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# Synthesis and characterization of AlN nanopowder by the microwave assisted carbothermal reduction and nitridation (CRN)

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Abstract Aluminum nitride (AlN) powder was successfully synthesized at low temperature via carbothermal reduction and nitridation (CRN) assisted by microwave heating. The synthesis processes of AlN powder were investigated with X-ray diffraction, FE-SEM, FT-IR and TGA/DSC. Aluminum nitrate was used as an oxidizer and aluminum source, urea as fuel, and glucose as carbon source. These starting materials were mixed with D.I water and reacted in a flask at 100°C for 20 minutes. After the reaction was finished, black foamy intermediate product was formed, which was considered to be an amorphous $Al_2O_3$ particles through intermediate product obtained by solution combustion synthesis (SCS) at the results of X-ray diffraction patterns and FT-IR. This intermediate product was nitridated at temperatures of 1300°C and 1400°C in $N_2$ atmosphere by a microwave heating furnace and then decarbonated at 600°C for 2 hours in air. It should be noticed from FE-SEM images that as nitridated particles, identified as AlN from X-ray diffraction patterns, are covered with carbon residues. After decarbonating the nitridated powders, the spherical pure AlN powders were obtained without alumina and their particle sizes were dependent on the nitridating temperature with high temperature of 1400°C giving large particles of around 70~100 nm.

Key words AlN powders, Urea, Microwave heating, Carbothermal combustion

## 1. Introduction

Aluminum nitride (AlN) has been used widely in semiconductor parts, metal printed circuit board (PCB) and Heat sink plate etc. due to its high thermal conductivity, high electrical resistance, low dielectric constant, low thermal expansion coefficient, good thermal shock resistance, good corrosion resistance and good thermal shock resistance [1, 2]. A lot of methods for synthesizing AlN have been reported such as direct nitridation [3], vapor phase synthesis [4] and Carbothermal reduction nitridation (CRN) [5-9]. CRN process produces AlN powder with high purity, high resistance against moisture, and high sinterability but has presented some limitations such as difficulty in mixing starting materials homogeneously and an increasing cost due to a high calcination temperature. Solutiion combustion synthesis (SCS) has been considered to be one of the most appropriate methods to prepare the oxide-based materials because it has some advantages [9, 10]. The combustion reaction in this method is so simple and instantaneous that it can save process energy. Furthermore, the synthesized ceramic powders exhibit the well-defined chemical compositions with homogeneous distribution of the elements.

In the present work, AlN powder was fabricated by CRN method assisted by microwave heating for rapid and uniform heating of reactants [11, 12]. Aluminum nitrate was used as an oxidizer and aluminum source, urea as fuel, and glucose as carbon source. The synthesis processes of AlN powder were investigated with X-ray diffraction (XRD, D/max Rigaku 2200V/PC), Field emission canning electron microscopy (FE-SEM), Fourier transform infra red (FT-IR, Thermo Scientific Nicolet iS10), Differential scanning calorimetry and Thermal gravimetry (DSC-TG, Netzsch STA 409 PC).

## 2. Experimental

Fig. 1 shows the experimental procedure for synthesis of the AlN powder by Solution Combustion Synthesis (SCS) in beaker and carbothermal reduction nitridation (CRN) with microwave furnace. The starting materials were aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Aldrich, 99 %), urea ($CO(NH_2)_2$ Aldrich, 99.0 %), and glucose ($C_6H_{12}O_6$, samchun, 98 %). The mixing molar ratio of urea to aluminum nitrate (U/Al) was 0.5, 1, 1.5 and glucose to aluminum nitrate (C/Al) was 0.5, 1

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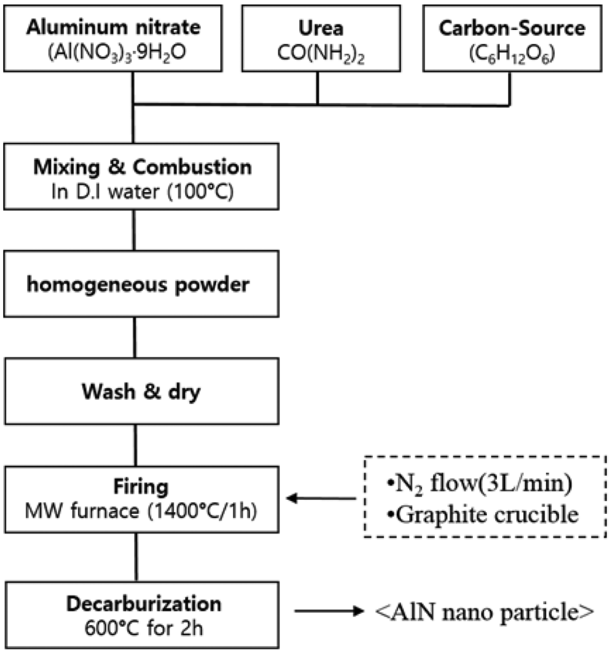

Fig. 1. Experimental procedure for synthesis of the AlN powder.

respectively. Aluminum nitrate, urea and glucose were completely dissolved in distilled water by a magnetic stirrer. This precursor solution was heated to 100°C in air on the heating mantle and kept there for 20 minutes. During the heating process, the precursor solution is initially evaporated and then becomes swollen suddenly to produce a yellow gelatinous matter with some black products contained inside it as shown in Fig. 2. In this SCS process, a lot of gases are released followed by the flame of combustion exothermic reaction which is contributed to a rapid increase of the reaction temperature reaching from 100°C to 169°C required to synthesize fine particles.

The intermediate products obtained by the SCS process were grounded completely to form homogeneous powders without agglomerated particles. After that, these intermediate powders were put into a graphite crucible and heated at 1300~1400°C in a flowing $N_2$ (3 L/min) by a microwave furnace (Unicera, UVAC-03, 3 kw, 2.4 GHz) as shown in Fig. 3. A 2.45 GHz microwave is generated by a generator placed below the quartz window whose power output can be 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 graphite crucible containing the intermediate powder was heated via the use of the SiC ring as susceptors at the center of the cavity.

Fig. 2. Combustion reaction from inside to surface lasted for several minute with flame.

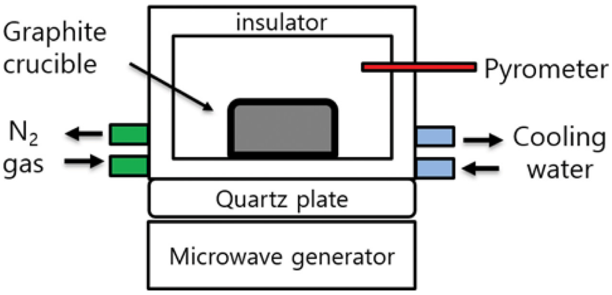

Fig. 3. A schematic illustration of the microwave chamber.

Temperature profile for the CRN step is divided into four stages considering the allowable temperature gradients, degassing and capability of furnace, etc. as shown in Fig. 4. Heating up from room temperature to 1000°C for 30 min, heating from 1000°C to 1400°C for 20 min. and then soaking at 1400°C for 60 min. finally cool down to room temperature for 70 min. During the heating, the furnace was flowed with $N_2$ gas of 3 L/min. in the furnace. Residual carbon in the nitridated product

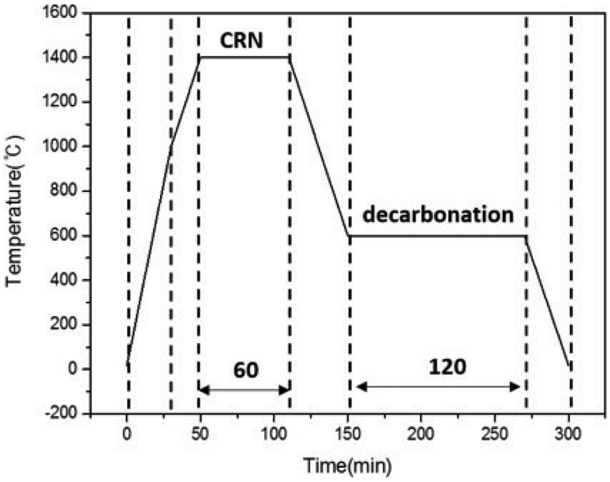

Fig. 4. Time to temperature schedule followed during the microwave heating and decarbonation.

was removed by firing in the electrical furnace at 600°C for 120 min in air condition. The synthesized powders were analyzed by X-ray diffraction, Field Emission Scanning Electron Microscopy, Differential scanning calorimetry and Thermal gravimetry and Fourier transform infra red.

## 3. Results and Discussion

The thermal behavior of the precursor under flowing nitrogen and argon are shown in Fig. 5. There is not nearly weight loss above 600°C because glucose, urea, nitrate and volatiles ($H_2O$, $CO_x$, etc.) were decomposed completely.

$$2Al(NO_3)_3 \cdot 9H_2O + 5CO(NH_2)_2 = Al_2O_3 + 5CO_2 + 8N_2 + 10H_2O \quad (1)$$

$$C_6H_{12}O_6 = 6C(s) + 6H_2O(g) \quad (2)$$

$$Al_2O_3(g) + 2C(s) = Al_2O(g) + 2CO(g) \quad (3)$$

$$Al_2O(g) + CO(g) + N_2(g) = 2AlN(s) + CO_2(g) \quad (4)$$

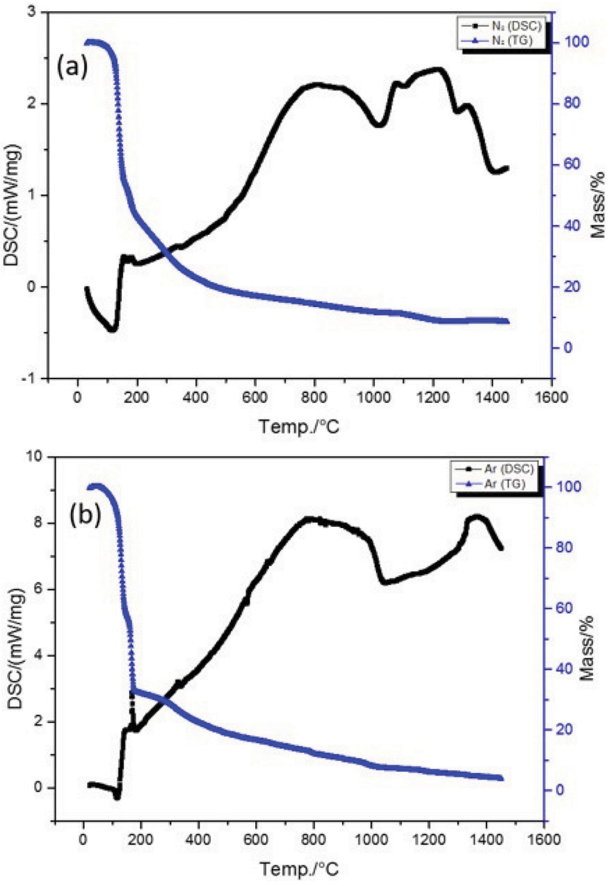

Fig. 5. The TGA/DSC curves of the precursor solution; argon flow condition (b) and nitrogen flow condition (a).

$$C(s) + CO_2(g) = 2CO(g) \quad (5)$$

The weight loss of about 10 % in the range of 50~150°C could be attributed to the evaporation of moisture from the precursor. The weight loss in the range of 150~200°C is about 40 % due to the decomposition of aluminum nitrate and urea Eq. (1). Between 200°C and 600°C, the 20 % weight loss is believed to originate from the decomposition and carbonization of glucose Eq. (2). All the exothermic peaks in the DTA curves corresponding to weight losses are broad and weak, implying that the precursor involves slow decomposition and carbonization without the combustion of carbon below 600°C in nitrogen atmosphere. In the range of 1000~1200° C, two more broad exothermic peaks are observed not at the argon flow condition Fig. 5(b) but nitrogen flow condition Fig. 5(a), which is likely to be attributed to the conversion reaction from alumina ($Al_2O_3$) to aluminum nitride (AlN) through the reaction equations Eq. (3), (4) and (5).

Fig. 6 illustrates the infrared spectrum of the intermediate product obtained by SCS step. There exist many absorption peaks that are due to the O-H stretching vibration of $H_2O$ (3360, 1614 $cm^{-1}$), $CO_3^{2-}$ groups (2361, 1385, 832 $cm^{-1}$), Al-OH (1087 $cm^{-1}$), and Al-O of amorphous $Al_2O_3$ (650~850 $cm^{-1}$) [13, 14]. The absorption peaks around 1614 $cm^{-1}$ and 1385 $cm^{-1}$ can be assigned to vibration of C=O group and the asymmetric vibration of H-N-H groups, respectively, which indicates the presence of ammonium, urea and urea derivatives [15]. It can be concluded from the investigation of infrared spectrum that the intermediate product obtained by SCS step are consisted of many substances besides amorphous $Al_2O_3$ particles composed of Al-O and/or Al-OH.

In the temperature range of 600~1000°C after SCS

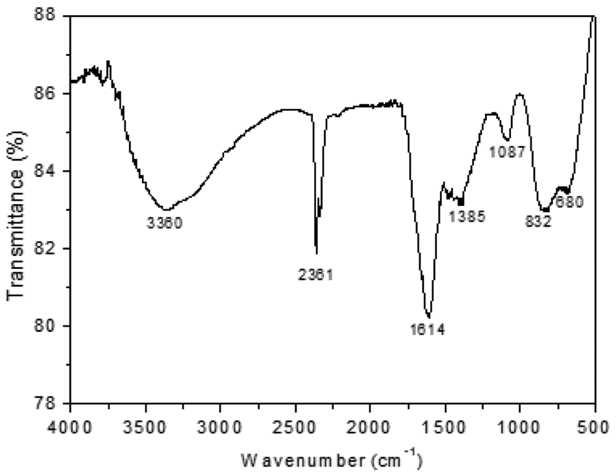

Fig. 6. Infrared spectra of precursor mixture after SCS step.

step, the additional exothermic reactions by the residues of ammonium, urea and urea derivatives seem to ignite and propagate in a self sustained manner throughout the intermediate product [13] and accelerate the conversion from the amorphous $Al_2O_3$ particles composed of Al-O and/or Al-OH to crystalline $Al_2O_3$ particles in microwave heating. It is considered that $Al_2O_3$ particles start to convert to AlN particles by reacting with C(s) and $N_2$(g) at about 1000°C in $N_2$ atmosphere and in further heating above 1000°C, the amount of AlN particles increases consuming remaining alumina particles through carbothermal reduction nitridation (CRN) [16, 17].

Fig. 7(a) and (b) present the X-ray diffraction patterns of the intermediate product after SCS step and the final powders after CRN step by microwave, respectively. It is evident from Fig. 7(a) that any obvious Bragg diffraction peaks are not detected in the intermediate product, which indicates that it is an amorphous phase consisted of many substances including Al-O as shown in Fig. (6).

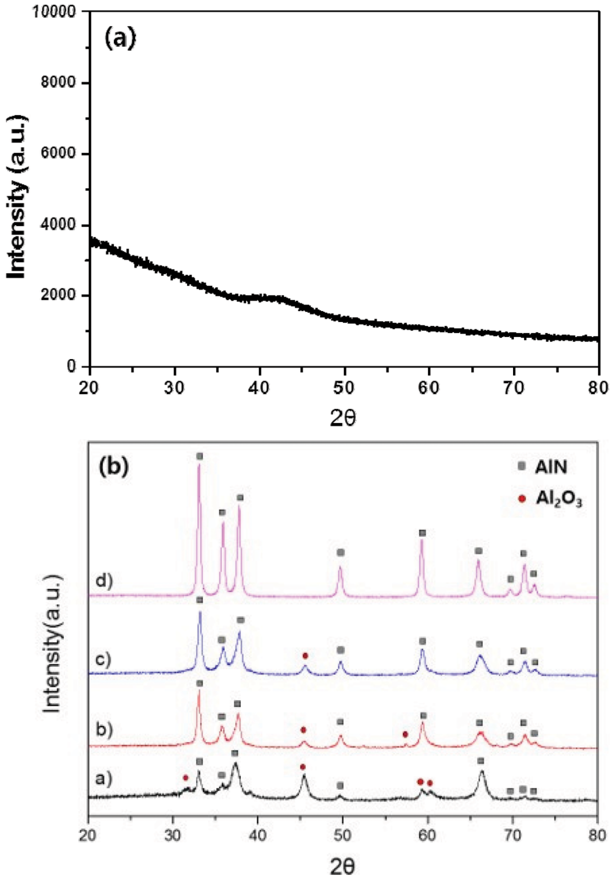

Fig. 7. X-ray diffraction patterns from (a) the intermediate product after SCS step and (b) the final powders after CRN step was processed at temperatures of 1300°C (The mixing molar ratio of urea to aluminum nitrate (U/Al) was a) 0.5, b) 1, c) 1.5 and d) 1.5 and glucose to aluminum nitrate (C/Al) was a) 0.5, b) 0.5, c) 0.5 and d) 1 respectively).

Fig. 7(b) presents the mixing molar ratio of urea to aluminum nitrate (U/Al) was a) 0.5, b) 1, c) 1.5 and d) 1.5 and glucose to aluminum nitrate (C/Al) was fixed a) to c) at 0.5 and d) at 1. After the CRN step at above 1300°C, the only AlN phases are observed without any $Al_2O_3$ phases as shown in sample d) which implies that the intermediate product is converted to AlN particles distributed in carbon matrix. The intensity of X-ray diffraction peaks is higher for the powder calcined at c) than at d) which is related to the crystallinity of particles. It is well known that the higher the intensity of X-ray diffraction peaks, the better the crystallinity.

Fig. 8 presents the FE SEM images of the precursor. The intermediate product after SCS step looks like ash without any crystalline particles as shown Fig. 8(a), which was identified as an amorphous $Al_2O_3$ phase located in carbon matrix from the FT-IR spectrum and the X-ray diffraction patterns in Fig. (6) and (7). In the SCS step, the precursor solution is dried for some minutes and then suddenly burned by combustion with gases generated during the reaction to give rise to the intermediate product. The powder after CRN step at 1300°C shows a lot of diffuse particles of about 60 nm in diameter, where some groups of particles are aggregated with being surrounded with thin layers and separated from other particles as shown in Fig. 8(b). The powder after CRN step at 1300°C and then decarburization at 600°C for 2 hours clearly consists of AlN particles of about 60 nm in diameter that are kept apart very well by the unreacted carbon as shown in Fig. 8(c), which may prevent the agglomeration of AlN particles and also ensure their homogeneity. It should be noticed that a considerable amount of residual carbon remains after finishing the CRN step, may be ascribed to the partial consumption of carbon during reaction. The powder after CRN step at 1400°C and then decarburization at 600°C for 2 hours has exhibited uniform and spherical particles of 70 to 100 nm in diameter as shown in Fig. 8(d).

## 4. Conclusion

Aluminum nitride (AlN) powder was successfully synthesized at low temperature via carbothermal reduction and nitridation (CRN) assisted by microwave heating. The synthesis processes of AlN powder were investigated with X-ray diffraction, FE-SEM, FT-IR and TGA/DSC. After the SCS reaction was finished, black

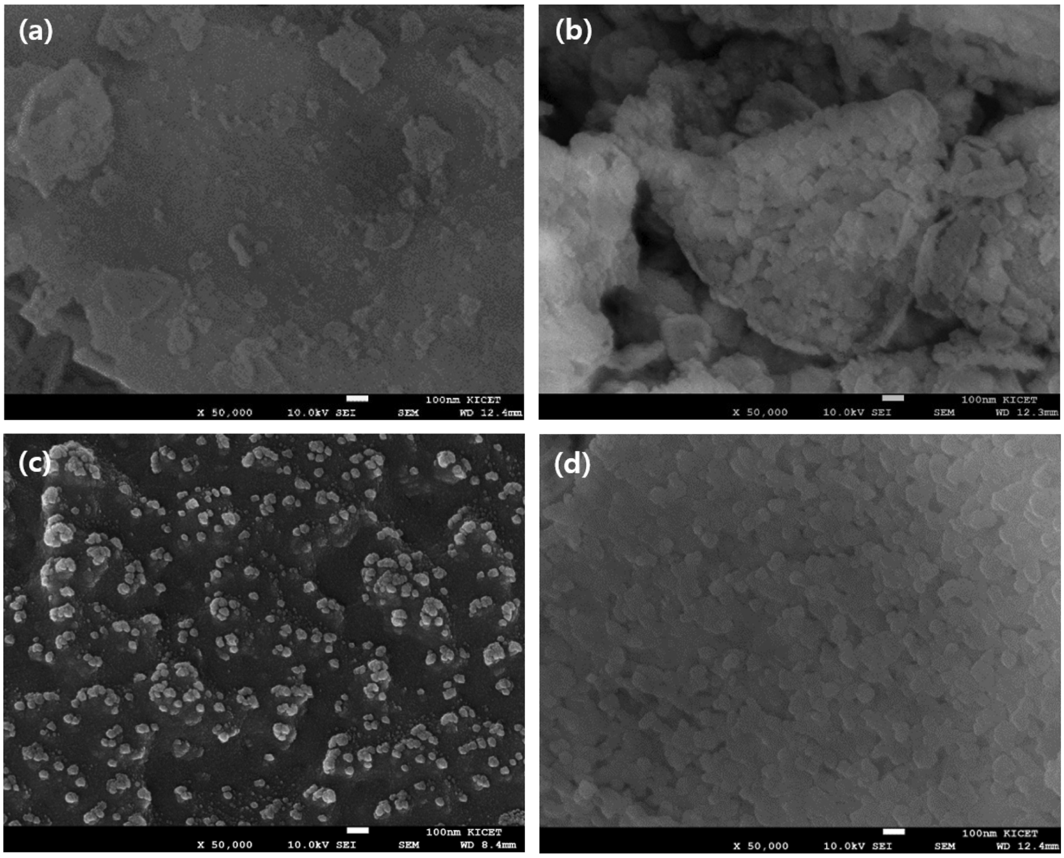

Fig. 8. FE-SEM photographs of (a) the intermediate product after SCS step, (b) the powder after CRN step at 1300°C, (c) the powder after CRN step at 1300°C and then decarburization at 600°C, and (d) the powder after CRN step at 1400°C and then decarburization at 600°C.

foamy intermediate product was identified as amorphous substances consisted of $Al_2O_3$ and organic residues derived from aluminum nitrate, urea and glucose from the results of X-ray diffraction patterns and FT-IR. The intermediate product is converted to AlN resided in carbon matrix in the process of the CRN at temperatures of above 1300°C in $N_2$ atmosphere by a microwave heating furnace. When the intermediate product was gone through CRN step at 1400°C and then decarburization at 600°C for 2 hours in air, the uniform and spherical particles of 70 to 100 nm in diameter were obtained without alumina and their particle sizes were dependent on the nitridating temperature with high temperature of 1400°C giving large particles of around 70~100 nm.

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