at approximately 1400 °C. However, this reaction is difficult to control and produces highly agglomerated AlN particles, which require crashing [9]. These disadvantages make the CRN process more attractive because its efficiency is higher and the resulting powder has a higher purity, lower hygroscopy, greater sinterability and uniformly sized particles [8,10]. However, the high temperature required in this method, which is typically between 1700 and 1900 °C, is the greatest obstacle facing large-scale production [11]. The addition of catalyst agents containing calcium (i.e., CaF_2, $CaCO_3$, $Ca(OH)_2$, and CaC_2) to the Al_2O_3–C powder mixture in the CRN processes allows for the AlN formation temperature to be decreased to 1350 °C [10].

A third production method is also employed via $Al(C_2H_5)_3$ nitriding in a gas phase reaction ($Al(C_2H_5)_3 + NH_3(g) \rightarrow AlN + 3C_2H_6$), which requires a high ammonia flow (1000 cm^3/min). This method produces fine AlN particles with a high purity but low oxidation resistance [9,12].

Other alternative but less widespread methods are being studied on the laboratory scale to prepare aluminium nitride. These methods include self-propagating high-temperature synthesis, SHS [8,13–15], aluminium cryomilling with a mixture of carbon and silica powders followed by heat treatment at high temperatures in a nitrogen atmosphere [11], filtered arc ion plating deposition [16], reactive radio frequency (RF) plasma spraying [17], and laser assisted chemical vapour deposition (LA-CVD) [18].

In general, nitriding processes require the destruction of oxide film covering Al particles to allow for direct contact between the metallic aluminium and the atomic nitrogen, which favours the formation of AlN. This nitriding reaction is more significant above the melting temperature of Al, and the conversion rate increases with temperature [19].

Herein, we propose a new and simpler method for the synthesis of AlN by direct nitriding, and this process involves milling of aluminium powder in an ammonia gas flow at room temperature. The milling process produces fresh Al surfaces, and simultaneously, the energy of

* Corresponding author.
E-mail address: jcintas@us.es (J. Cintas).

http://dx.doi.org/10.1016/j.powtec.2015.10.023
0032-5910/

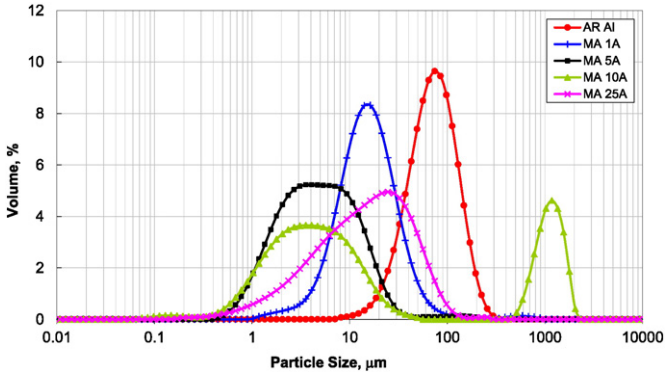

Fig. 1. Granulometric curves of the mechanically alloyed powders under a flowing ammonia atmosphere and AR Al.

the process allows for the decomposition of the flowing NH_3 regardless of the fact that the process takes place at room temperature.

2. Material and methods

The starting material consisted of atomized elemental aluminium powder (AS 61, Eckart) with a purity level higher than 99.7% and a mean particle size of 80.5 μm. A high-energy attritor ball-mill [20] was used to process the aluminium powder in a water-cooled stainless steel vessel with a capacity of 1400 cm^3. The mill contained 72 g of powder and 3600 g of balls (diameter of 4.65 mm, and charge ratio of 50:1) [21]. 3 wt.% of the micropowder organic wax (ethylene bis-stearamide) was used to balance the welding and fracture processes of the Al powders during milling [22]. All of the milling experiments were carried out with a rotor speed of 500 rpm under continuous ammonia gas flow (1 cm^3/s) for 1, 3, 5, 7.5, 10, 15 and 25 h. The ammonia gas (Air Liquide) had a purity higher than 99.96%. The milled powders were heat treated at 650 °C. In addition, the powders milled for 25 h were also heat treated under the same conditions (time and atmosphere) but at 1000 °C both in the powder form and as compacts after cold compaction at 1000 MPa. All of the heat treatments in this study were performed for 1 h and carried out under vacuum (5 Pa).

Granulometric characterization of the milled powders was carried out using a laser diffraction analyser (Malvern Mastersizer 2000), and the powder morphology was studied using a scanning electron microscope (SEM, Philips XL-30, working at 15 kV, 10 mm WD and 1000× and 5000×). X-ray diffraction analysis (XRD, Bruker D8 Advance, using CuKα radiation, a step size of 0.015° and a time step of 0.5 s) was used to identify and quantify the phases as well as to measure their crystallite size. The XRD studies were carried out on the milled and heat-treated powders. A universal testing machine (Instron 5505) with a load cell of 100 kN was used to test the compressibility of the powders. The nanocrystalline nature of the AlN powder was confirmed by transmission electron microscopy (TEM, Phillips CM200 and FEI Talos, both operated at 200 kV). The TEM studies were carried out on cold-pressed and sintered compacts prepared from powders milled for 25 h.

3. Results and discussion

3.1. Granulometry and morphology

Seven experiments with different milling times were performed to study the influence of the ammonia flow on the mechanical alloying of the aluminium powder. The effect of the milling duration on the powder characteristics and the conversion rate from aluminium to aluminium nitride were studied.

Fig. 1 shows the particle size distribution of the as-received aluminium (AR Al) and the mechanically alloyed powders under an ammonia flow for 1, 5, 10 and 25 h (MA 1A, MA 5A, MA 10A and MA 25A, respectively).

As expected, the average particle size of the mechanically alloyed powders decreased compared to that of AR Al (80.5 μm). However, due to the smaller particle size, the powders exhibited a greater tendency to agglomerate, resulting in a broader size distribution and in some cases, the appearance of humps for larger sizes (MA 10A). Therefore,

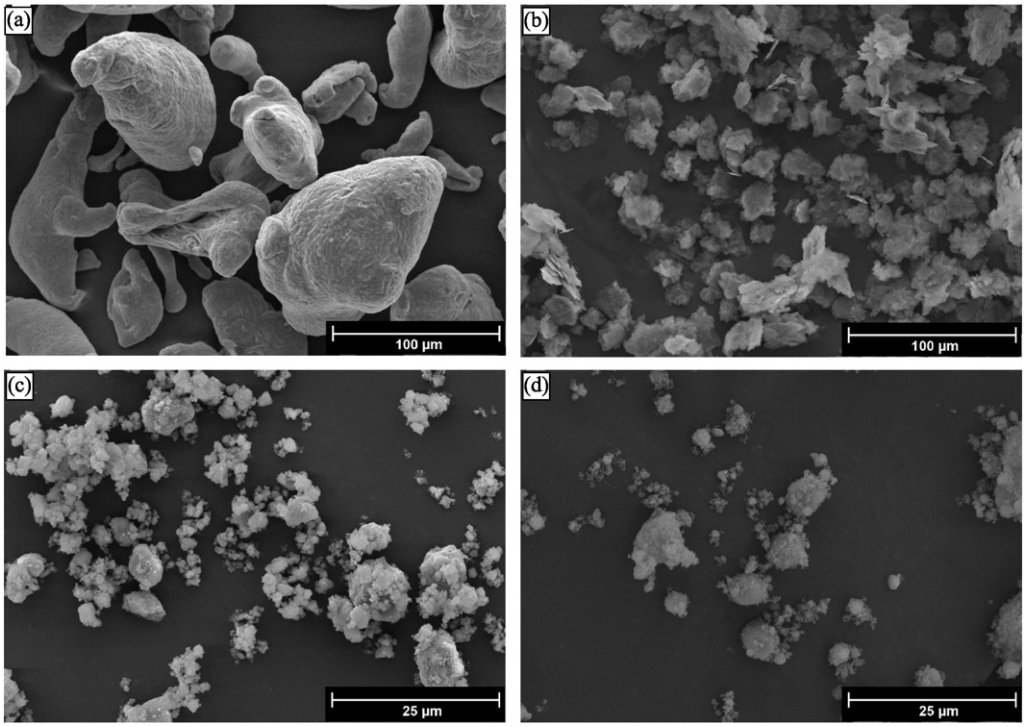

Fig. 2. SEM-SE images of a) AR Al, b) MA 1A, c) MA 5A and d) MA 25A powders. Note the higher magnification of the last two images.