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A combined experimental and theoretical investigation of the Al-Melamine reactive milling system: A mechanistic study towards AlN-based ceramics

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ABSTRACT

A versatile ball milling process was employed for the synthesis of hexagonal aluminum nitride (h-AlN) through the reaction of metallic aluminum with melamine. A combined experimental and theoretical study was carried out to evaluate the synthesized products. Milling intermediates and products were fully characterized via various techniques including XRD, FTIR, XPS, Raman and TEM. Moreover, a Boltzmann distribution model was proposed to investigate the effect of milling energy and reactant ratios on the thermodynamic stability and the proportion of different milling products. According to the results, the reaction mechanism and milling products were significantly influenced by the reactant ratio. The optimized condition for AlN synthesis was found to be at Al/M molar ratio of 6, where the final products were consisted of nanostructured AlN with average crystallite size of 11 nm and non-crystalline heterogeneous carbon.

1. Introduction

Nowadays, the demand for technically important nanoceramics with fascinating properties is quickly growing. However, the use of these nanoceramics is considerably restricted due to some difficulties related to the synthesis of nanoceramics. The main challenges are attributed to the accessibility to the expensive high-tech instrumentations and the low manufacturing yield which hinder large-scale production and increase the costs [1]. Therefore, the development of simple and non-expensive fabrication routes for the high yield preparation of nanoceramics is demanded. Among the various synthetic methods, mechanochemistry is known as a versatile and environmentally friendly approach for the synthesis of nanoceramics at ambient conditions [2,3]. Mechanochemistry is a branch of chemistry in which chemical reactions are induced through the input of mechanical energy [2,3]. This approach offers a unique opportunity for the synthesis of organic, inorganic and carbon-based nanomaterials [2–7]. Conventional high-energy ball milling, in which the activation energy is provided by the ball impacts, is frequently used for inducing mechanochemical reactions [8]. The process brings many advantages in comparison to the conventional wet chemical- and thermally-assisted routes, including solvent-free synthesis, increased reaction rates at low temperature, overall simplicity and very low production costs [2,3].

Among the nanoceramics fabricated by ball milling, nitrides of the group III have attracted significant attention due to their outstanding optical and electrical properties [9]. Nitrides are

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commercially synthesized by the carbothermal reduction of metal oxides in a flowing N_2/NH_3 gas mixture or through direct nitridation of metals at elevated temperatures [10–13]. Among the nitrides, AlN is of particular interest for electronic applications due to its unique properties, including a large band gap (6.2 eV), a low dielectric constant, high thermal conductivity and a low linear thermal expansion coefficient [11,14,15].

The mechanochemical synthesis of AlN has to date consisted of ball milling of Al or Al_2O_3 under N_2 or NH_3 atmosphere [16,17]. Although the process benefits from a room-temperature solid-state procedure, it still suffers from some serious drawbacks, such as the prolonged milling times and the requirement of pressurized toxic gaseous atmosphere [16,17]. The substitution of the gaseous atmosphere with a solid source of nitrogen would be a promising noteworthy approach. However, the choice of a proper, safe and non-explosive solid nitrogen-rich compound is challenging. It has been previously demonstrated that solid nitrogen-containing organic compounds (SNCOCs) such as cyanamide [18], dicyanamide [19] and melamine [20] have been feasibly employed for the simultaneous thermal reduction/nitridation of metal oxides. Various metal nitrides have been successfully fabricated at relatively high temperatures through this solid-state technique. Recent investigations revealed that the SNCOCs can be used for the synthesis of nitrides through the ball milling process [21,22]. In this case, the metal nitride is prepared by the milling of a SNCOC with the corresponding metallic element at room temperature. So far, the synthesis of metal nitrides such as AlN and TiN has been respectively reported through the mechanochemical reaction of Al and Ti with melamine, diaminomaleonitrile and urea [21–23]. Recently, we proposed the first stepwise mechanistic approach for the mechanochemical synthesis of nanostructured AlN through a detailed theoretical and experimental investigation of the Al-melamine system [24]. The results demonstrated that at the stoichiometric reactant ratios, the reaction was mainly governed by the polymerization of melamine and the formation of a carbon nitride (CN_x) phase. However, there is still a lack of knowledge regarding to the mechanochemical nitridation reactions induced by ball milling, the role of reactants ratio on the reaction mechanism and the structural characteristics of final products. The current study aims to investigate the effect of various amounts of reactants on the structures and types of the final products in the ball milling process. Moreover, the optimized experimental conditions for the synthesis of AlN are proposed.

2. Experimental procedures

2.1. Sample preparation

Al (Goodfellow, 99.5% purity, −120 mesh) and melamine (Khorasan Petrochemical Co., 99.8% purity, −325 mesh) powders were used as-received without any further purification. The powders were mixed with different Al-to-melamine molar ratios (Al/M) of 2, 4, 6 and 10. In each experiment, 3 g of the powder mixture was loaded into a hardened steel vial along with 10 mm diameter hardened steel balls to give a ball-to-powder weight ratio of 50:1. No additive or process control agent (PCA) was added to the mixture. Charging and discharging of the vials were done in a purified argon-filled glove box (less than 1 ppm O_2 and H_2O) to protect the materials from surface oxidation. Milling experiments were conducted using a Retsch PM-400 planetary ball mill at a rotating speed of 300 rpm. The milling was performed at room temperature for various times. The milling times were adjusted for the samples with various Al/M ratios based on the reaction completion times (monitored by XRD and FTIR).

For the phase characterization of carbonaceous by-product, a small quantity of powder milled for 6 h with Al/M = 6 was added to a 10 M aqueous solution of NaOH and stirred for 2 h at 85 °C. After centrifugation of the suspension, the resulting sediment was stirred again with 37% HCl at room temperature for 1 h. The remaining black particles were removed by centrifugation and washed with distilled water until it reached neutral pH value of 6–7. XRD and Raman measurements were carried out on this sample after overnight drying at 85 °C.

2.2. Materials characterization

X-ray diffraction (XRD) patterns were measured using a Philips X'Pert X-ray diffractometer with Co Kα radiation (λ = 0.17889 nm). Rietveld refinement was used to analyze the crystallite size of the milled products. Fourier transform infrared spectroscopy (FTIR) spectra were collected at room temperature over the range of 4000-400 cm^{-1}, using a ThermoNicolet Avatar 370 infrared spectrometer with KBr pellet technique. The X-ray photoelectron spectroscopy (XPS) experiments were carried out at room temperature in an ultra-high vacuum system equipped with a SPECS PHOIBOS 100 hemispherical electron analyzer. Raman analysis was performed using a DXR SmartRaman with an exciting laser wavelength of 532 nm and a resolution of 1 cm^{-1}. High resolution transmission electron microscopy (HRTEM) measurements were conducted by a Tecnai F30 (FEI company) microscope, operating at 300 kV.

2.3. Computational details

Ab initio density functional theory (DFT) calculations are performed using the projector augmented waves method, as implemented in VASP. Electron exchange and correlation energies are obtained with the generalized gradient approximation, as proposed by Perdew, Becke and Ernzerhof (PBE). The kinetic energy cutoff was set to 600 eV. The structures were optimized using a conjugate gradient method and the energy convergence criterion was set to 1.0e-6. For the molecular calculations, no Van der Waals interactions were included, assuming that the molecules are sufficiently separated in the experiments.

3. Results and discussion

The XRD patterns of powder mixtures milled for various times at different Al/Melamine (Al/M) ratios are presented in Fig. 1a–d. The weak peaks at $30° \leq 2\theta \leq 35°$ arise from the sample holder. It is inferred from the patterns that the final milling product changes by the variation of the Al/M ratio. In the system with Al/M = 2 (Fig. 1a), the peaks indexed to the reactants disappear after 12 h, suggesting that the reaction between Al and melamine has occurred. The peaks appearing at the milling times longer than 18 h are assigned to 2-cyanoguanidine ($C_2H_4N_4$) which is a dimer of cyanamid. No peaks corresponding to AlN are observed in the patterns (Fig. 1a), probably as a result of very fine crystallite size. However, the formation of AlN in the final product (sample milled for 24 h) is inferred from FTIR analysis, as is shown in the next section.

As the Al/M ratio increases to 4 and 6 (Fig. 1b and c), broad peaks of hexagonal AlN appear and become dominant, implying reaction of the Al particles with melamine and then, the formation of AlN. When the Al/M ratio exceeds 6 (Al/M = 10, Fig. 1d), an aluminum carbonitride (AlC_xN_{1-x}) phase is formed instead of AlN. The chemical composition of this phase was found to be $Al_{10}C_1N_9$, as determined by XPS analysis. Since the carbonitride phase is a nitrogen rich phase, it can be expected that the crystal structure should be similar to hexagonal-AlN. The peak appeared at $2\theta = 52.3°$ in some patterns is ascribed to iron contamination resulted from the milling