Journal of Ceramic Processing Research. Vol. 22, No. 3, pp. 258~263 (2021)
(Received 11 February 2020, Received in revised form 26 June 2020, Accepted 16 July 2020)
https://doi.org/10.36410/jcpr.2021.22.3.258

JOURNAL OF
Ceramic Processing Research

Synthesizing of nano-sized AlN powder with alumina balls

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In this study, a new method called the dynamic carbothermal reduction and nitridation (DCRN) method was used for nano sized aluminium nitride (AlN) powder production. The carbothermal reduction process was carried out in an atmosphere controlled modified rotary-type tube furnace in the new method and reactants are rolled with Al_2O_3 balls continuously during the process. This is a novel approach in synthesizing AlN powders. This study shows that high quality uniax homogeneous particles of nano sized aluminium nitride (AlN) powder could be produced using this method (DCRN) from aluminium hydroxide ($Al(OH)_3$) starting powders as low as 1450 °C. Produced powders were characterized by X-ray diffractometer (XRD) and field emission scanning electron microscopy (FESEM) analyses. As the result, nano-sized AlN powders were synthesized at 1450 °C for 1.5 hrs under by dynamic carbothermal reduction and nitridation (DCRN) method used Al_2O_3 balls.

Keywords: Aluminium nitride, dynamic carbothermal reduction, aluminium hydroxide, powder synthesis

Introduction

Aluminium nitride (AlN) is a Group III nitride compound that has been investigated for many micro-electromechanical systems (MEMS) applications and it has been evolved since the end of the 20th century owing to the progress in electronic industry [1, 2]. It is particularly important due to the variety of performance. AlN is an important structural ceramic material due to its high melting temperature (2200 °C) and good mechanical properties [3]. AlN has the high thermal conductivity (theoretical value of 320 $W \cdot m^{-1} \cdot K^{-1}$), high mechanical strength, low dielectric constant (8.0 at 1 MHz) and its thermal expansion coefficient is 4.8×10^{-6} K^{-1} at 20-500 °C, nontoxicity (when compared to BeO as a competing material), high electric breakdown field (1.8×106 $V \cdot cm^{-1}$) and excellent chemical stability [4, 5, 6]. AlN is a promising material for electronic substrates such as passivation and dielectric layers, protective coatings, and optical devices [7]. With a low value of electron affinity, high chemical and thermal stability, it should be a good candidate for field emission applications [8]. Its high thermal conductivity makes it possible to employ in the production of insulation plate for LED technology [9], ceramic substrates [10], buffer layer for surface acoustic wave (SAW) [11] and film bulk acoustic wave resonator (FBAR) based microwave filters [12] applications. In addition to the electronic industry, AlN is widely used for the production of composite materials [13]. AlN can also be used for structural applications, such as melting crucible [14], cutting tools [15] and ballistic armor [16].

There are a lot of methods in synthesizing AlN powders, including direct nitridation of Al [17], carbothermal reduction and nitridation (CRN) of Al_2O_3 [18], microwave plasma processing [19], solvent thermal method [20], solid-gas reaction of aluminium sulfide (Al_2S_3) with ammonia [21] and a wet chemical method [2]. However, it is still important to investigate the new methods for the synthesis of very low particles size and morphology control of AlN powders that are important in process stage of this material.

The CRN process is more attractive and economical route since it results in AlN powders with higher purity, higher resistance against moisture and higher sinterability than the widely used direct nitridation process. Because of this, CRN has been preferred widely used by many companies to manufacture AlN powders. Initially a powder mixture with Al_2O_3/C molar ratio of 1:3 is heated at around 1600 °C or above temperatures under a nitrogen gas flow for long periods of time to synthesize the AlN powders [18]. $Al(OH)_3$ are also used as an aluminium source for the CRN method [22, 23]. When $Al(OH)_3$ is used, the molar ratio of $Al(OH)_3$ and carbon is 1:6 following according to the stoichiometric equation below:

$$Al(OH)_{3(s)} + 6C_{(s)} + N_{2(g)} \rightarrow AlN_{(s)} + 3HCN_{(g)} + 3CO_{(g)} \quad (1)$$

According to this reaction, firstly hydrogen and nitrogen react to form HCN, depending on the amount of carbon. The remaining carbon provides the reduction in nitrogen media so AlN is formed [23].

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In the current study, the process was carried out in a specially designed rotary type tube furnace used Al_2O_3 balls and the process is named as dynamic carbothermal reduction (DCRN). The traditional carbothermal reduction technique up to now is used exclusively in a static system, where the reactants do not move during the whole reaction. Whereas, in the new DCRN method used in this study, reactants are rolled continuously with or without having balls in the system. This motion is a great advantage to reduce the time to complete the reaction for a given temperature or to lower the temperature for given time. Additionally, this result in finer size (nano) powders due to the grinding action of the balls compared to classical CRN process. Here, the parameters of aluminium nitride powder production using a new approach, DCRN process from aluminium hydroxide and carbon black as the raw material were investigated and the obtained results were presented.

Experimental

As a starting raw material for Al source, aluminium hydroxide powder which compose of gibbsite (γ-$Al(OH)_3$) from Merck was used. Carbon black from Körfez Petrokimya was used as reducing agent. The properties of the raw materials were given in Table 1. After pre-determined weight ratios, powders ($Al(OH)_3$/C molar ratio of 1:21) were prepared a homogenous mixture. Powder mixture and alumina balls (a certain amount) were charged into a cylindrical reactor made of graphite that both ends having holes for allowing gas flow. The used graphite reactor is shown in Fig. 1.

Cylindrical graphite reactor placed in the middle of the alumina tube furnace run at different test parameters under N_2 gas flow. Schematic view of the system is shown in Fig. 2. Before heating, the furnace was vacuumed and then flushed with N_2 gas to eliminate any oxygen before the reaction. The flow rate of nitrogen was 60 $L \cdot h^{-1}$. The residual carbon remained after DCRN was removed by firing the products in air at 680 °C for 1.5 hrs. Flow chart of aluminium nitride (AlN) production by DCRN process was given in Fig. 3.

It is better first to clarify about the original aspect of the method that its operating principle is based on the thermo-mechanical approach in rotating furnace. Unlike the conventional CRN process where powders are stable during reaction, here in DCRN process powders with and without having ceramic balls rotate by means

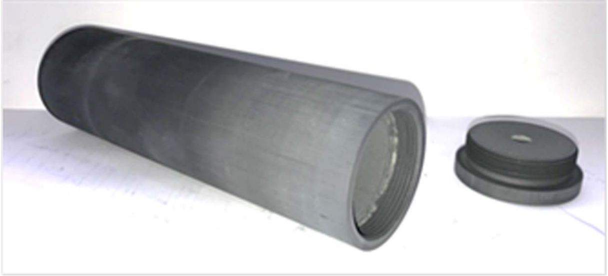

Fig. 1. The photograph of used graphite reactor in DCRN process.

Table 1. Properties of aluminium hydroxide ($Al(OH)_3$) and carbon black (C) as raw materials

Material	Powder Size	Impurity (wt.%)							
		Fe	Na	O	Cl	SO_4	Si	S	Ca
$Al(OH)_3$	<150 µm	0.01	0.30	-	0.01	0.05	-	-	-
C *	20 nm	1.88	4.09	45.77	-	-	12.49	11.94	13.04

*Loss of ignition (LoI) is 99.95wt.% after fired at 900 °C for 1 hour in O_2 atmosphere. Remaining ash was analyzed by Energy Dispersive Analysis (EDX).

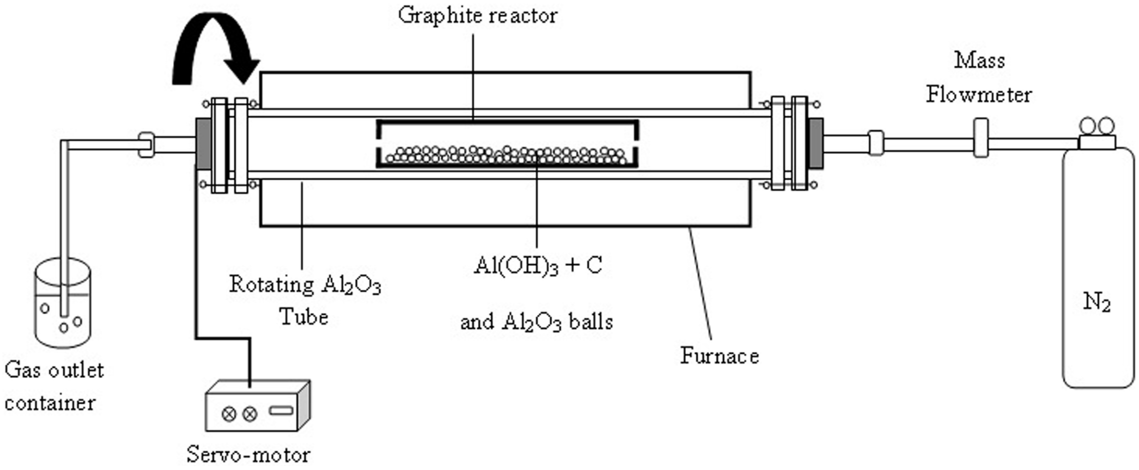

Fig. 2. The system of powder production by DCRN process.

of servo motor moves continuously during the process. It is believed that the diffusion becomes faster in or out of the raw materials with this rotation. In addition, thanks to this motion, time required to complete the reaction is much less as well as more homogeneous and finer particle size is obtained compared to static system (CRN process).

For the DCRN process, high temperature horizontal type atmosphere controlled furnace (Protherm, max. 1600 °C) was used using 60 mm outer diameter RCA alumina tube. The furnace was modified so that alumina tube is rotating with the help of 3-volt DC servo motor and gear system. Alumina tube was placed on top of an assemble carried using 4 bearings two on each site so as to rotate the tube easily and freely with predetermined speed if required. Heating and cooling of the furnace was set to 5 °C·min^{-1} due to the limit of alumina tube in order to avoid thermal shock [24]. After DCRN process product powders (i.e., AlN powders) having some amount of excess carbon was subjected to the removal excess carbons using Protherm PLF-130/18 model furnace in open air atmosphere. The schematic representation of nano sized AlN powder production was given in Fig. 4. It can be seen here before and after the process.

Phases present in the products were identified by X-ray diffractometer system (Rigaku, model D/Max-2200/PC, Japan) using monochromatic Cu Kα radiation operated at 50 kV and 300 mA. The analysis was performed at a rate of 2 °C·min^{-1} and between 10° to 90° 2θ. Morphologies were observed by scanning electron microscopy (SEM; JEOL, model 6060 LV, USA) and field emission scanning electron microscopy (FESEM; FEI Quanta FEG-450, Japan).

Results and Discussion

Fig. 5 shows the microstructure and XRD pattern of the raw material used as an Al source in synthesizing AlN via DCRN. According to the XRD analysis, it is seen that the structure consists of gibbsite (γ-$Al(OH)_3$) (the card number is 01-070-2038). In the SEM analysis, pure $Al(OH)_3$ powder (as given in Table 1) has very

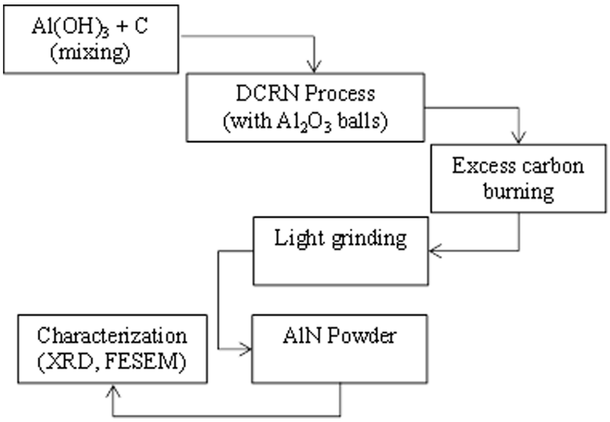

Fig. 3. Flow chart of nano-sized AlN powder production by DCRN process.

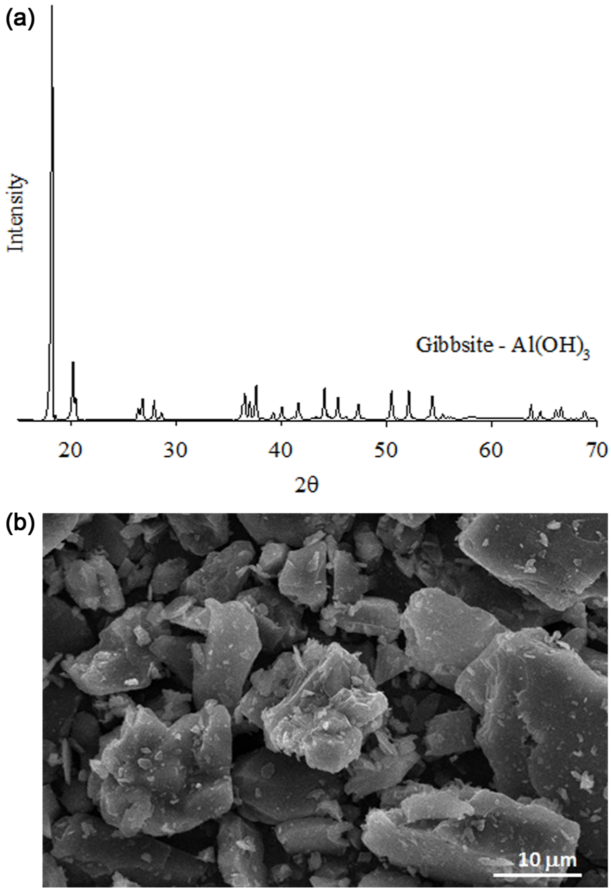

Fig. 5. (a) XRD and (b) SEM analyses of the raw material, aluminium hydroxide ($Al(OH)_3$).

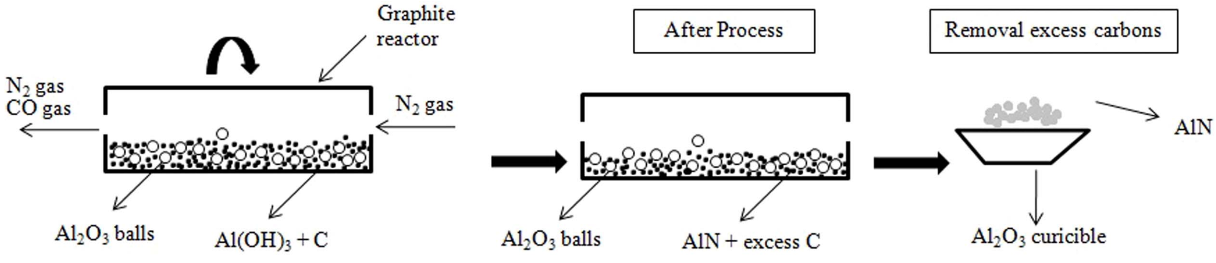

Fig. 4. Schematic representation of nano sized AlN powder production.

course particle size and wide particle size distribution with irregular and flat-faced shape particles.

In Fig. 6 gives the XRD pattern of the products synthesized by DCRN at 1450 °C for 1.5 hrs with different ball to powder (B/P) ratios process under 60 L·h^{-1} N_2 gas flow and reactor speed of 2 rpm. The samples were fired in an open air to remove the excess carbon at 680 °C for 90 min after DCRN process. According to XRD results, AlN powder (the card number is 01-076-0565) was produced with very high conversion rate under these parameters at all the experiments. Conversion rate was monitored using 1/ 10000 g sensitive balance which is used in weighting the reactants and product powders before and after DCRN. $Al(OH)_3$ is fully converted to AlN at 1450 °C for 1.5 hrs reaction using 60 L·h^{-1} N_2-flow rate with a reactor speed of 2 rpm in the DCRN process in all B/P ratios (Fig. 6). Also peak intensities are much higher compared to commercial AlN powders from Alfa Aesar. According to the literature [25], the production of AlN by CRN method was realized in 1550 °C for 2 hrs, in this study (DCRN) it was obtained in a much lower temperature and time. Wang et al. [26] studied AlN synthesis from Al_2O_3 with Y_2O_3 addition by CRN process and they obtained completely transformation in 1700 °C for 2 hrs. Similarly, they produced AlN powder with CaF_2 addition in another study and they have achieved the best result at 1800 °C for 2 hrs [27]. Xi et al. [28], reported the AlN ceramics synthesized by carbothermal reduction using the mechanical activated Al_2O_3. There, AlN synthesis was occurred at 1600 °C from the original Al_2O_3 powders. The temperature and time of production were reduced with activated Al_2O_3 powder by high-energy ball milling for 20 hrs. Hu et al. [29], synthesized AlN powder at 1500 °C for 2 hrs with $Al(OH)_3$ raw materials by carbothermal reduction nitriding process. On the other hand, it has been shown that with this study, more easily and very fine AlN powders can be produced by DCRN process.

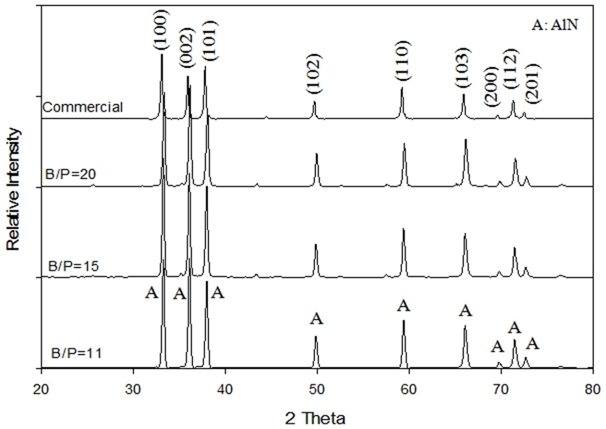

Fig. 6. XRD patterns of the products synthesized at 1450 °C for 1.5 hrs with different ball to powder (B/P) ratios.

Fig. 7 shows FESEM photographs of the powders synthesized via DCRN at 1450 °C for 1.5 hrs. It is observed that synthesized AlN powder has very small grains and a homogeneous morphology compared to

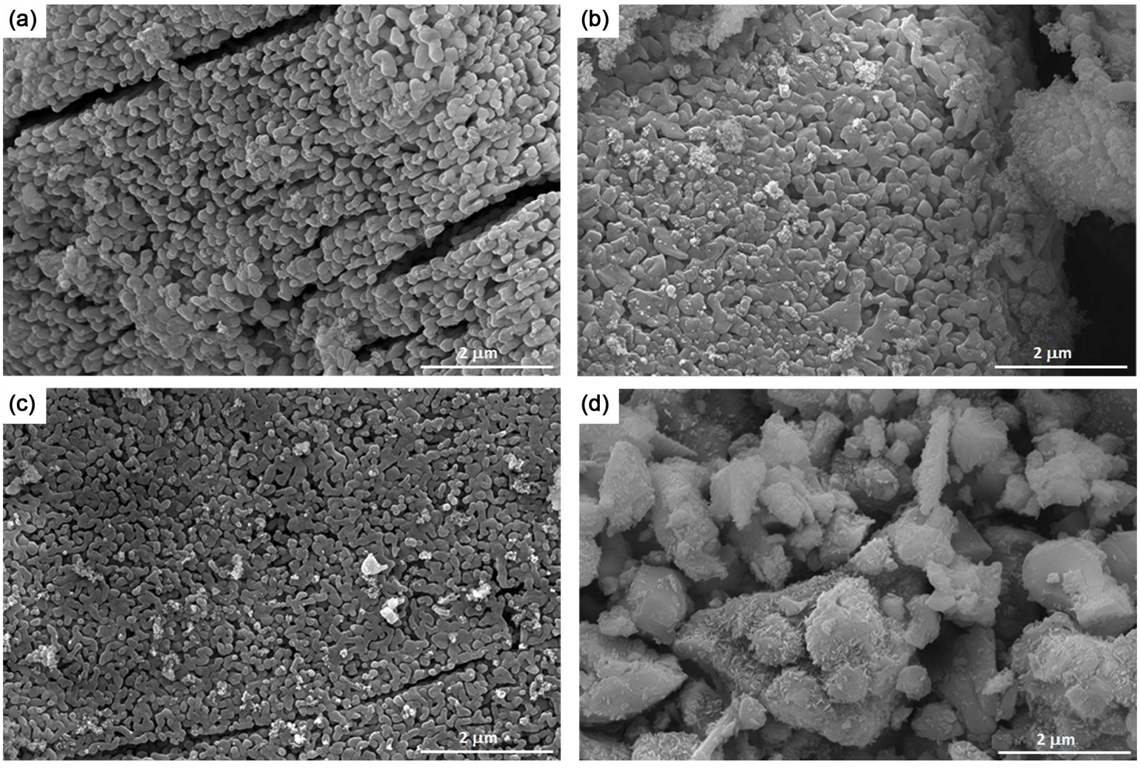

Fig. 7. FESEM photographs of the products synthesized at 1450 °C for 1.5 hrs using different ball to powder ratio of (a) B/P=11, (b) B/P=15, (c) B/P=20 and (d) Alfa Aeser AlN powder.

commercial AlN powders from Alfa Aesar. It is seen that the product was composed of homogeneous rounded shape equax nano size particles (≤90 nm). The resulting product of narrow size distribution of very fine equiax AlN powders were produced in a relative short period of time and lower reaction temperature compared to conventional static system of CRN method [30]. It is seen that the particle size of the products decreases as the ball to powder (B/P) ratio increases in the reactor (from (a) to (c) in Fig. 7). Therefore, the better result was obtained for B/P=20 given in Fig. 7(c). With the presence of balls in the graphite reactor in the reaction zone, the particles were ground and thus smaller grain size was obtained. This situation is the most important point of this study. It is a great advantage of using DCRN method for synthesizing nano-sized powders that does not require any further heat treatment when compared to the methods such as sol-gel technique. In addition, the used starting raw materials are relatively small amount compared to other chemical methods [31].

Increasing reactor speed from 2 rpm to 4 rpm further decreased the particle size as it can be seen clearly in Fig. 8. Increase in reactor speed however resulted in bimodal particle size distribution. Small particles are around or below 80 nm in size whereas mean size of the big particles are around 125 nm. Therefore, the optimum condition was determined as 2 rpm for the reactor speed for this particular experimental study.

To prove the effectiveness of the study for produce nano-size AlN powder, the powder was synthesized under the same condition by DCRN process without Al_2O_3 balls. XRD analysis of the produced powders by DCRN process at 1450 °C for 1.5 hrs for B/P=20 with and without balls shows that there is no effect on the phase formation (Fig. 9). On the other hand, there is a strong evidence by which having balls into the reactor made it possible to produce nano-sized powders which are in the range of below 90 nm compared with the situation where no balls used (Fig. 10). Kang et al. [32]

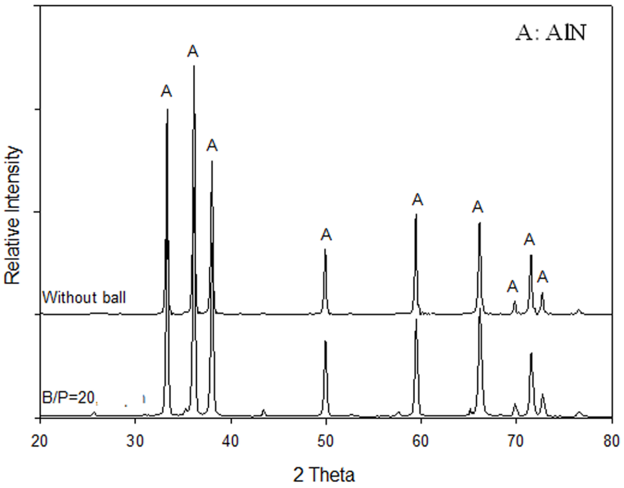

Fig. 9. XRD patterns of the products synthesized at 1450 °C for 1.5 hrs with Al_2O_3 ceramic balls and without balls.

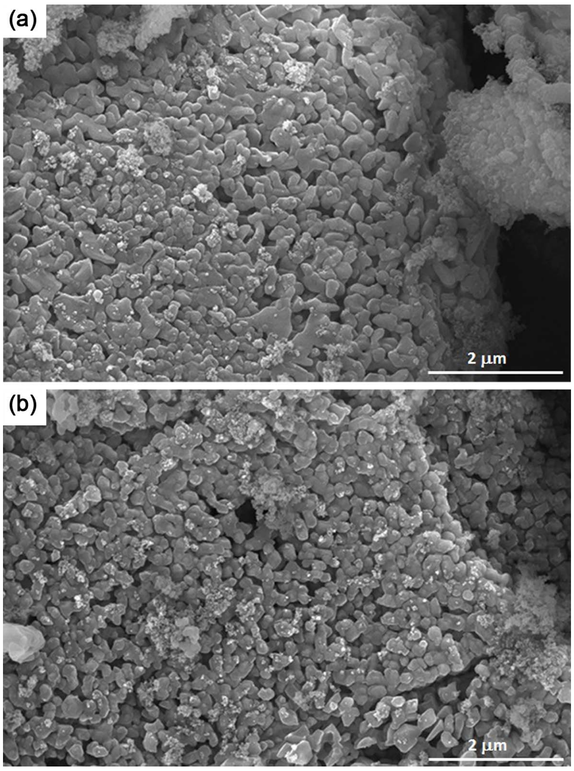

Fig. 8. FESEM images of the products synthesized at 1450 °C for 1.5 hrs with B/P=15 at different reactor speeds (a) 2 rpm and (b) 4 rpm.

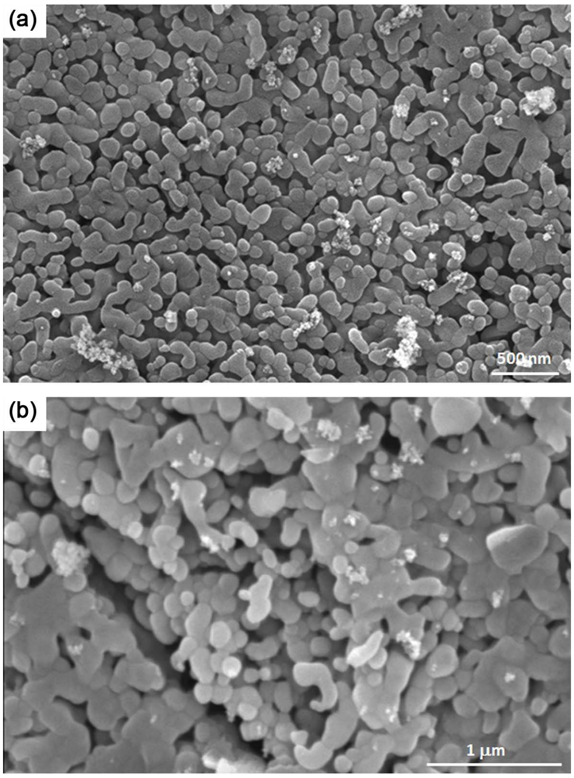

Fig. 10. FESEM photographs of the products synthesized at 1450 °C for 1.5 hrs a) with balls (B/P=20) and b) without balls (Scale bar in "a" is 500 nm and in "b" is 1 µm).

synthesized AlN powder by carbothermal reduction and nitridation process at 1700 °C for 3-4 hrs. They obtained a mean particle size of 1.6 mm in synthesized final products. In this study, nano sized AlN powder was produced at a very low reaction temperature (1450 °C) and time (1.5 hrs) by dynamic carbothermal reduction and nitridation process. Considering all the results, it was seen that nano-sized AlN powder production was realized by using balls during DCRN process. Furthermore, this production took place in a relatively short time and at low temperature. This is an important advantage for the synthesis of valuable and expensive nano-sized advanced ceramic powders such as AlN.

Conclusion

In this study, it is aimed to produce nano-sized AlN powder from coarse Al $(OH)_3$ powder. For this, the DCRN method which can produce good quality powder has been applied. Also, Al_2O_3 balls were used during the process to produce finer size powder. By using this novel approach it is possible to have shorter the reaction time and relatively lower temperatures to synthesize powders. Therefore, nano-sized (below 90 nm) AlN powders were synthesized at 1450 °C for 1.5 hrs under 60 $L \cdot h^{-1}$ N_2-gas flow with 2 rpm reactor speed using ceramic balls and $Al(OH)_3$ powders with B/P ratio of 20 into the graphite reactor.

Acknowledgments

Author acknowledge TUBITAK for the financial support provided to the Project (Nu. 115M562). The author would also like to thank the Sakarya University Scientific Research Council (SAU-BAP) and Prof. Dr. Ali Osman Kurt and Nurşen Mutlu.

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