

Synthesis of Fine AlN Powders by Foamed Precursor-assisted Carbothermal Reduction-nitridation Method

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Abstract: A modified carbothermal reduction-nitridation (CRN) method was proposed to synthesize fine AlN particles using γ -Al₂O₃ and sucrose as raw materials which were pre-treated as cellular foams. The reaction procedure and the produced AlN were investigated by XRD, SEM and TEM. XRD result suggests that γ -Al₂O₃ transferred into AlN without transformation into α -Al₂O₃. HRTEM shows that γ -Al₂O₃ particles are covered by amorphous carbon from sucrose inhibiting the transformation of α -Al₂O₃ from γ -Al₂O₃ in the synthesis procedure. The foamed structure is of benefit to the diffusion of N₂ and the produced CO. The minimum reaction temperature is 1450 °C for full conversion of Al₂O₃ to AlN. SEM photographs show the particle size of synthesized AlN is 50 nm. This study demonstrated an efficient way to synthesize fine AlN powders which are urgently required for the manufacture of advanced AlN ceramics.

Key words: aluminum nitride; foams; particles; synthesis

Aluminum nitride (AlN) is one of the most important advanced ceramics and an ideal substrate material for semiconductor package because of the remarkably high thermal conductivity, low dielectric constant, high electrical resistivity, high mechanical strength, and low thermal expansion coefficient that matches well with silicon^[1-4]. As well known, the property of the advanced ceramics are critically influenced by the characterization of raw powders. The manufacture of advanced AlN ceramics is the same case. It is still a challenge to fabricate high quality AlN powders with efficient sintering activity. Presently, the most practical method to synthesize AlN ceramic powders is the carbothermal reduction-nitridation (CRN) of Al₂O₃^[5]. Compared with direct nitridation from aluminum^[6], the CRN process is more appropriate to synthesize AlN powder, since it produces powders with high purity, high uniformity, high yield and low cost^[7-10]. However, the CRN process requires high synthesis temperature^[11], which leads to particle growth and agglutination. Furthermore, it is important to mix carbon and alumina particles in a very small scale, because the CRN reaction is the reaction involved two solid phases. Otherwise, much higher temperature and longer time are necessary in order to convert all Al₂O₃ into AlN^[12-14].

In order to decrease the synthesis temperature and time, much attention was attracted on using fine alumina and carbon particles or precursors. For example, γ -Al₂O₃^[15], Al(OH)₃^[16], and γ -AlOOH^[16] were used instead of α -Al₂O₃. And nano-sized carbon particle was used to replace graphite particles. However, their effects are very limited in the respect of synthesis temperature and particle size. Other research work focused on applying soluble precursors which may transform into alumina and carbon afterwards. The idea is that the mixture of solution could reach atom level, compared with the mixture of solid particles. Mylinh, *et al*^[17] prepared AlN particles using phenol resin as precursor at a temperature above 1700 °C. Baik, *et al*^[18] employed sucrose as carbon source and converted Al₂O₃ fully to AlN at 1600 °C. Chu, *et al*^[19] prepared Al/C precursor by combustion synthesis using a mixed solution of aluminum nitrate, glucose, and urea, which was then nitrided into pure AlN at 1500 °C. Jung, *et al*^[20] obtained AlN particles by calcining basic dicarboxylate Al(III) complexes under flowing nitrogen at 1450 °C for 15 h. These efforts focused on reactants, but didn't effectively decrease the synthesis temperature. The reason is that it is difficult for nitrogen to diffuse into the interior of the reactant through the gap between

Received date: 2019-01-28; Modified date: 2019-05-12

Foundation item: National Key R&D Program of China (2017YFB0310500); National Natural Science Foundation of China (51772309)

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the sub-micron particles, as well as for CO escaping as by-product. Besides, the using of aluminum organics lead to much higher cost which will, of course, restrict the application of obtained AlN powders.

To accelerate the reaction, the diffusion of N_2 into the interphase draws our attention. Recently, we employed a slurry foaming method, which is normally used to make ceramic foams^[21-22], to prepare porous γ - Al_2O_3 /carbon foam, where plenty of connected pores act as channels for N_2 transportation during the following CRN procedure^[23]. In this method, Al_2O_3 starts to transfer to AlN at 1400 °C, and is completely converted at 1550 °C for only 2 h.

In the present work, we combined the foaming technology with sucrose as carbon source to ensure all γ - Al_2O_3 particles are covered by the resulting carbon. Excessive sucrose was used in order to form residual carbon to avoid the particle growth and agglutination of AlN powders. The effects of reaction temperature and sucrose/ Al_2O_3 ratio on the nitridation rate and morphology of AlN powder were investigated.

1 Experimental

Commercial γ - Al_2O_3 with the average particle size of 13 nm (purity 99.99%, specific surface area 120 m²/g, Dalian Hiland Photoelectric Material Co., Dalian, China), and sucrose ($C_{12}H_{22}O_{11}$, purity 99.5%; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as starting raw materials. The weight ratio of sucrose to alumina was 2.0. The corresponding carbon addition is 1.2 times of that required for the reduction of alumina. The existence of excess carbon, which originally covered on alumina particles, is expected to separate the formed AlN particles to avoid the agglutination. The forming procedure was described elsewhere^[23]. Sucrose, γ - Al_2O_3 , and copolymers of isobutylene and maleic anhydride^[24-25] (Isobam104# and Isobam600AF, Kuraray; Osaka, Japan) were dispersed in deionized water. Then, Emal TD (triethanolamine laurylsulfate, with 40% active content, Kao Chemical Co., Tokyo, Japan) was added into the mixed slurries, which were then vigorously stirred for 3 min to generate foams. After gelation and drying, the sucrose/ Al_2O_3 precursor foams were pyrolysed for 1 h at 1000 °C with a heating rate of 10 °C/min in flowing N_2 in a graphite furnace (High-Multi 10000, Fujidempa Kogyo Co., Tokyo, Japan). Following CRN reaction was carried out at 1250–1600 °C for 2 h. After synthesis, residual carbon in the nitridation product was removed by firing at 650 °C in air for 6 h.

The crystalline phase of the synthesized products was examined by X-ray diffraction (XRD, D8-Advance A25,

Bruker Co., Karlsruhe, Germany) with Cu K α radiation and a scan speed of 0.1 (°)/s. The AlN conversion fraction was determined on the basis of the relatively peak intensity of the AlN phase in XRD patterns. The morphologies of the products were observed by scanning electron microscopy (SEM, Hitachi, S-4800, Tokyo, Japan). A field-emission transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) was used for high resolution transmission electron microscopy (HRTEM). Differential thermal analysis/thermo gravimetric analysis of sucrose was studied in N_2 using a thermal analyzer (TG/DTA, Netzsch, STA449C, Germany). The oxygen content of the resultant AlN powder was measured by Oxygen-Azote mensuration equipment (TC600C, Leco Co., Chicago, America).

2 Results and discussions

In order to confirm the carbonization of sucrose, the TG/DTA curves of sucrose pyrolysis procedure from room temperature to 1000 °C in N_2 atmosphere is presented in Fig. 1. Two endothermic peaks take place at 172.9 and 219.4 °C, revealing the carbonization of sucrose with a carbon yield of 21.41wt% according to the TG curve. The corresponding carbon addition is about 1.2 times of that required for the reduction of alumina, which agrees well with the design.

The SEM images of the foam heated at 1000 °C in N_2 are shown in Fig. 2(a). The pyrolysis foam sustains the cellular structure of the precursor foam, where large number of spherical cells and interconnected windows act as the transportation channels for N_2 and the by-product CO. Fig. 2(b) shows the microstructure of the produced foam after CRN reaction at 1550 °C. It could be observed that the struts and walls of the cells become loose with more interconnected windows.

Fig. 3 shows X-ray diffraction patterns of the products from the foam with sucrose/ Al_2O_3 ratio of 2.0. It can be

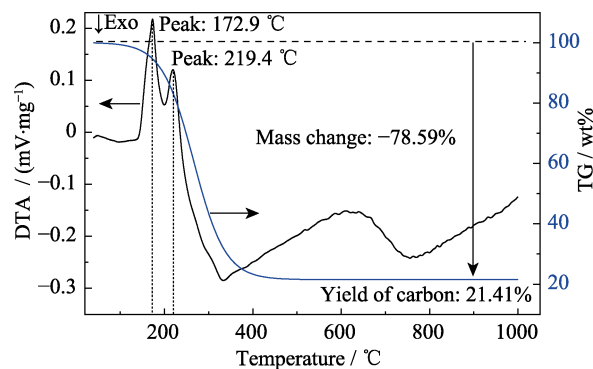


Fig. 1 DTA and TG analysis of sucrose pyrolysis procedure from room temperature to 1000 °C in N_2 atmosphere

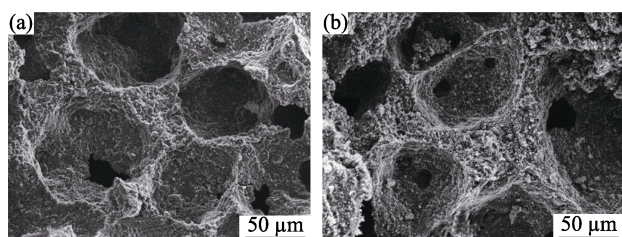


Fig. 2 SEM images of the foam heated at (a) 1000 and (b) 1550 °C with sucrose/ Al_2O_3 ratio of 2.0

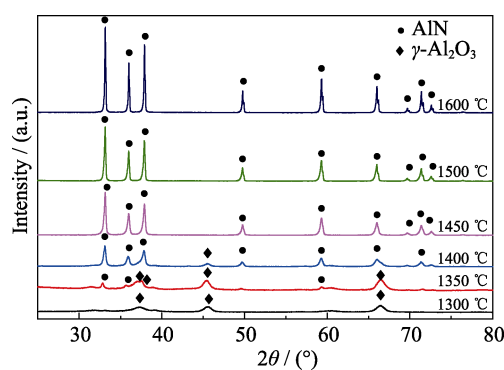


Fig. 3 XRD patterns of the sucrose/ Al_2O_3 powders synthesized at different temperatures

clearly seen that only $\gamma\text{-Al}_2\text{O}_3$ phase is detected in the sample heated at 1300 °C, which implies that the produced carbon is amorphous and the nitridation reaction did not occur at this temperature. The diffraction peaks of AlN start appearing at 1350 °C, and become stronger as the heating temperature increases. When the heating temperature is higher than 1450 °C, only AlN diffraction peaks are detected, which infers that all alumina is transferred to AlN. It is notable that in the temperature range of 1300–1400 °C, the unreacted alumina exists as $\gamma\text{-Al}_2\text{O}_3$ instead of $\alpha\text{-Al}_2\text{O}_3$. It suggests that in the present case $\gamma\text{-Al}_2\text{O}_3$ is transferred into AlN without any transformation into $\alpha\text{-Al}_2\text{O}_3$. However, in our previous work where nano-sized carbon black was used, all $\gamma\text{-Al}_2\text{O}_3$ was changed to $\alpha\text{-Al}_2\text{O}_3$ at 1300 °C, which is consistent with the thermal stability of $\gamma\text{-Al}_2\text{O}_3$ in literature that $\gamma\text{-Al}_2\text{O}_3$ is transferred to $\alpha\text{-Al}_2\text{O}_3$ at around 1200 °C^[26]. This phenomenon probably originates from the C/ $\gamma\text{-Al}_2\text{O}_3$ core shell structure.

Fig. 4 shows morphologies of the corresponding particles synthesized at different temperatures. Fig. 4(a) is the microstructure of products after pyrolysis where the CRN reaction didn't happen yet as indicated by the XRD results in Fig. 3. There are shuttle-like dark particles which are surrounded by the gray carbon decomposed from sucrose. The dark particles should be $\gamma\text{-Al}_2\text{O}_3$ which remains until 1300 °C as shown in Fig. 3. In Fig. 4(b),

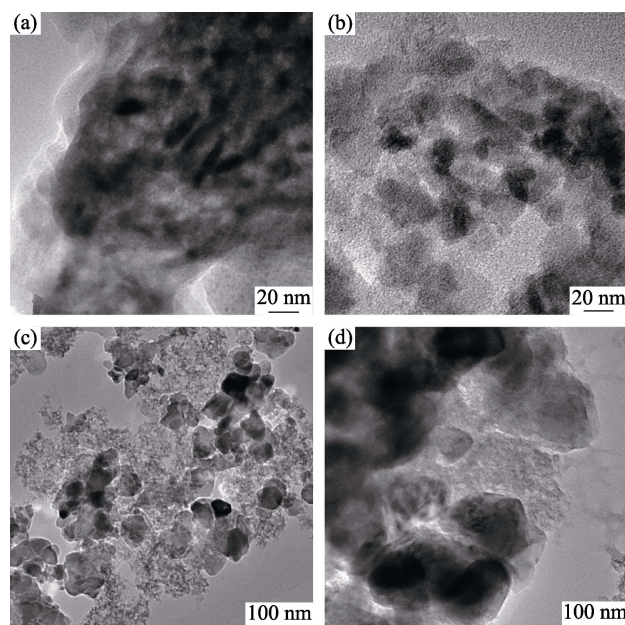


Fig. 4 TEM images of particles heated at different temperatures (a) 1250 °C; (b) 1350 °C; (c) 1450 °C; (d) 1550 °C

however, it can be found that the dark particles have spherical shape with a diameter about 20 nm. The change of particle morphology relates to the transformation of Al_2O_3 to AlN, which is confirmed by XRD results. As the synthesis temperature increases to 1450 and 1550 °C, the diameters of the spherical particles increase to about 50 and 200 nm, as shown in Fig. 4(c, d). It is noted that the AlN particles are separated by the residual carbon, which could avoid the growth of AlN, because carbon are very stable in the synthesis temperature range.

The HRTEM image of the particles after pyrolysis at 1250 °C is shown in Fig. 5(a) with a selective electron diffraction spot pattern indicated in Fig. 5(b). The periodic lattice in Fig. 5(a) has a periodic distance of 0.458 nm, which is proximate to the interplanar distance of {111} plane of $\gamma\text{-Al}_2\text{O}_3$. The diffraction spots in Fig. 5(b) is consistent with the diffraction pattern of the $\gamma\text{-Al}_2\text{O}_3$ phase along the [011] zone axis, with spots corresponding to crystal plane {111} and {400}. It is obvious that the inside dark particles are $\gamma\text{-Al}_2\text{O}_3$, which is consistent with the XRD results (Fig. 3). The $\gamma\text{-Al}_2\text{O}_3$ particles are covered by amorphous carbon with the boundary appearing a quasi-ordered structure, with an interplanar distance thickness of 0.395 nm. The boundary layer is considered as the critical factor for the existence of $\gamma\text{-Al}_2\text{O}_3$ at high temperature. Confined by the boundary layer, the growth of $\gamma\text{-Al}_2\text{O}_3$ is prevented even the temperature is over 1200 °C. Hence, the nucleation of $\alpha\text{-Al}_2\text{O}_3$ becomes difficult. Another reason might be attributed to the surface energy barrier from the interlayer.

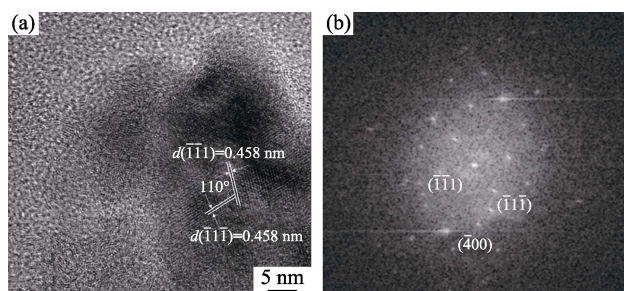


Fig. 5 (a) HRTEM image of particles synthesized at 1250 °C and (b) selective electron diffraction pattern

The formation of AlN is directly from γ -Al₂O₃ in the present study, which has much larger specific surface area than that of α -Al₂O₃. Compared with our previous study^[23], this transformation procedure is beneficial to the CRN reaction. Fig. 6 shows the microstructures of the AlN particles synthesized at different temperatures after de-carbon calcination. The particle size increases from about 50 nm to 200 nm as the reaction temperature raises from 1450 °C to 1600 °C, which are much smaller than that reported in previous study^[23], where the average AlN particles size is 300 nm when synthesized at 1450 °C.

In an early study where sucrose was also used as carbon source^[18], the minimum reaction temperature for full conversion of Al₂O₃ to AlN is 1600 °C, even a fine and reactive precursor boehmite was used. The high reaction temperature results in agglutination of the produced AlN particles. The lower minimum full conversion temperature at 1450 °C in our study, which could be attributed to porous structure of foamed precursor, is the key to gain fine particle size. The interconnected channels make it possible that the rapid diffusion of N₂ and easy removal of produced CO, eliminating the screening effect of CO^[11]. Considering the chemical reaction formula of the

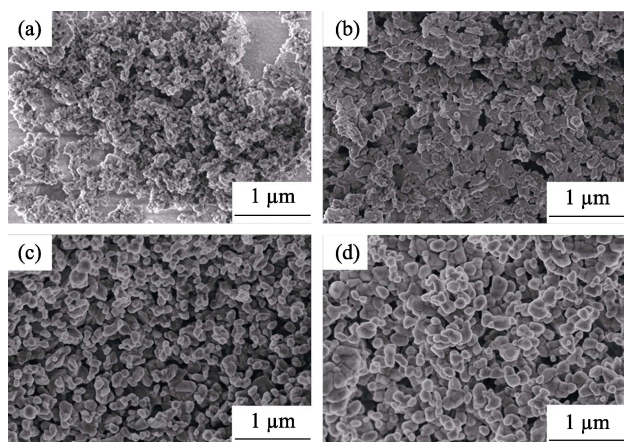


Fig. 6 SEM photographs of the AlN powders synthesized at different temperatures for 2 h
(a) 1450 °C; (b) 1500 °C; (c) 1550 °C; (d) 1600 °C

Table 1 Nitrogen and oxygen content of AlN powders with various sucrose/Al₂O₃ ratios and synthesizing at 1550 °C

Element content/wt%	Sucrose/Al ₂ O ₃		
	2.0	2.5	3.0
Nitrogen	29.3	29.4	30.2
Oxygen	2.4	2.0	1.6

CRN, lower pressure of CO corresponds to lower energy barrier for the AlN formation and thus higher reaction rate^[27].

The nitrogen and oxygen content of the AlN powder synthesized at 1550 °C with different sucrose/Al₂O₃ weight ratio are also investigated and are listed in Table 1. An increase of nitrogen from 29.3wt% to 30.2wt% can be seen with the oxygen decreasing from 2.4wt% to 1.6wt% when sucrose/Al₂O₃ weight ratio increases from 2.0 to 3.0. Taken the low cost and non-pollution of sucrose and the simple starting materials mixing process into consideration, the current modified CRN process shows great potential for a convenient and efficient method to fabricated AlN powder.

3 Conclusions

AlN powders were synthesized by the novel sucrose/ γ -Al₂O₃ foam assisted CRN method. The inter-connected channels in the foam structure facilitates N₂ and CO diffusion and supplies larger effective reaction area. The γ -Al₂O₃ particles, covered by the pyrolytic carbon from sucrose, convert directly to AlN without the appearance of α -Al₂O₃. The residual carbon from extra sucrose can effectively avoid the growth of AlN particles. Size controllable AlN particles from 50 nm to 200 nm can be obtained by correspondingly varying the synthesis temperature from 1450 °C to 1600 °C.

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碳热还原氮化法结合泡沫前驱体制备超细氮化铝粉体

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摘要: 本研究使用改良的碳热还原氮化法合成超细氮化铝粉体。以 γ 氧化铝和蔗糖作为铝源和碳源, 先预处理制备成多孔泡沫, 再通过碳热还原氮化法合成氮化铝粉体。反应过程和产物通过 X 射线衍射分析、SEM 和 TEM 确定。X 射线衍射分析表明整个反应过程不存在氧化铝的相转变。高分辨透射电子显微镜显示 γ - Al_2O_3 颗粒被无定型碳包裹, 从而抑制了 γ - Al_2O_3 到 α - Al_2O_3 的相转变。泡沫的多孔结构促进了氮气的扩散和反应副产物的释放, 使得最低反应温度降低至 1450 °C。SEM 结果表明得到的氮化铝颗粒粒径大约为 50 nm。本研究合成的氮化铝粉体可用于制备高热导氮化铝陶瓷。

关键词: 氮化铝; 泡沫; 粉体; 合成

中图分类号: TQ174 文献标识码: A