

Low temperature synthesis of AlN nanopowders by the microwave assisted combustion method

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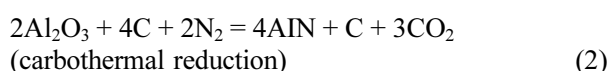
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Aluminum nitride (AlN) powder was calcined at low temperature through the carbothermal reduction nitridation (CRN) assisted by microwave heating. Their phase formation and microstructure were investigated with X-ray diffraction (XRD) and transmission electron microscopy (TEM). The starting materials such as aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea (NH_2CONH_2) and glucose anhydrous ($\text{C}_6\text{H}_{12}\text{O}_6$) were dissolved by stirring with a magnetic bar at 100 °C for 25 min and then the precursor solution was dried at oven. The mixing molar ratio of urea to aluminum nitrate = 1.6 and that of glucose to aluminum nitrate = 1.0 were selected, respectively. The dried precursor mixtures were calcined at 1200 ~ 1500 °C for 60 min. in N_2 atmosphere by a microwave heating furnace and then carburized at 700 °C for 2 hrs in air. The homogeneous AlN powders, free of alumina, were obtained by calcining at temperatures above 1300 °C. The particle size of AlN powder increases monotonically with increasing the calcination temperature. From TEM micrographs, the AlN powders calcined at 1300 °C and 1500 °C were found to be around 30 nm and 90 nm, respectively.

Key words: Aluminum nitride (AlN), Nano particle, Synthesis, Microwave combustion, carbothermal.

Introduction

Aluminum nitride (AlN) has been used widely in thermal dissipation applications such as IC packaging materials, heat sinks and high thermally conductive composites due to its high thermal conductivity, high electrical resistivity, good corrosion resistance and thermal expansion coefficient similar with Si-wafer [1]. There are various methods for synthesizing AlN powder such as direct nitridation, self-propagating high temperature synthesis (SHS), chemical vapor synthesis (CVD), and carbothermal reduction-nitridation (CRN), etc. The main methods to produce AlN powder commercially are as follows [2-7]: one is the direct nitridation of Al with N_2 and the other is the carbothermal reduction of Al_2O_3 with carbon black in the presence of N_2 as shown below.



The CRN process can produce the AlN powder having high purity, high resistance against moisture, and high

sinterability. However, it is difficult to obtain the pure AlN powder by calcining at low temperature for this process. A lot of efforts have been made in order to solve the above problem. Nano-sized AlN powder was calcined at about 1400 °C using carbothermal reduction and nitridation of a precursor which was made from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Citric acid, NH_4NO_3 and NH_4OH [8]. Terao *et al.* [9] obtained the pure AlN powder over 1300 °C using gas reduction nitridation of alumina nanopowder using an NH_3 - C_3H_8 gas mixture. Yamakawa *et al.* [10] calcined single phase nanosized AlN over 1200 °C using gas-reduction-nitridation of aluminum hydroxide, $\text{Al}(\text{OH})_3$ powders with a mixture of NH_3 and C_3H_8 gases. It was reported that AlN powder was obtained using carbothermal reduction of the mechanical activated Al_2O_3 at 1250 °C but there existed unknown phase due to a probable contamination [11].

The conventional synthesis of AlN takes a long reaction time caused by slow diffusion rates in solids and can give inhomogeneous properties due to the temperature difference according to the firing place. In contrast to the conventional method, the microwave technique has a lot of advantages for the preparation of inorganic materials such as short reaction time, enhanced reaction kinetics, and reactant selectivity during energy transfer from the microwave field. Meanwhile, there are limited reports available on the microwave heating synthesis of AlN [12-15].

In this study, we prepared AlN powder by the carbothermal reduction-nitridation (CRN) method assisted

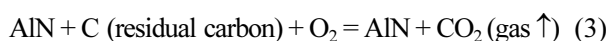
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with the microwave heating. The variation of phase formation and microstructure as a function of synthesis temperature were investigated with XRD and TEM. Also, the decomposition behavior of the mixed precursor powder was analyzed by TG-DTA.

Experimental Procedure

Fig. 1 shows the schematic diagram of fabrication process of AlN nano-particle by carbothermal reduction and nitridation method with microwave furnace. The starting materials were $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$, and $\text{C}_6\text{H}_{12}\text{O}_6$. The mixing molar ratio of urea to aluminum nitrate and glucose to aluminum nitrate were fixed at 1.56 and 1.04, respectively. Aluminum nitrate, urea and glucose were completely dissolved in water in order to obtain a combustion precursor solution. A gelatinous mass was formed by evaporating the solution at around 100°C on a hot plate. With further heating, the gelatinous mass boiled and swelled with releasing a lot of gas. The whole process took about 20 minutes and finally a black foamy mixture of alumina and carbon ($\text{Al}_2\text{O}_3 + \text{C}$) was obtained. For proceeding the nitridation of Al_2O_3 , the precursor mixture was put into a graphite crucible and heated in a flowing N_2 gas of 3 L/min. at temperature of $1200 \sim 1500^\circ\text{C}$ by a microwave furnace (Unicera, UVAC-03, 3 kw, 2.4 GHz). Fig. 2 is a schematic illustration of the microwave furnace. The graphite crucible containing the precursor mixture was placed on the ring typed SiC susceptor at the center of the cavity. Microwave at 2.45 GHz was generated by a generator placed below the quartz window whose power output was continuously adjustable in the range of 0-3 kW. The heating rate was controlled by adjusting the microwave power and the microwave cavity was cooled by circulating water.

The temperature profile for synthesizing AlN powder is shown in Fig. 3. The temperature profile was divided into four stages considering the allowable temperature gradients, degassing and capability of furnace, etc. Heating up from room temperature to 1000°C for 30 min, heating from 1000°C to 1500°C for 25 min. and then soaking at 1500°C for 60 min. finally cool down to room temperature for 180 min. Before heating, the furnace was vacuumed and then flushed with N_2 gas to eliminate oxygen in the furnace. Residual carbon in the nitridated product was removed by firing for 120 min. in air at 700°C in a box furnace and its reaction is shown below.



Phase analysis was performed on X-ray diffractometer (Siemens, DE/D500D) using Cu K_α radiation. The chemical reaction and decomposition of the precursor mixture was investigated with TG/DTA (Shimadzu,

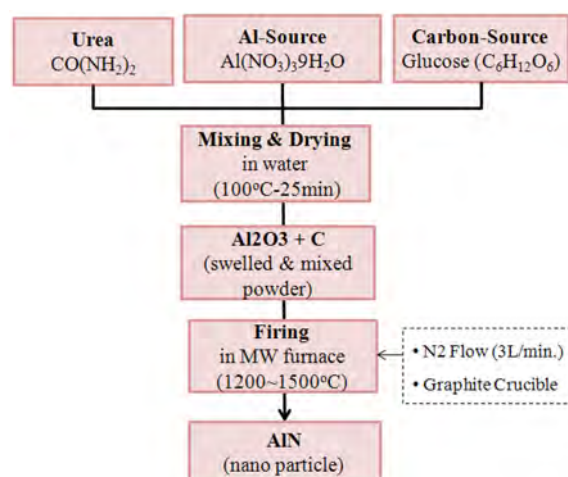


Fig. 1. Experimental procedure for synthesizing the AlN powder.

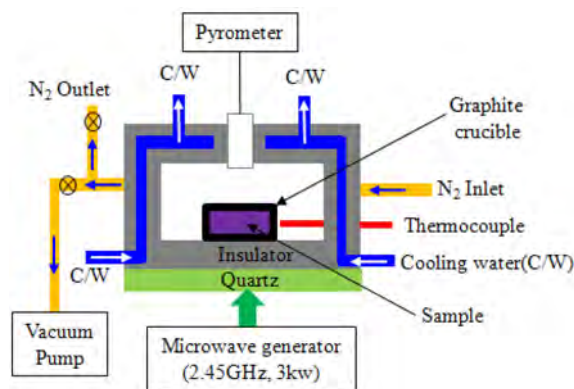


Fig. 2. A schematic illustration of the microwave heating furnace.

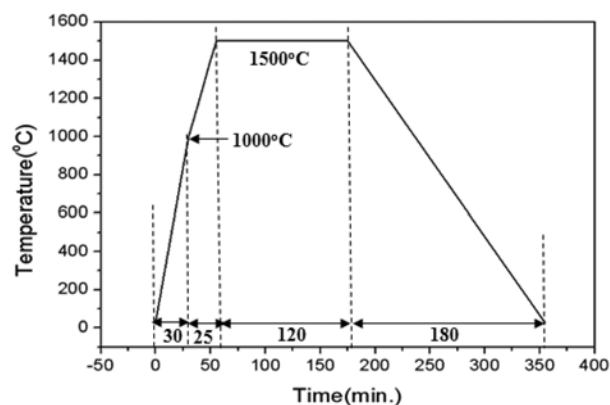


Fig. 3. Temperature profile of the microwave furnace for synthesizing the AlN powder.

DTG-60H). The particle sizes and morphologies of the nitridation products were observed by TEM (Jeol, JEM-4010).

Results and Discussions

The high temperatures required for the formation of ceramic powder are usually accomplished by the exothermicity of the reactions occurring between the

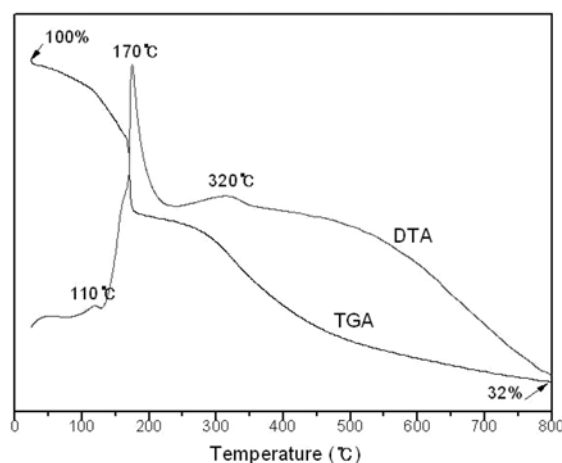


Fig. 4. DTA/TG curves of a precursor gel formed by heating the solution mixture of aluminum nitrate, urea and glucose at 100 °C.

decomposition products of metal nitrate (oxidizer) and urea/glucose (fuel) during combustion. Stoichiometric compositions of the metal nitrates, urea and glucose were calculated using the total oxidizing and reducing valencies of the components which provide as numerical coefficients for stoichiometric balance so that the equivalent ratio is unity and the energy generated by the combustion is at a maximum. According to the concepts used in propellant chemistry, the elements Al, C and H have reducing valencies of + 3, + 4 and + 1, respectively. Oxygen has a oxidizing valency of -2 and the valency of nitrogen is zero. Thus, the oxidizing and the reducing valencies of aluminum nitrate, urea and glucose become -15, + 6 and + 24, respectively. To synthesize the aluminum nitride (AlN) by combustion route, crystalline $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (total valencies -15) can be taken as Al source. Direct use of propellant chemistry criterion to determine the urea and glucose required to balance the total oxidizing and reducing valencies in the mixture, leads to: $1(-15) + n(+6 + 24) = 0$. A redox mixture is considered to be stoichiometric when $n = 0.5$. In our mixture, the mixing molar ratio of urea to aluminum nitrate and glucose to aluminum nitrate were fixed at 1.6 and 1.0, respectively, which means that the fuel in our precursor composition is rich in comparison with aluminum nitrate (oxidizer).

Fig. 4 shows the DTA/TG curves of a precursor gel formed by heating the solution mixture of aluminum nitrate, urea and glucose at 100 °C. As can be seen in the DTA curve, one strong exothermic peak at 170 °C and two weak broad peaks near 110 °C and 320 °C are observed. The high exothermic reaction at 170 °C, accompanied by a drastic mass loss, seems to be attributed to the decomposition of urea which is a strong reducing agent [16]. The abrupt mass reduction between 110 °C and 170 °C is another evidence of the removal of moisture and the decomposition of urea during the combustion. The weight loss at a lower rate

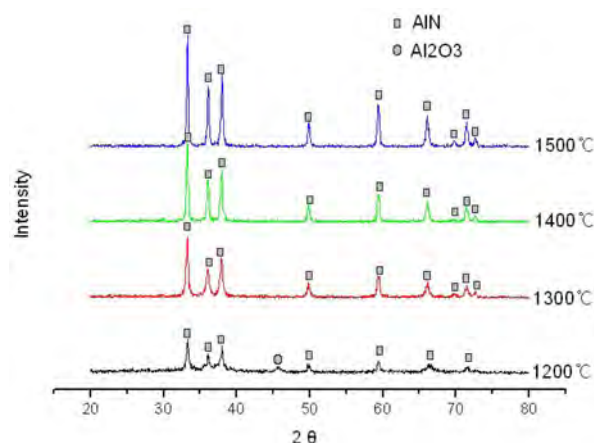
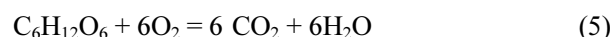
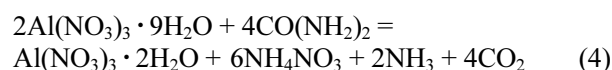


Fig. 5. X-ray diffraction patterns of the AlN powders synthesized at different temperatures.

between 320 °C and 800 °C is presumably due to the decomposition of aluminum nitrate and/or the oxidation of CO_2 of some carbon from the pyrolysis of glucose [17].



There is no evidence for the compound formation in TG-DTA curves.

Fig. 5. shows the X-ray diffraction patterns of the powders calcined at 1200 ~ 1500 °C using the microwave heating furnace and nitrated at 700 °C in order to remove residual carbon. A weak peak due to the residual Al_2O_3 was observed at $2\theta = 46^\circ$ for the powers calcined at 1200 °C. It is noticed that the pure AlN phase appeared for the powers calcined above 1300 °C as shown in Fig. 4, which is lower than the other result calcined with the conventional furnace [18]. Therefore, the microwave furnace is considered to be more useful than conventional one in respect of a fast and homogeneous synthesis of the AlN powder at low temperature. It is also observed that the intensity of X-ray diffraction patterns becomes stronger and sharper with increasing the calcining temperature, which seems to be related with the crystallinity and the particle size of the calcined powder.

The average crystalline size was calculated according to XRD patterns using the peak corresponding to hexagonal (100) plane and Scherrer formula as follows:

$$D(\text{nm}) = \frac{0.89\lambda}{B \cos \theta} \quad (6)$$

Where D is the crystalline size; λ is the wavelength of the X-ray diffraction (for CuK radiation, $\lambda = 1.5406 \text{ \AA}$); θ is the Bragg angle; B is full width at half maximum intensity (FWHM).

Figs. 6(a) and 6(b) show the variation of the (100)

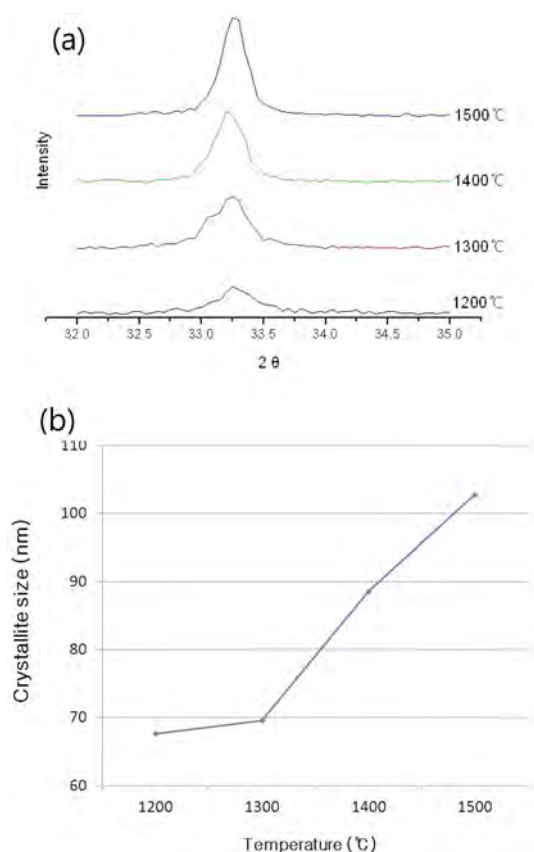


Fig. 6. The variation of (a) the (100) XRD pattern and (b) the average crystallite size as a function of the calcining temperature.

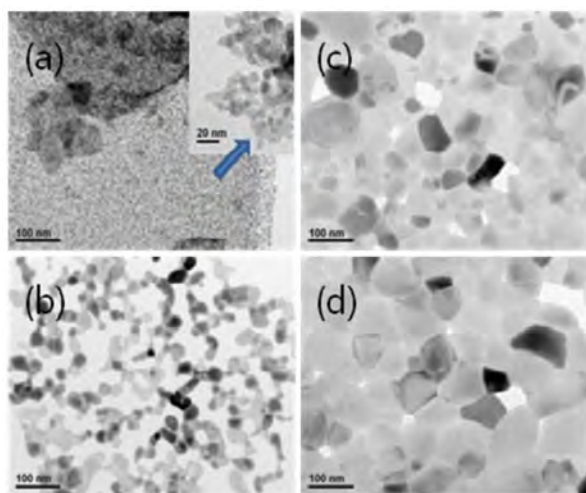


Fig. 7. TEM images of the AlN powders synthesized at (a) 1200 °C, (b) 1300 °C, (c) 1400 °C and (d) 1500 °C.

peak of X-ray diffraction and the average crystallite size as a function of calcining temperature, respectively. It is shown that the (100) peak becomes narrower in shape and stronger in intensity. The crystallite size was found to be 67 nm for the powders calcined at 1200 °C. The crystallite size increased with higher calcination temperatures and the maximum size was found to be 102 nm for powders calcined at 1500 °C.

The TEM images of AlN powders calcined at

1200 ~ 1500 °C are presented in Figs. 7(a)-(d). It is shown that the particle size grows and the particle shape becomes facet with increasing the calcination temperature. The facet shaped particles seems to be related with the formation of sintering necks and interconnections due to the agglomeration of the particles. The size of the AlN powders were found to be around 30 nm at 1300 °C, which was smaller than the value of 70 nm calculated based on XRD data. Meanwhile, the size of the AlN powders calcined at 1500 °C was about 90 nm, which is relatively consistent with the result derived from XRD data.

Conclusions

The 100% pure AlN powders were calcined at low temperature of 1300 °C from aluminum nitrate, urea and glucose by the microwave assisted combustion synthesis method. An elevation of the calcination temperature from 1200 to 1500 °C leads to the formation of larger particles. The SEM micrographs show that the particle size of nano-crystalline AlN powders were found to be near 30 nm at 1300 °C and 80 ~ 100 nm at 1500 °C. It is thought that the microwave assisted combustion synthesis method is useful for obtaining the pure AlN powder with ease at low temperature.

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