

# Polymer Network Gel Method for Surperfine AlN Powder Preparation

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**Abstract.** To research mixing uniformity of precursor was helpful to improve the quality of the powder late processing. Layered problems of the precursor comprised of aluminium source and of carbon source were well solved by the polymer network method. High quality raw precursor was synthesized by new process which contained polyacrylamide-gel method and carbothermal process. The synthesized precursor was investigated to obtain porous structure precursor. The results showed that sucrose was more suitable for the preparation of AlN precursor. The effect of reaction temperature and heating time on the phase composition of AlN powder were also studied. In this work, ultrafine nano-sized AlN powder was prepared at low temperature.

## 1 Introduction

There are many scholars devoted to the low temperature preparation of density AlN ceramic, in order to exert its features such as high thermal conductivity, good electrical resistivity, high melting temperature, good thermal shock resistance, wide band gap, low dielectric constant and high mechanical strength, etc, which may be useful for high integration of semiconductor substrate and electronics packaging applications. High quality raw material (AlN precursor) is believed to be one of the ways to achieve this purpose. For this, we improved the traditional preparation technology, and studied the effect of improvement process on the preparation of ultrafine aluminium nitride.

At present, it was shown that carbothermal reduction method [1-5], high energy ball-milling method [6, 7], mechanical activated method [8, 9], sol-gel technique [10-13], direct-nitridation[14,15] and chemical vapour deposition[16-19], were widely used for the preparation of AlN. However, these synthesis processes suffering from various problems, including inferior crystal structure, non-uniform microstructure and complex process as well as high cost of raw material. So improving the uniformity of precursor, technological process and recovery rate become the key technologies which need to resolve during the preparation of AlN powder.

In this work,  $C_3H_5NO$  was used as monomer.  $C_7H_{10}N_2O_2$  was used as crosslinking network.  $(NH_4)_2S_2O_8$  was used as initiator. And  $Al(NO_3)_3 \cdot 9H_2O$  was used as Aluminium source for its lower prices. The precursor was prepared by polyacrylamide gel method, which was best solved the layered phenomenon of Al and C source. The polymer gel network was produced by functional groups activation of the double bond using acrylamide as monomer. The activity of ion was reduced by the effect of gel network blocking. And the reunion opportunity in the process of precipitation and

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sintering was also decreased. These results would lay the foundation for the further studies on the ultrafine of AlN powder.

## 2 Experimental

### 2.1 Technological process of AlN precursor

A certain amount of monomer, network agent and initiator (weight ratio of 5:1:1) was added into 0.3 mol/l of aluminum nitrate solution, and was magnetically stirred for 30min. The temperature in this titration process was controlled below 0°C. Meanwhile, carbon sources (sucrose or active carbon) were prepared. Here the molar ratio of C and Al was 6:1. After 3.42 g of sucrose was added into the mixture and stirring for 60min. Then ammonia solution was dripped into the mixtures with the concentration ratio of 1:2 and 3 - 5 ml/min dripping speed. When titration was finished, the reaction mixture was continued to stir for 120min. The prepared wet gel was obtained until the mixture was aggregated at 65°C for 120min. Final AlN precursor was obtained while the wet-gel directly drying at 85°C for 120min in the vacuum drying oven.

All raw materials (Al (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NH<sub>3</sub>·H<sub>2</sub>O, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, C<sub>3</sub>H<sub>5</sub>NO, C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) used in the preparation of AlN precursor were 99% in purity.

The synthesis of nanosized AlN powder was carried out in vacuum carbothermal reducing furnace. The AlN precursor was heated in a flowing nitrogen gas at various temperatures in the range of 1100-1500°C for 120min. And the flow rate of nitrogen was 10 l/min. Residual carbon in each nitridation product was removed by firing in air at 640°C for 240min[20].

### 2.2 Characterization

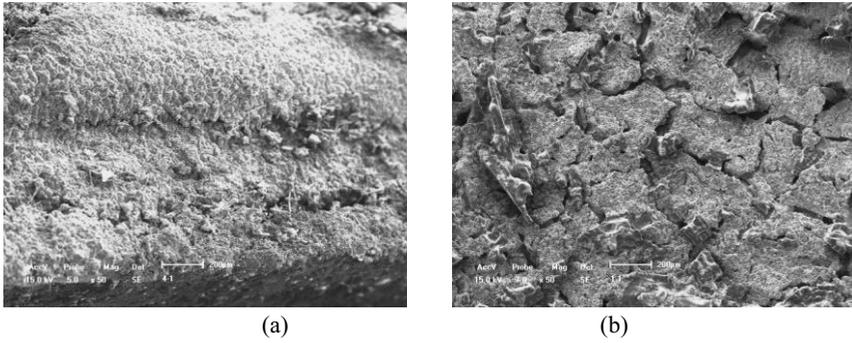
Phase analysis of the nitridation reaction products for AlN precursor calcined at different temperature were carried out by X-ray diffraction (XRD, PhilipPw3040/60) using monochromatic Cu K $\alpha$  radiation with the X-ray wavelength of 0.154nm, operated at 20kV.

Microstructures of the reaction products were observed using field emission scanning electron microscopy (SEM, SSX-550, Shimadzu Corporation). Element distributions of sample were analyzed by energy dispersive X-ray spectroscopy (EDS). Here EDS was used to assist the SEM analysis.

## 3 Results and Discussion

### 3.1 Effect of different carbon sources on the precursor

AlN precursors were synthesized by means of polyacrylamide gel method with ammonia as precipitant, sucrose and activated carbon as carbon source, respectively. Here the molar ratio of C to Al was 2:1. The SEM images of AlN precursor synthesized by different carbon source were shown in Fig.1. It was evident that the section of AlN precursor which used activated carbon as carbon source presents obvious layers. However, AlN precursor with sucrose that contains a homogeneous mixture of very fine alumina and carbon particle can be obtained in this work. Compared with active carbon, sucrose was more suitable for well-proportioned precursor. Sucrose was used as carbon source based on the above reason.

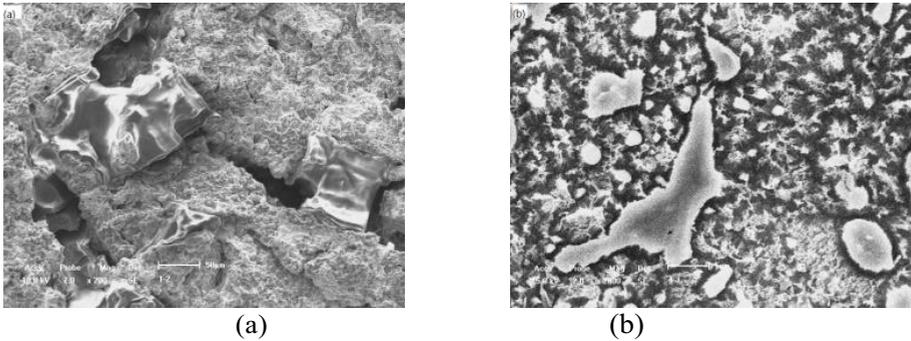


**Figure 1.** SEM images of AlN precursor prepared by ammonium hydroxide with different carbon source (a) sucrose (b) activated carbon

**3.2 Effect of sucrose on the uniform precursor**

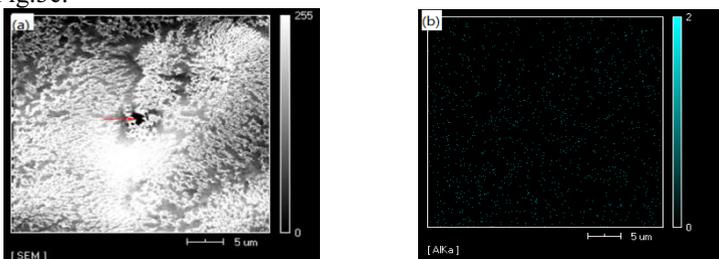
The SEM images of AlN precursor under different magnification were shown in Fig.2. The sample was observed under low magnification. And there was no obvious stratification in it (see Fig.2(a)).

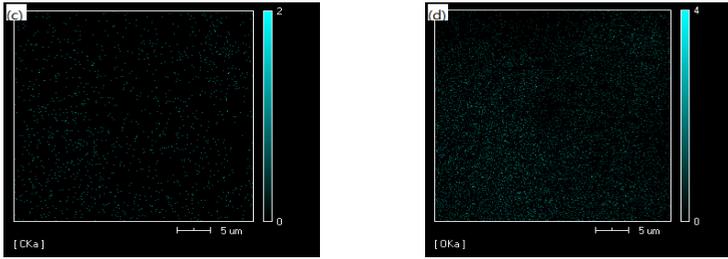
To further study the microstructure and distribution of precursor sample, it was magnified 2000 times by SEM, as shown in Fig.2(b). Meanwhile, the microstructure of the precursor was porous structure. It would suggest that adding liquid sucrose may accelerate the formation of network structure. The elementary and crosslinking reaction of polymeric hydrogel and small molecule of liquid sucrose can explain this phenomenon very well.



**Figure 2.** SEM images of AlN precursor under different magnification (a) 200times magnification (b) 2000times magnification

Fig.3 shows surface scanning images of AlN precursor using ammonium hydroxide and sucrose as raw material. Fig.3a shows that AlN gel precursor has crosslinked and the network structure formed. As shown in Fig.3b, c and d, elements composition and distribution in AlN precursor were also studied by lateral scanning. Fig.3b, c and d show the distribution of Al, C and O atoms in aluminum nitride precursor, respectively. Continuous and uniform distribution of C atoms in AlN precursor was clearly seen from Fig.3c.





**Figure 3.** Surface scanning images of AlN precursor

### 3.3 Effect of reaction temperature on the phase composition of AlN powder

So far, detailed reaction mechanism for the synthesis of AlN powder by carbon thermal reduction method was unclear. Based on some research [21], the nitridation reaction of AlN powders prepared by carbon thermal reduction may be suggested as the following equation:



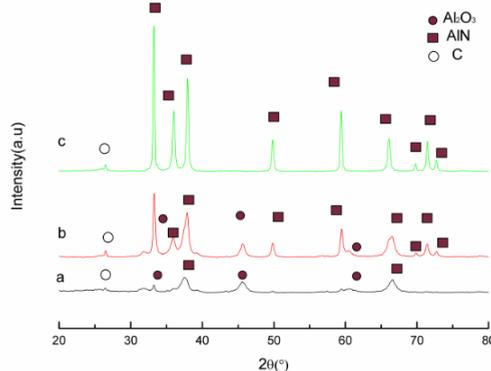
The Gibbs free-energy values for reaction were calculated to confirm a driving force. According to some theories in some paper [22], the initial reaction temperature is 1400°C. A series of AlN powders were prepared at various temperatures by the carbothermal reduction method using AlN precursor as raw material.

Fig.4 shows the reaction products of AlN precursor under various temperatures. The XRD patterns of AlN precursor and products that were calcined at different temperature for 2h were shown in Fig.4.

From Fig.4a, the XRD pattern of the sample obtained at 1400°C showed that AlN phase was formed together with the diffraction peaks of  $Al_2O_3$  and C. This suggests that the AlN precursor was not completely sintered.

Compared with JCPDS Card No.25-1133, some diffraction peaks represent the existence of AlN. Fig.4b shows that the intensities of AlN peaks increased when the temperature was up to 1450°C. The diffraction peaks of  $Al_2O_3$  was still detected in the sample, as Fig.4b shown.

However, when the sample was obtained at 1500°C, only AlN and small amounts of C were present without any other detectable peaks (see Fig.4c). The presence of excess carbon in the reaction product possibly prevented the growth of AlN particle [23].

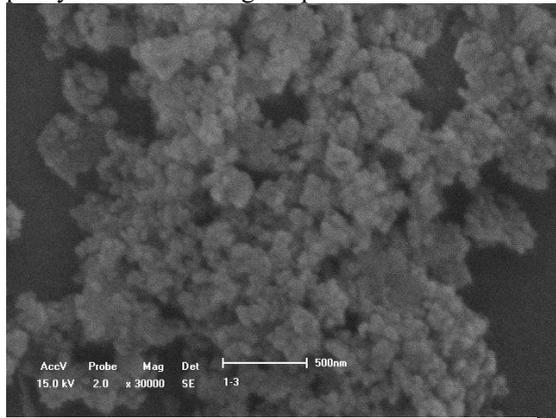


**Figure 4.** XRD patterns of reaction products obtained at different temperature for 2h.

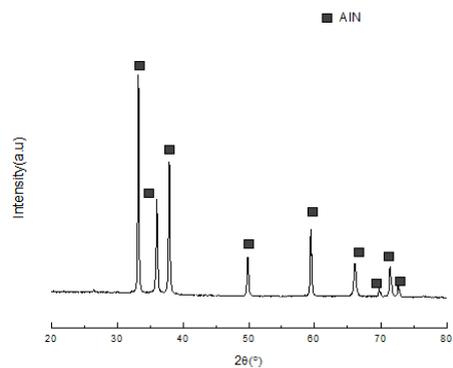
### 3.4 The superfine AlN powder

AlN powder was prepared by carbon thermal reduction method sintering 1500°C for 2h using AlN precursor as raw material. The superfine AlN powder can be obtained by reaction product sintering at 650°C for 4h to remove excess carbon. Fig.5 shows the SEM image of AlN powder synthesized at 1500°C for 2h. No abnormal large particle can be observed and the average particle size was likely to be 40-80nm. Since the presence of excess carbon in the mixture possibly inhibited the growth of AlN grain [23], the particles of synthesized AlN powder observed in Fig.6 are very fine.

The XRD patterns of the final AlN powders are shown in Fig. 5, the main peaks can well correspond to the characteristic peaks of hexagonal AlN. It can be seen clearly that single AlN phase was found in the synthesis powder calcined at 1500°C heated for 2h. It can be seen clearly that single AlN phase was found in the synthesis powder calcined at 1500 heated for 2h. Compared with the sintering temperature of conventional synthesis method, the powder prepared by this process was purity and the sintering temperature was lower.



**Figure 5.** SEM image and XRD pattern of AlN powder synthesized at 1500°C for 2h



**Figure 6.** XRD pattern of AlN powder synthesized at 1500°C for 2h

## 4 Conclusions

In this paper, aluminum and carbon source were homogeneously distributed in the AlN precursor with sucrose. Optimum process for AlN powder which prepared by carbon thermal reduction method was 1500°C for 2h followed by heating at 650°C for 4h to remove any extra carbon. The superfine AlN powder with smaller size was successfully synthesized by using above process. Meanwhile, this synthesis process is superior to the traditional preparation process with single aluminum and carbon source. It can lower the reaction temperature and reduce heating time for conversion of AlN precursor. And the process in this paper could be suitable to the preparation of high density ceramics.

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