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Synthesis of nanostructured AlN by solid state reaction of Al and diaminomaleonitrile

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ABSTRACT

The solid state reaction of diaminomaleonitrile (DAMN) with aluminum via both mechanochemical and thermal treatment routes was studied by X-ray diffraction and Fourier transform infrared spectroscopy. During the milling process, the reaction starts with the deammoniation of the DAMN molecules, followed by the formation of nanostructured AlN powder as the main solid product after milling for 7 h. The reactivity of the mixed powder was also investigated during the conventional thermal treatment process using differential scanning calorimetry, derivative thermogravimetry and thermogravimetric analysis. The results reveal that DAMN starts to polymerize at 192 °C by the elimination of the amine groups. Furthermore, increasing the annealing temperature leads to the formation of a nitrogen-containing carbonaceous material with the structure similar to non-crystalline carbon. However, no evidence for the formation of AlN was observed in the annealed samples even at temperatures as high as the Al melting point.

1. Introduction

Metal nitrides are a wide group of ceramic materials with individual properties and extensive industrial applications. Among the others, group III-nitrides present a large potential for applications in optoelectronic devices [1,2]. One of the group III-nitrides which attracted much attention during recent two decades is the aluminum nitride. Some unique features, such as high thermal conductivity, low dielectric constant, low linear thermal expansion coefficient and large band gap (6.2 eV), make AlN a potential candidate for electronic industrial applications like electronic packages, heat sinks and optical devices [3–6].

AlN can be synthesized by a variety of techniques, such as carbothermal reduction [6], direct nitridation process [7,8], chemical vapor deposition (CVD) [9,10], metalorganic chemical vapor deposition (MOCVD) [11], organometallic procedure [12], solvothermal process [13], combustion synthesis [14] and mechanochemical synthesis [15,16]. Among these methods, mechanochemical synthesis through ball milling stands out as the easiest way for the fabrication of nitrides without requiring any controlled atmosphere condition and high technological equipment [17]. Milling can also be used as a pre-treatment step, namely "mechanical-activation", for other synthesizing methods, especially when a significant reduction in reaction temperature is desirable [18,19].

Most of the research on mechanochemical synthesis of AlN have been performed by the solid–gas metathesis (SGM) route, which consists of the reactive milling of Al or Al_2O_3 under N_2 or NH_3 atmosphere [15,16]. Yet, the full conversion of the reactants into AlN can hardly be achieved in a reasonable time due to the high stability of N_2 and the poor contacting of the reactant materials (solid–gas). Moreover, in most cases, processing in a controlled atmosphere is also required. In order to overcome these limitations, the gaseous nitrogen-rich phase should be substituted with solid nitrogen-containing (SNC) compounds to improve the contact between reactants and to promote the formation of the nitride product [20].

Recently, it has been demonstrated that organic SNC compounds can be used for synthesizing metal nitrides by the solid state metathesis (SSM) route. Based on this procedure, various metal oxides were heated in the presence of cyanamide [21] or one of its oligomers, such as disyanamide [22], melamine [23] and carbon nitride (C_3N_4) [24], in sealed conditions. As a result, the formation of a wide variety of metal nitride nanoparticles, such as AlN, GaN, VN and TiN, was reported using this processing route.

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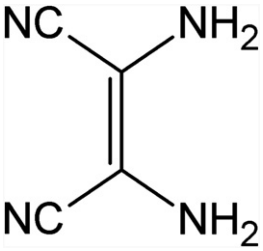

Fig. 1. Chemical structure of the DAMN molecule.

However, the high temperature required for the reaction completion (about 1150 °C in the case of AlN [21–23]) represents a serious drawback. Hence, there is the need for the reduction of the reaction temperature and for performing the tests in ambient atmosphere. To achieve these purposes, high-energy ball milling can be used as an alternative technique to the conventional thermal treatment processing. With regard to this, Zhang et al. introduced a milling procedure for synthesizing AlN by mechanochemical reaction of Al and melamine [25]. They successfully synthesized nanocrystalline AlN just after 14 h of milling at room temperature. Recently, we reported a mechanistic approach for the reaction which takes place during this milling process [26]. However, the specific symmetry of melamine s-triazine ring makes the mechanism difficult to be fully interpreted.

In this work, we developed a simple mechanochemical process for synthesizing AlN using a tetramer of cyanogen, the diaminomaleonitrile (DAMN), as a source of nitrogen. In contrast to cyanamide, cyanogen and its oligomers have not been used for formation of nitrides yet. DAMN is a low-cost organic compound with a high nitrogen content (the chemical structure of the DAMN molecule is illustrated in Fig. 1). The specific chemical geometry of nitrogen bonding in the DAMN molecule makes it more favorable than melamine or other materials with s-triazine rings from the viewpoint of chemical bond evolutions and may permit to follow the degradation and polymerization of the molecule during both mechanochemical and thermal treatment methods.

2. Experimental procedure

Al powder (purity 99.5%, Mashhad Powder Metallurgy Co.) was mixed with diaminomaleonitrile (purity 98%, Fluka) with a molar ratio of 4:1. The mixed powder (1.5 g) was charged into a steel vial together with stainless steel balls of two different sizes (10 and 8 mm) to give a ball to powder weight ratio of 50:1. After sealing the vial valve, milling process was conducted using a planetary ball-mill (manufactured by Khorasan Co.) in ambient atmosphere with rotating speed of 300 rpm for various times up to 12 h. Thermal analysis was carried out using a Netzsch 409 PC Luxx calorimeter at a heating rate of 10 °C/min under argon atmosphere. Phase analysis of the samples was performed by X-ray diffraction (XRD) using a Philips X'Pert X-ray diffractometer with Cu$K\alpha$ radiation (λ=0.154060 nm). In order to measure crystallite size of the milled products, the Rietveld method was used and the diffraction data were collected over a 2θ range of 4°–90° with a step width of 0.02°. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a ThermoNicolet Avatar 370 infrared spectrometer at room temperature with the KBr pellet technique. The measurements were obtained in the range 400–4000 cm^{-1} at a resolution of 2 cm^{-1}. Scanning electron microscopy (SEM) investigations were conducted using a Gemini 1530 (Zeiss) microscope operating at 20 kV.

High resolution transmission electron microscopy (HRTEM) investigations were performed using a Tecnai F30 (FEI company) microscope, operating at 300 kV. Samples were prepared by sonication of the powder in ethanol and putting a drop of suspension on a copper grid.

3. Results and discussion

3.1. Mechanochemical process

3.1.1. XRD analysis

Fig. 2 illustrates the phase evolution of the powder mixture during the milling process. The starting material (0 h) consists of a mixture of Al and DAMN. After milling for 6 h, the XRD pattern shows a significant broadening of the diffraction peaks belonging to Al and DAMN, which can be ascribed to grain refinement and to the introduction of lattice defects. No trace of AlN is detectable at this stage. Along with additional peak broadening for the Al and DAMN phases, the pattern of the powder mixture milled for 7 h reveals the presence of broad AlN diffraction peaks with very low intensity. With further milling up to 12 h, the peaks of the Al and DAMN reactants are no longer visible, whereas the intensity of the AlN peaks is remarkably increased, which indicates that the mechanochemical reaction is complete at this milling stage. The AlN XRD peaks are rather broad, which implies the formation of a nanocrystalline AlN structure. This is corroborated by Rietveld structure refinement, which reveals a mean crystallite size of about 18 nm for the AlN powder milled for 12 h.

3.1.2. FTIR characterization

The FTIR spectra for the powder mixture after different milling times are shown in Fig. 3. In order to identify possible bond changes occurring during milling, the IR spectrum of the pure as-received DAMN is also plotted in Fig. 3 (0 h). The main band characteristics of the DAMN arise from several functional groups; the bands obtained at 3200–3450 cm^{-1} correspond to the stretching vibration mode of the amine groups. The strong and sharp bands at 2166 and 2213 cm^{-1} are due to the stretching vibration mode of the nitrile groups. Other transmittance peaks at 1600–1650 cm^{-1}, 1200–1400 cm^{-1} and below 750 cm^{-1} result from the C=C and C–N bond stretching and the C–C bending and rotational vibrations, respectively.

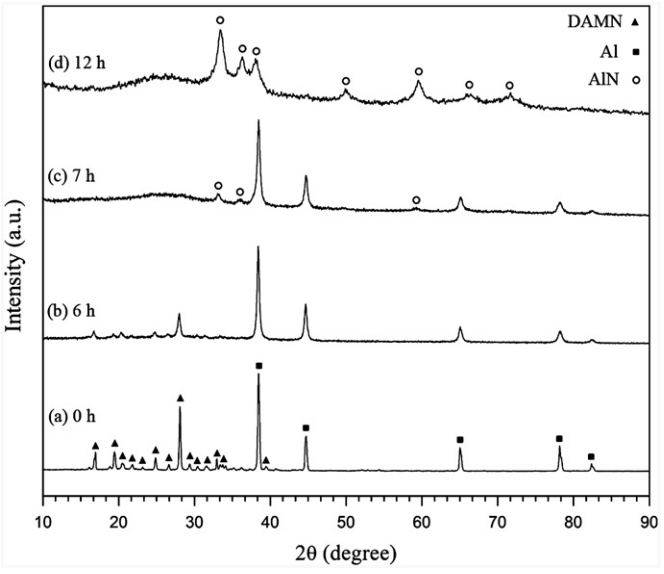

Fig. 2. XRD patterns of the powder mixture after milling for various times.