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Journal of the European Ceramic Society 29 (2009) 795–799

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Influence of carbon on the synthesis of AlN powder from combustion synthesis precursors

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Received 9 August 2007; received in revised form 1 July 2008; accepted 11 July 2008
Available online 21 August 2008

Abstract

AlN powders were synthesized by carbothermal reduction of combustion synthesis precursors. Water-soluble organics and carbon black were used as carbon sources. The effects of carbon on the synthesis of AlN powders were studied. Results showed that AlN powders were synthesized directly from γ-Al_2O_3 without γ-Al_2O_3 to α-Al_2O_3 phase transition when water-soluble organics were used as carbon sources, and the nitridation of the precursors could be completed at 1400 °C. However, AlN powders were synthesized from the nitridation of α-Al_2O_3 when carbon black was used as carbon source, and the reaction temperature for a complete conversion increased to 1500 °C. The particles of AlN powders synthesized with water-soluble organics was smaller than the particles of AlN powders synthesized with carbon black and their particle size distribution was sharper. The specific surface area of synthesized AlN powders increased with the increase of carbon content in the precursors.

Keywords: Aluminum nitride; Carbon; Combustion synthesis; Phase transition; Particles

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1. Introduction

Recently aluminum nitride (AlN) has attracted much attention for its remarkable properties, including high thermal conductivity (theoretical value is 320 $W\,m^{-1}\,K^{-1}$), high electrical resistivity ($>10^{16}\,\Omega\,m$), a low dielectric constant (8.8 at 1 MHz) and a low dielectric loss (3–10 at 1 MHz), as well as a low thermal expansion coefficient (20–500 °C, $4.6 \times 10^{-6}\,K^{-1}$) close to that of silicon. This combination of properties makes AlN an extremely attractive material for electronic applications.[1,2] At present, there are two primary methods to prepare AlN powders commercially[3,4]: (1) direct nitridation of Al with N_2 or NH_3; (2) carbothermal reduction of Al_2O_3 with carbon black in the presence of N_2. Comparatively, AlN powders produced by carbothermal reduction method have better properties in many aspects including purity, sinterability and stability against humidity. However, carbothermal reduction method has also some disadvantages, such as the notorious difficulty to homogeneously mix the starting materials, the high cost based on the high calcination temperature and the need for high purity Al_2O_3 and carbon black for the fabrication of high purity AlN powders. A lot of work has been done in the past few years to improve carbothermal reduction method and reduce the fabricating cost. For example, Silverman[5] synthesized AlN powders from colloidal aluminum oxide precursors trapped in a polymer matrix and Jung and Ahn[6] prepared AlN powders from a (hydroxo)(succinato)aluminum(III) complex. These researches show that the particle size and the mixing homogeneity of staring materials have a great influence on the carbothermal reaction conditions and the properties of the synthesized AlN powders. Therefore the selection of raw materials and the preparation of a homogeneous mixture of $Al_2O_3 + C$ precursor have become one of the most important technologies for the synthesis of AlN powder by carbothermal reduction method.[7–13]

In 1988, low-temperature combustion synthesis was reported for the first time by Kingsley and Patil.[14] They dissolved a certain amount of aluminum nitrate (oxidizer) and urea (fuel) into water and then put the resulting solution contained in a dish into a muffle furnace. The solution underwent a series of reactions, such as boiling, dehydration, foaming, swelling, and then glowed to incandescence. The entire combustion process was over in less than 5 min, and finally a voluminous and foamy alumina

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doi:10.1016/j.jeurceramsoc.2008.07.019

powder with high specific surface area was obtained. Due to the igniting temperature and the combustion temperature being rather low compared with Self-propagating high-temperature synthesis (SHS), they called this process a low-temperature combustion synthesis (LCS). Low-temperature combustion synthesis has many advantages. It saves energy because the heat needed to drive the chemical reaction is provided by itself and not by an external source. The combustion reaction is simple and instantaneous. And it can produce ceramic powders with high sinterability, high specific surface area, well-defined chemical compositions, and homogeneous distribution of the elements.[14–18]

From the above discussion, a new process to prepare a homogeneous mixture of ($Al_2O_3 + C$) precursors can be suggested. If carbon sources are added to the solution of aluminum nitrate and urea, mixed homogeneously in liquid phase and then heated, low-temperature combustion reaction between aluminum nitrate and urea can be used to prepare $Al_2O_3 + C$ precursors. In this paper, different kinds of carbon source, such as, glucose, sucrose, water-soluble starch, citric acid, and carbon black, were added to the solution of aluminum nitrate and urea, and precursors of alumina and carbon was prepared by using low-temperature combustion synthesis process. The influence of carbon source and carbon content on the phase transformation behaviors of the precursors, as well as the particle size and morphology of synthesized AlN powders, were investigated.

2. Experimental

The starting materials included aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 99% in purity), urea ($CO(NH_2)_2$, 99% in purity), carbon black (specific surface area 126.4 m^2/g, 99% in purity), and water-soluble carbon sources, such as glucose ($C_6H_{12}O_6 \cdot H_2O$, 99% in purity), sucrose ($C_{12}H_{22}O_{11}$, 99% pure), citric acid ($C_6H_8O_7 \cdot H_2O$, 99% in purity), and water-soluble starch ($(C_6H_{10}O_5)n$, 99% in purity). Firstly, a solution was prepared by dissolving a certain amount of aluminum nitrate and urea in water. The mixing molar ratio of urea to aluminum nitrate was fixed at 1.5. Then different kinds of carbon source were added to the solution. In order to study the influence of carbon content on the synthesized AlN powders, the molar ratio of glucose to aluminum nitrate was varied in the C/Al moral ratio range of 3–12 in the starting materials. The solution was heated on an electrical furnace whose temperature could be controlled. In the range of 90–100 °C, a gelatinous mass was formed by the evaporation of the solution. As heating continued, the solution suddenly boiled and swelled, and a lot of gas was given off. The whole process only took several minutes and finally a black foamy mixture of alumina and carbon ($Al_2O_3 + C$) was obtained. The nitridation reaction of the precursors was performed in a vertical graphite furnace. The samples were held in a graphite crucible. Before heating, the furnace was vacuumed and then flushed with nitrogen repeatedly to eliminate oxygen before the reaction. The precursor mixture was heated in a flowing nitrogen gas at various temperatures in the range of 1200–1600 °C for 120 min. The flow rate of nitrogen was 3 L/min. Residual carbon in each nitridation product was removed by firing in air at 700 °C for 60 min.

Phase analysis of the precursor and the nitridation reaction products calcined at different temperatures was performed on an X-ray diffractometer using Cu Kα radiation (XRD, Rigaku, D/max-RB12). The particle sizes and morphologies of the nitridation products were observed by scanning electron microscopy (SEM, LEO, JSM-6301F). The specific surface areas of the precursors and the nitridation products were determined by the single-point of Brunauer–Ematt–Teller (BET) method.

3. Results and discussion

3.1. Effects of carbon source on the phase transition behaviors

Fig. 1 shows X-ray diffraction patterns for the precursor prepared with glucose as carbon source after being calcined at different temperatures. As shown in Fig. 1, only γ-Al_2O_3 phase was detected in the sample calcined at 1200 °C. Both γ-Al_2O_3 and AlN coexisted in the samples calcined at 1300 °C and 1350 °C. In the samples calcined at above 1400 °C, only AlN was detected. No α-Al_2O_3 phase was detected during the whole nitridation process.

Fig. 2 shows X-ray diffraction patterns for the precursor prepared with carbon black as carbon source after being calcined at different temperatures. It can be seen clearly that only α-Al_2O_3 phase is found in the sample calcined at 1200 °C. In the sample calcined at 1300 °C, α-Al_2O_3 is still the dominant phase, although AlN phase begins to form. Traces of α-Al_2O_3 still exist in the sample calcined at 1400 °C. Only AlN phase is found in the sample calcined at 1500 °C.

Table 1 summarizes the phase transitions of these combustion precursors during their nitridation reaction process, as well as combustion phenomena during the preparation of the precursors

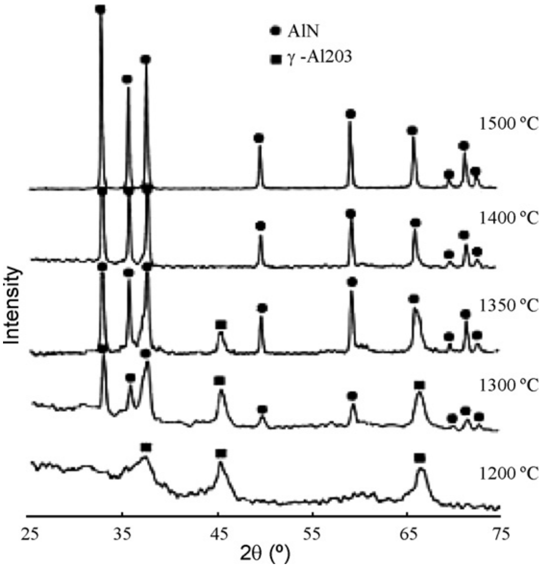

Fig. 1. X-ray patterns for the precursor prepared with glucose as carbon source after being calcined at different temperatures.

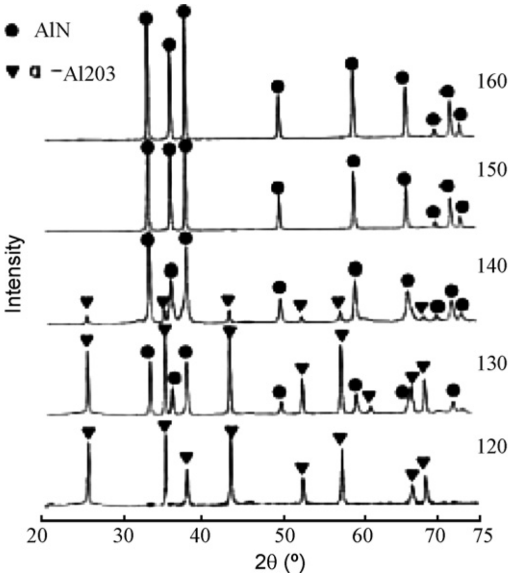

Fig. 2. X-ray diffraction patterns for the precursor prepared with carbon black as carbon source after being calcined at different temperatures.

when different carbon sources were used. As shown in Table 1, when water-soluble organics such as sucrose, water-soluble starch and citric acid are used as carbon source, smouldering might have been occurred in the combustion process, and the phase transition behaviors are the same as that of glucose, that is, AlN is synthesized through the direct nitridation of γ-Al_2O_3 without γ-Al_2O_3 to α-Al_2O_3 phase transition. However, when carbon black is used as carbon source, a flame has been occurred during combustion, and only AlN and α-Al_2O_3 phase are detected when the reaction temperature is higher than 1200 °C, which indicates that AlN is synthesized through the direct nitridation of α-Al_2O_3 in this system. The reasons for carbon sources influencing the phase transitions of these precursors are not yet known. Further experiments are needed to reveal these reaction mechanisms.

3.2. Nitridation reaction

Fig. 3 shows the effect of calcination temperature on the conversion ratio of Al_2O_3 to AlN for the precursors prepared with different sources, calculated on the basis of the relatively peak intensity of AlN phase in XRD patterns. As shown in Fig. 3, for the precursors prepared with water-soluble organic materials as carbon source, there is almost no difference in their nitridation rate, and nitridation reaction proceeds very rapidly in the temperature range of 1200–1400 °C. By contrast, nitridation reaction proceeds slowly for the precursor prepared with carbon black as carbon source, and a complete conversion to AlN requires a calcination temperature about 1500 °C. These results can be due to the particle size and mixing homogeneity of the raw materials, as well as the phase transition behavior during the nitridation process. Both aluminum source and carbon source are water-soluble materials when water-soluble organics are used as carbon sources, and they can mix homogeneously at molecular level after dissolving in water. As combustion takes place, the aluminum compound is transformed into very fine alumina particles by the heat generated in the combustion reaction and uniformly dispersed into the carbon matrix, which is formed by the dehydration and decarbonization of water-soluble organics. However, in the present work it was very difficult to disperse carbon black particles uniformly in water due to their hydrophobic properties, although stearic acid was used as surface-active agent when carbon black was used as carbon sources. The particle size of carbon black was larger than that of water-soluble organic molecules. The difference in the mixing homogeneity of the raw material and the particle size of carbon sources may be one reason for the different reaction rate of the precursors prepared with different carbon sources. The phase transition behaviors during the nitridation process may be another reason for the different reaction rate of these precursors. It is well known that γ-Al_2O_3 has high reactivity because of its high specific surface area. If this active γ-Al_2O_3 was directly nitrided to yield AlN without γ-Al_2O_3 to α-Al_2O_3 phase transition, the reaction proceeded very rapidly.[19] However, the reactivity decreased rapidly when γ-Al_2O_3 eventually transformed into α-Al_2O_3. Therefore, the direct nitridation of active γ-Al_2O_3 without the formation of α-Al_2O_3 may explain

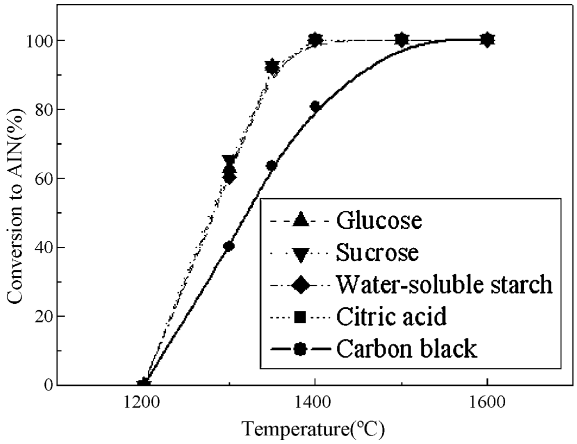

Fig. 3. Relationship between conversion to AlN and reaction temperature.

Table 1
Phase transition behaviors during nitridation process and combustion phenomena during preparation process of the precursors prepared from different carbon sources

Carbon sources	Combustion phenomena	1200 °C	1300 °C	1400 °C	1500 °C	1600 °C
Glucose	Smouldering	γ-Al_2O_3	γ-Al_2O_3 AlN	AlN	AlN	AlN
Sucrose	Smouldering	γ-Al_2O_3	γ-Al_2O_3 AlN	AlN	AlN	AlN
Water-soluble starch	Smouldering	γ-Al_2O_3	γ-Al_2O_3 AlN	AlN	AlN	AlN
Citric acid	Smouldering	γ-Al_2O_3	γ-Al_2O_3 AlN	AlN	AlN	AlN
Carbon black	Flame	α-Al_2O_3	α-Al_2O_3 AlN	α-Al_2O_3 AlN	AlN	AlN

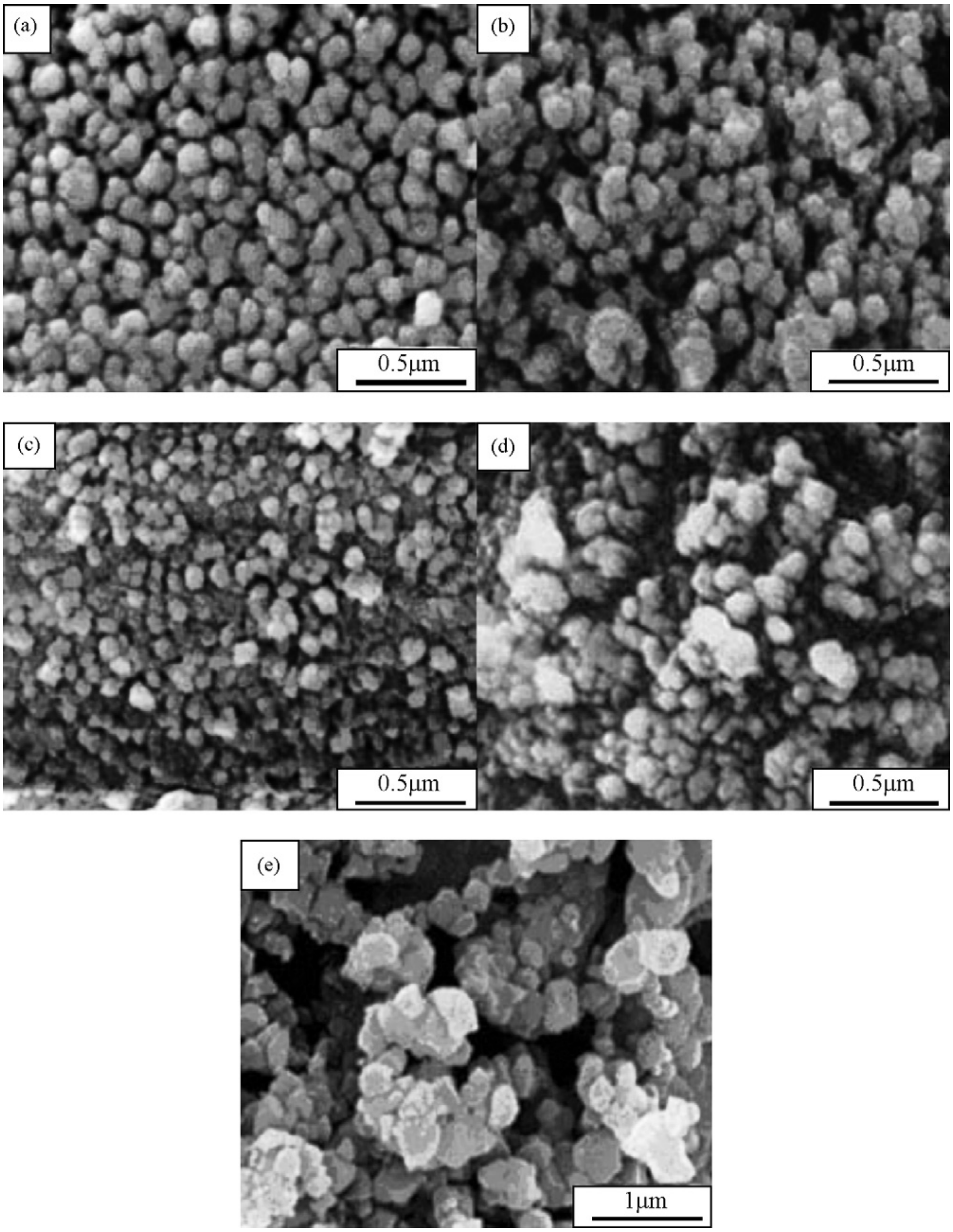

Fig. 4. SEM photographs of AlN powders synthesized from different carbon sources (a, glucose; b, sucrose; c, water-soluble starch; d, citric acid; e, carbon black).

the more rapid reaction rate for the precursors prepared with water-soluble organic materials as carbon sources.

3.3. SEM observation of AlN powders

Fig. 4 shows the SEM photographs of AlN powders synthesized from the precursors prepared with different carbon sources. As shown in Fig. 4, AlN powders synthesized with water-soluble organic materials as carbon source consist of very fine spherical particles (particle size about 100 nm) and their particle size distribution is sharp. The particles of AlN powders synthesized with carbon black as carbon source seem to be larger than those of the powders synthesized with water-soluble organic materials as carbon source, and their size distribution is wider. These differences can be easily explained by considering the differences of the particle size and the mixing homogeneity of the raw materials

3.4. Effect of carbon content on the specific surface area of AlN powders

Glucose was used as a water-soluble carbon source to study the influence of carbon content on the specific surface area of the synthesized AlN powders. The molar ratio of carbon to aluminum (C/Al) in the combustion synthesis precursors was changed by varying the molar ratio of glucose to aluminum nitrate in the starting materials. Fig. 5 shows the relationship between the specific surface area of AlN powders synthesized at 1500 °C for 2 h and the C/Al molar ratio in the precursors. The specific surface area increased with the increase of the

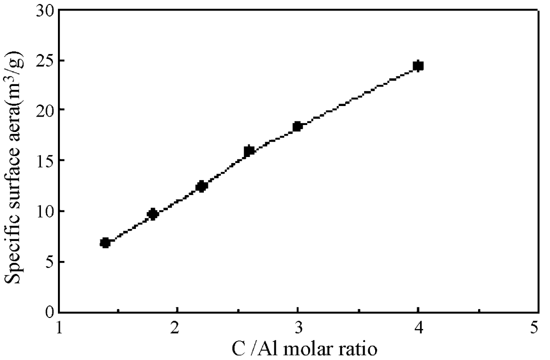

Fig. 5. Effects of C/Al molar ratio on the specific surface area of AlN powders.

C/Al molar ratio in the precursors. These results indicate that an increase of carbon content facilitates the synthesis of AlN powders with finer particle size and better dispersability. It is generally accepted that the heat generated in the combustion reaction is almost a constant when the ratio of fuel (urea) to oxidizer (aluminum nitrate) in the starting materials is fixed and the reaction is under the same conditions.[20] In our experiment, the heat generated in the combustion reaction not only transformed aluminum compound into alumina, but also made the glucose dehydrated and decarbonzied to form carbon matrix. The heat consumed by the dehydration and decarbonization of organic carbon sources increased in line with the amount used. It was found that, when the amount of water-soluble organic materials increased to a certain amount, the heat generated in the combustion reaction was insufficient for the dehydration and decarbonization of these organic carbon sources and the precursor prepared became a hard brown lump. As the heat used for the dehydration and decarbonization of organic carbon sources was increased, the heat that transformed aluminum compound to alumina decreased and finer alumina particles were obtained. These finer alumina particles dispersed into a larger amount of carbon matrix, which caused the particle size of synthesized AlN powders to become finer and the specific surface area of the powders to increase.

4. Conclusions

Carbon sources had a great influence on the synthesis of AlN powders by carbothermal reduction of combustion synthesis precursors. AlN powders were synthesized directly from γ-Al_2O_3 when water-soluble organic materials were used as carbon sources, while AlN powders were synthesized from the nitridation of α-Al_2O_3 when carbon black was used as carbon source. The reaction rate for the precursors with water-soluble organics as carbon sources was faster. The particles of AlN powders synthesized with water-soluble organics as carbon sources were smaller and their particle distribution was sharper. The carbon content had a great influence on the particles of AlN powders. The specific surface area of synthesized AlN powders increased with the increase of carbon content in the precursors. The increase of the carbon content in the precursors facilitated the synthesis of AlN powders with fine particle size and good dispersability.

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