Journal of Solid State Chemistry 190 (2012) 8–11

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

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

Formation of nanocrystalline h-AlN during mechanochemical decomposition of melamine in the presence of metallic aluminum

S.A. Rounaghi [a,*], A.R. Kiani Rashid [a], H. Eshghi [b], J. Vahdati Khaki [a]

[a] Department of Materials Engineering, Ferdowsi University of Mashhad, P.O. Box No. 91775-1111, Mashhad, Iran
[b] Department of Chemistry, Ferdowsi University of Mashhad, P.O. Box No. 91775-1436, Mashhad, Iran

ARTICLE INFO

Article history:
Received 28 November 2011
Received in revised form
31 December 2011
Accepted 2 January 2012
Available online 8 January 2012

Keywords:
Melamine
Aluminum nitride
Mechanochemical decomposition
Infrared spectroscopy
X-ray diffraction
Thermal analysis

ABSTRACT

Decomposition of melamine was studied by solid state reaction of melamine and aluminum powders during high energy ball-milling. The milling procedure performed for both pure melamine and melamine/Al mixed powders as the starting materials for various times up to 48 h under ambient atmosphere. The products were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The results revealed that Al causes melamine deammoniation at the first stages of milling and further milling process leads to the s-triazine ring degradation while nano-crystallite hexagonal aluminum nitride (h-AlN) was the main solid product. Comparison to milling process, the possibility of the reaction of melamine with Al was also investigated by thermal treatment method using differential scanning calorimeter (DSC) and thermo gravimetric analyzer (TGA). Melamine decomposition occurred by thermal treatment in the range of 270–370 °C, but no reaction between melamine and aluminum was observed.

1. Introduction

Aluminum nitride is one of those advanced materials attracted many attentions in two recent decades. This modern ceramic is known for its great properties such as high thermal conductivity (320 W/m K), low dielectric constant, low liner thermal expansion coefficient similar to the silicon and its large band gap (6.2 eV) which can emit a wavelength as short as 210 nm in deep ultraviolet region [1–3]. Such unique features make AlN a great candidate for high technology industrial applications like electronic packages and substrates, heat sinks, light emitting diodes (LEDs) and laser diodes (LDs) [3,4].

In spite of such unique features, the application of AlN has been limited to its production cost. AlN is industrially synthesized by either carbothermal reduction or direct nitridation processes [5], but it can be attained by many other ways in laboratory-scale methods such as chemical vapor deposition (CVD) [6,7], metalorganic chemical vapor deposition (MOCVD) [8], organometallic procedure [9,10], solvothermal process [11,12], combustion synthesis [13,14] and mechanochemical synthesis [15,16]. Regardless of the method, the most of these procedures must be conducted both at high temperatures and under nitrogen atmosphere. Some others like organometallic and solvothermal techniques also require very high toxicity materials as reactants [10,11]. Relatively, mechanochemical synthesis can be considered as the just way performed without any of the above limitations.

In recent decades, mechanochemical synthesis has been paid attention to as an attractive and facile route for production of hardly synthesized nano materials at room temperature which cannot be easily prepared by other methods. It takes place by solid state reaction of reactant materials that the activation energy of the reaction is provided mechanically via a high energy ball mill [17]. Most of the recent researches conducted on the production of AlN via the mechanochemical route were done with the milling of aluminum or aluminum oxide under nitrogen or ammonia atmosphere [15,16]. However, recently, some solid nitrogen-containing materials such as melamine ($C_3H_6N_6$) and urea have been proposed for synthesizing nitride ceramics [18–20]. These materials exhibit an improvement in contact of reactant materials comparing with gaseous atmosphere leading to the reduction of reaction time [21]. Melamine is a chemical compound that has a number of industrial uses, including the production of laminates, glues, dinnerware and adhesives. It contains 66% nitrogen by mass that can be recognized as a safe and suitable source of nitrogen. This makes it possible to synthesize of a wide range of metal nitrides from their oxides by low temperature treatments methods [22]. Zhang et al., [18] also applied melamine as the row material for production AlN by the mechanochemical reaction, but they did not report any evidence mechanisms for the reactions may take place during the milling.

* Corresponding author.
E-mail addresses: s.a.rounaghi@gmail.com (S.A. Rounaghi), heshghi@ferdowsi.um.ac.ir (H. Eshghi).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2012.01.005

In spite of high potential of melamine in preparing metal nitrides in both thermal and mechanochemical routes, its decomposition behavior during these processes has not been discussed yet. In this research, we so focused on structural changes and bond evolutions of reactant materials during high energy ball-milling of melamine with Al as a process for preparation of AlN. Subsequently, effect of the milling process and Al powder on melamine decomposition was discussed and compared with the thermal treatment method.

2. Experimental procedure

Melamine powder (purity 99.8%, Khorasan Petrochemical Co.) was mixed with Al powder (purity 99.5%, Mashhad Powder Metallurgy Co.) with the molar ratio of 1:6.

Three gram of mixed powder was milled in a planetary ball mill under air atmosphere at room temperature on rotating speed of 300 rpm. The milling media was consisted of stainless steel balls with different diameters, 10 mm and 8 mm (half–half) and the ball to powder ratio was adjusted on 50:1. Milling process was conducted at various times up to 48 h. Similar milling conditions were applied on 3 g pure melamine powder (without Al) also milled up to 48 h. In both cases, the characterization of products was utilized by Philips X'Pert X-ray diffractometer with Cu K_α (λ=0.154060 nm). Fourier transformation infrared spectroscopy (FTIR) measurements were carried out at room temperature using a Brucker TENSOR 27 infrared spectrometer. The transmission spectra were obtained from the specimens embedded in a KBr matrix. The sample was mixed up with the KBr powder and pressed into a pellet for the measurement. To study the reactions may occur by heating the mixed powder (Al/Melamine), thermal analysis was performed by Netzsch 409 PC Luxx instrument with a heating rate of 10 °C/min in argon atmosphere.

3. Results and discussion

3.1. Milling the mixed powder

Figure 1 illustrates the evolution of initial powders after various milling times. Conspicuous changes can be observed only after 7 h milling. There are some small peaks indexed to the hexagonal AlN in the pattern at this time. This shows the reaction has been occurred in initial mixed powder, but the main parts of reactants still exist. Milling for 8 h disappears the reactants peaks and makes AlN as the dominant product. Furthermore, AlN peaks are relatively broadened specially by increasing milling time. So, the mean crystallite size of AlN was measured by Scherer's equation:

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where D is the mean crystallites size in nm, λ the radiation of wavelength (Cu $K_\alpha 1$, 0.15406 nm), β the full width at half of the maximum in radians and θ is the Bragg-angle. The AlN crystallite size was calculated in different milling time and the results were illustrated in Fig. 2. As can be recognized, the mean grain size is in nano range and it reduces and reaches to a steady state by increasing milling time. There are many parameters in deformation such as stress mode, strain rate, milling temperature etc. which influence on nanostructure formation during high energy ball-milling and it is difficult to distinguish the effect of each parameter from the others. Nevertheless, it has been demonstrated at the early stage of milling the dislocation density

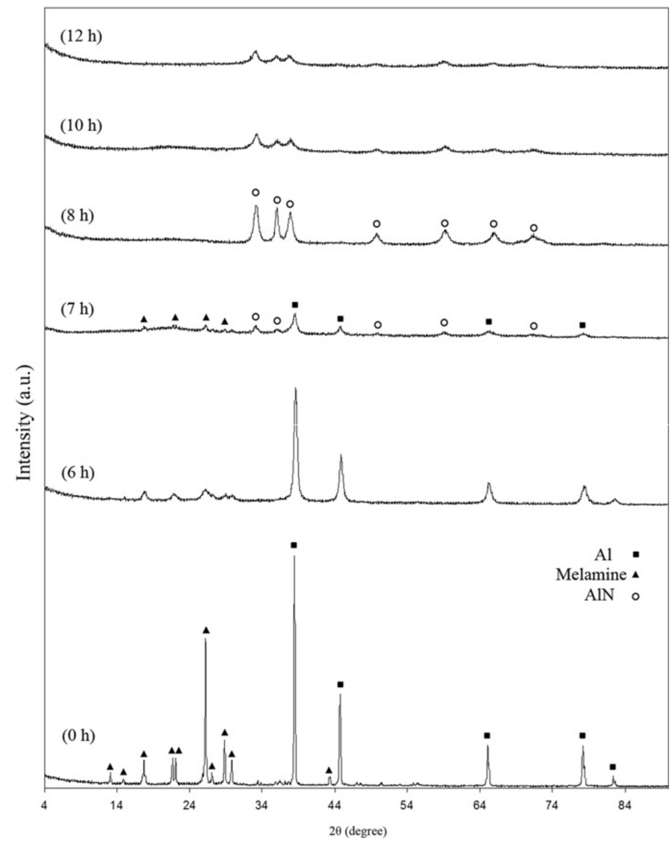

Fig. 1. The XRD patterns of mixed powder after various milling time.

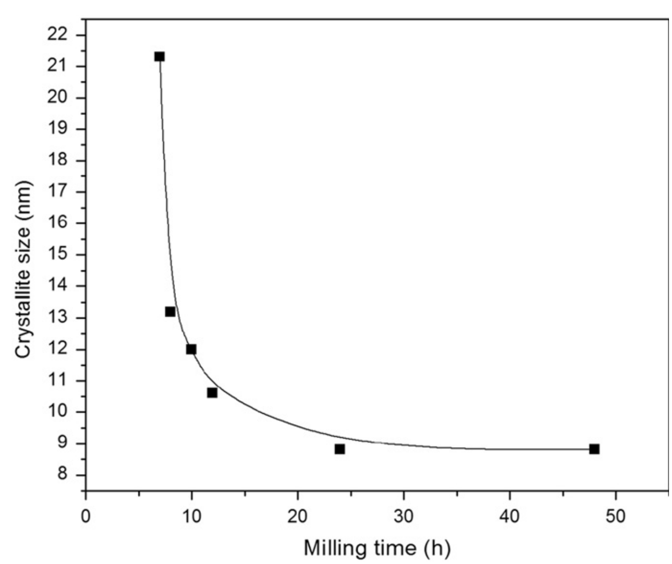

Fig. 2. The evolution of mean crystallite size of synthesized AlN powder versus milling time.

increases and dislocation cell structures develop [23]. The size of dislocation cells decreases with further deformation while reaches to a critical value. Then cellular structure transforms to granular to reduce the energy and very fine and equiaxed new grains form by continues dynamic recovery and recrystallization mechanism [23]. Once nano grains formed, no more refinement achieved by increasing milling time since further deformation can take place by grain boundary sliding [24] so the grain sizes reach to the steady state as shown in Fig. 2.