Synthesis of Nano-Size AlN Powders by Carbothermal Reduction from Plasma-Assisted Ball Milling Precursor*

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Abstract Nano-size aluminum nitride (AlN) powders have been successfully synthesized with a high efficiency method through annealing from milling assisted by discharge plasma (p-milling) alumina (Al₂O₃) precursors. The characterization of the p-milling Al₂O₃ powders and the synthesized AlN are investigated. Compared to conventional ball milling (c-milling), it can be found that the precursors by p-milling have a finer grain size with a higher specific surface area, which lead to a faster reaction efficiency and higher conversion to AlN at lower temperatures. The activation energy of p-milling Al₂O₃ is found to be 371.5 kJ/mol, a value that is much less than the reported value of the unmilled and the conventional milled Al₂O₃. Meanwhile, the synthesized AlN powders have unique features, such as an irregular lamp-like morphology with uniform particle distribution and fine average particle size. The results are attributed to the unique synergistic effect of p-milling, which is the effect of deformation, fracture, and cold welding of Al₂O₃ powders resulting from ball milling, that will be enhanced due to the introduction of discharge plasma.

Keywords: aluminum nitride, ball milling, thermal temperature, plasma, alumina

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(Some figures may appear in colour only in the online journal)

1 Introduction

Aluminum nitride (AlN), as a substrate material for integrated circuits, has attracted growing attention due to its potential applications in the fields of high thermal conductivity, a modest coefficient of thermal expansion, high electrical resistivity and thermal stability [1−3]. In the past few decades, carbothermal reduction nitridation (CRN) has been the most frequently used method to manufacture AlN powders in industry because the AlN prepared by the CRN method exhibit many excellent advantages, such as high purity and sinter-ability. Additionally, the morphology of AlN powders can also be controlled due to the endothermic reaction [4]. Despite these, this prepared method also shows some deficiencies, which mainly include the difficulty to uniformly mingle the precursors, the expensive cost for high annealing temperature, and the low efficiency for the fabrication of AlN powders [5]. For the sake of further improving the CRN technique and decreasing the synthesized cost, a great quantity of researches have been carried out. For example, Kulkarni et al. [6] synthesized nano-particles of AlN by using the thermal plasma, and Liu et al. [7] investigated ultra-fine AlN particles that were synthesized by mechanical ball milling. These researches have shown that the particle size and the activation energy of precursors have an important effect on the synthesized conditions of CRN and the physical properties of prepared AlN. Hence the acquisition of refined and highly reactive precursors has turned into one of the most significant technological issues with regard to the preparation of AlN by the CRN technique.

The mechanical milling assisted by discharge plasma (p-milling) is a promising technique and has been used to effectively manufacture a variety of nanostructured materials, such as nanocrystalline metallic and ceramic materials, and amorphous alloys. This technique combines the mechanical milling and discharge plasma to process materials by submitting powders to a mechanical milling mode, which effectively enhances chemical reaction by the effect of continuous deformation, fracture, and recrystallization, and finally the fine products are produced with highly activated state and various bulk defects [8,9]. Such products as the precursor in the CRN process can effectively improve the synthesis efficiency and reduce the fabrication cost when compared with conventional ball milling (c-milling) and other techniques conventionally used to synthesize AlN [10−12].

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In this work, we reported a method for synthesizing AlN powders by p-milling. The particle size, specific surface area, crystallite size and morphology of p-milling Al₂O₃ and prepared AlN were investigated, respectively.

2 Experimental details

The mechanical milling is carried out in a high energy vibration ball grinding mill, as shown in Fig. 1. The milling medium is stainless steel balls and the original Al₂O₃ powders (purity 99.99 %) as the precursor are sealed in the milling vial, which is filled with N₂ to prevent oxidation of products. The ratio of the balls to powder is 30:1 by weight. The AC high voltage power is supplied and connected to the electrode bar, discharge plasma is generated on the surface of the electrode bar inside the milling vial. The circulation of water is used to cool the milling vial during milling in order to prevent the temperature rise. In our experiment, the milling time is set as 10 h, 20 h, 30 h, and 40 h. After p-milling, the products are mixed with carbon with a mole ratio of 1:4, and then the CRN processes of the mixture are carried out in a graphite furnace with a flowing nitrogen atmosphere (1 L/min); the annealing process would last 2 h between 1200°C and 1600°C. Finally, the excess carbon would be removed in air by heating.

The crystalline structure of the p-milling precursor and prepared AlN is identified by the X-ray diffraction (XRD Bruker D8 Focus Germany) analysis. The differential scanning calorimetry analysis and thermal gravimetry (DSC-TG) analysis of the p-milling precursor are calcined up to 1550°C in a flow of nitrogen atmosphere of 100 mL/min. A Hitachi S-4800 field scanning electron microscope (SEM) is used to characterize the product morphology. Microstructures of products are studied by transmission electron microscopy (TEM). The component of impurity in the synthesized AlN powders is characterized using an inductive coupled plasma emission spectrometer (ICP Optima 2000DV USA).

3 Results and discussion

3.1 The XRD and SEM analysis of precursors under different milling times

Fig. 2 shows typical XRD patterns of precursors under two milling types (p-milling and c-milling) with various milling times. It is observed that there are only Al₂O₃ diffraction peaks and no AlN phase is obtained. Compared with the unmilled Al₂O₃, the diffraction peaks become smaller and broader with the rising of the milling time. In addition, the diffraction peaks of p-milling Al₂O₃ are also smaller and broader than those of c-milling Al₂O₃. This is attributed to the introduction and accumulation of the micro-strain of the mixed powder by the simultaneous fracturing and deformation effect from p-milling. Moreover, grain refinement and lattice distortion may also be responsible for these characteristics.

![Fig.2 The typical XRD patterns of precursor under various milling times](image-url)
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pear in Fig. 4(c) and (d), which are produced by gathering from a large number of small Al₂O₃ particles. In addition, a TEM photograph of p-milling Al₂O₃ powders for 40 h milling time is presented in Fig. 4(e). It seems that the Al₂O₃ powders have been refined to reach the nano-sized level and even amorphous oxide can also be observed under a long milling time. The selected area electron diffraction of p-milling Al₂O₃ powders is presented in Fig. 4(f).

![Fig. 3](image1.png)  
**Fig. 3** The specific surface area and the crystallite size of Al₂O₃ as a function of milling time

![Fig. 4](image2.png)  
**Fig. 4** The SEM and TEM images of p-milling Al₂O₃ at different milling times

3.2 The kinetic reaction of p-milling Al₂O₃ during CRN process

Fig. 5(a) shows the DSCTG curves from Al₂O₃ by p-milling for 40 h under a heating rate of 15 K/min. Some interesting phenomena are that two obvious endothermic peaks can be found at about 1130°C and 143°C, respectively, and two corresponding large weight losses also appear at these temperatures, which indicate that there is a two-step CRN process. Firstly, a reduction reaction takes place between p-milling Al₂O₃ powders and adding of carbon, which causes the Al₂O₃ powders to be broken down into the gaseous aluminum and the low state aluminum oxide, then the broken products have a nitriding reaction with flowing N₂ to synthesize AlN powders. This mechanism of chemical reaction has good agreements with the gas phase reaction model presented in Ref. [13].

![Fig. 5](image3.png)  
**Fig. 5** (a) The DSC-TG curve of p-milling Al₂O₃ for 40 h and (b) the activation energy of p-milling Al₂O₃ powders

To determine the activation energy of the reaction from p-milling Al₂O₃ powders the Kissinger equation is used in Fig. 5(b). The heating rate (β) and the endothermic peak temperature (T) follow the formula:

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{RA}{E}\right) - \frac{E}{RT},
\]

where \(E\) is the activation energy and \(R\) is the gas constant of 8.314 J/(mol·K). The heating rate \(\beta\) is set as 5 K/min, 15 K/min, and 25 K/min, respectively. The activation energy for the synthesized AlN is determined to be equal to 371.5 kJ/mol, a value which is much less than the value of 529 kJ/mol of unmilled Al₂O₃ and the value of 457 kJ/mol of the milled Al₂O₃ without plasma [14]. Therefore, p-milling can effectively reduce the activation energy in the CRN process.

3.3 The XRD and SEM analysis of synthesized AlN powders

The typical XRD patterns of Al₂O₃ powders for 40 h of milling time under two milling types at different temperatures are shown in Fig. 6(a) and (b), respectively.
It can be seen that there are only the diffraction peaks of Al₂O₃ at 1200°C, while no AlN diffraction peaks are observed. When temperature is increased to 1300°C, the new AlN phase is formed and both AlN and Al₂O₃ diffraction peaks exist simultaneously. As the temperature continues to increase up to 1400°C, only diffraction peaks of AlN are detected in Fig. 6(b), while AlN and Al₂O₃ diffraction peaks still exist at the same time in Fig. 6(a). An interesting result is that two different AlN lattices are produced at 1600°C under two milling types, namely, fcc AlN and hcp AlN. This implies that the p-milling can obviously improve the AlN conversion rate and effectively lower the annealed temperature compared to other synthesized technologies. Meanwhile, the corresponding AlN conversion rate can be exhibited in Fig. 7. It can be seen that the conversion rate of AlN under p-milling has reached 100% at 1400°C, while it is only 75% under c-milling. Additionally, no AlN is formed under un-milling, even at 1600°C.

The SEM and TEM images of p-milled Al₂O₃ that have been calcined at 1600°C are presented in Fig. 8. The synthesized AlN powders exhibit the irregular lamp-like morphology with particle size about 1 µm. Moreover, the large number of AlN whiskers with higher crystallinity can also be observed. The corresponding SEAD depicted in Fig. 8(c) and (d) shows that the synthesized AlN is fcc and hcp AlN, which are in agreement to the XRD patterns (Fig. 6). In addition, the component analysis of impurity in synthesized AlN powders at 1600°C is also detected in Table 1. It is found that the synthesized AlN powders have a small amount of metal impurity elements, including Ni, Cr, and Fe, the corresponding weight percent is 0.0514 wt%, 0.7463 wt%, and 0.0974 wt%, respectively. This indicates that the small amount of metal impurity elements have little impact on the characteristic of synthesized AlN.

**Table 1.** The component analysis of impurity in synthesized AlN powders at 1600°C

<table>
<thead>
<tr>
<th>Component</th>
<th>Intensity</th>
<th>Conc. Units</th>
<th>Conc. Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (231.604)</td>
<td>12300.8</td>
<td>1.562 mg/L</td>
<td>0.0514 wt%</td>
</tr>
<tr>
<td>Fe (238.204)</td>
<td>338218.2</td>
<td>22.69 mg/L</td>
<td>0.7463 wt%</td>
</tr>
<tr>
<td>Cr (267.716)</td>
<td>115956.0</td>
<td>2.961 mg/L</td>
<td>0.0974 wt%</td>
</tr>
</tbody>
</table>

3.4 The mechanisms of prepared AlN by p-milling

The mechanisms of synthesis of AlN powder by p-milling is a complex process involving the formation of small particles and the generation of large fresh surface areas. During the p-milling process, the discharge plasma can produce lots of electron flow and ion flow with high energy, which impact on the surface of precursors with high speed to lead to a rapid rising temperature of precursors even vaporization by transforming in the form of heating. This phenomenon would make the precursor produce an explosion to exhale a large number of thermal stresses and expansion. Meanwhile, the effects of plastic deformation, fracture, and...
cold welding are produced by the fierce collision between milling balls and precursors, which cause large amounts of lattice deformation produced, such as dislocations, twin crystal and also situates lots of atoms of precursors in the crystal lattice in highly activated states \[15,16\]. In addition, the charged particles from plasma may pass through the interface into the crystal lattice, which would effectively enhance the diffusion ability of internal atoms, lower the internal barrier and stimulate the lattice atoms across the internal barrier \[8,10,11\].

4 Conclusions

In this study the p-milling technique is used to synthesize AlN powders with a high efficiency. It is shown that the p-milling Al$_2$O$_3$ exhibits a fine crystallite size with high specific surface area. The activation energy for p-milling Al$_2$O$_3$ is determined as 371.5 kJ/mol. Moreover, it is shown that the synthesized AlN powders have an irregular lamp-like morphology and a uniform distribution with particle size about 1 $\mu$m. Finally two different AlN lattices are produced at 1600°C and a set number of AlN whiskers are also observed.

References


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