

Optimisation study for making aluminium nitride using an improved carbothermal reduction-nitridation process

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In order to obtain a high thermal conductivity, impurities such as oxygen and carbon should be removed from aluminium nitride (AlN) during its synthesis using a carbothermal reduction-nitridation (CRN) process. In this study, AlN powders were prepared under various conditions (1550–1750 °C, 0.5–4.0 hrs, nitrogen at 75–399 ml/min) using mixtures of alumina (Al₂O₃) and carbon black (C) at different molar ratios of 0.28 to 0.40. Residual carbon of the synthesized AlN powder was removed in a decarbonisation step using an electric furnace (600–900 °C, 0.5–4.0 hrs). The synthesis of AlN from alumina-carbon black mixtures of Al₂O₃/C molar ratio of 0.31 (5% excess carbon black) at optimum conditions of 1700 °C for 3–4 hrs and air decarbonisation (annealing) at 750 °C for 2 hrs produced product containing 385 ppm C and 0.62 wt% O₂, lower than for current commercial products.

Key words: Aluminum nitride, Carbothermal reduction, Nitridation, Decarbonisation, Carbon.

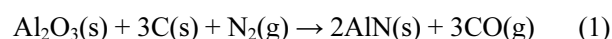
Introduction

The increasing demand for high performance electronic devices has been continuously met with circuits using aluminium nitride (AlN) materials having high thermal conductivity to faster dissipate heat. AlN also possesses high thermal expansion coefficient close to silicon, high electrical insulation capacity, low dielectric constant and good mechanical properties. Several techniques have been used to synthesize AlN, details of which were recently reviewed [1]. For the production of AlN powders, direct nitridation using nitrogen and aluminum powder [2], carbothermal reduction-nitridation using aluminum hydroxide and carbon black (CRN) [3] and vapor phase reaction [4] have been trialed. Since the 1950s, many studies on the synthesis of AlN using the CRN process have been conducted, advancing the field leading to wider application of this technique commercially to produce AlN powders for ceramic fabrication.

The CRN synthesis requires an aluminum oxide (Al₂O₃) to be reduced at high temperature (1700–1950 °C) [1] using different carbon sources such as carbon black, nut shell or organic compounds [1, 3, 5] in a nitrogen atmosphere. The CRN method has also presented some limitations such as difficulty in producing homogeneous mixes of starting materials, high cost due to elevated nitridation temperature, and

the requirement of pure precursors for the fabrication of high purity AlN powders. In addition, to produce granular AlN from powders, additives have been widely used for sintering high quality AlN ceramics. Among them, the rare-earth oxides such as Y₂O₃ have been used widely [6, 7]. Other additives such as CaF₂ [8, 10] and YF₃ [9] or combination of all these [7] were also used to improve the synthesis of AlN granules.

The formation of AlN using Al₂O₃, C and N₂ is represented by the following reaction:



In order to obtain a high thermal conductivity as a primary requirement for high quality AlN, oxygen and carbon contents in the AlN powders should be lower than 1 wt% O₂ and 1000 ppm C as achieved by the current commercial products [11–13].

Oxygen is a typical contaminant of AlN due to unreacted aluminum oxide (Al₂O₃) or intermediate product oxynitride (AlON) as thermodynamically predicted by Nakao et al. [9] at different conditions of temperature, CO and N₂ partial pressure. There are other oxides containing aluminum and oxygen (such as AlO, Al₂O, Al₂O₂), which might be formed and remained in the final product [1].

As typically shown by Wang et al. [7], excess carbon at least at a carbon/alumina molar ratio of 4.26 (mass ratio of 0.5) needs to be used and mixed thoroughly with Al₂O₃ for 24 hrs to ensure complete carbothermic reduction before nitridation. However, excessive unreacted carbon, Al₂O₃ and CO remaining will contaminate the

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produced AlN and have to be further removed to ensure their contents in the final product lower than specifications of 1% oxygen and 1000 ppm (0.1%) carbon.

Several studies were reported in the literature on the thermodynamics and of different AlN systems [14-19], showing different phase formations. These studies postulated the formation of other deleterious species such as Al_2O , AlO_2 , etc. formed at different conditions of partial pressures of N_2 , CO , CO_2 and O_2 .

This paper presents results of an optimisation study on the synthesis of AlN powder using Al_2O_3 and carbon black as raw materials based on carbothermal reduction-nitridation conditions followed by decarbonisation to remove residual carbon and oxygen. The study also includes modelling of the thermodynamics of the synthesis conditions using Outotec HSC software [20].

Material and Methods

In this study, high-purity alumina (A0001 Grade 99.998% purity, mean particle size 1.2 mm, Pos-Hial Co) and carbon black (Hiblack 170 Grade 99.9% purity, 0.058 mm, Orion Engineered Carbons Co) were used as starting materials for the preparation of high purity AlN powders.

Alumina and carbon black were mixed (1000 rpm) at 95 °C for 24 hrs using a Lodiger Mixer (LDH-0.1, Sejitech Co) at different $\text{Al}_2\text{O}_3/\text{C}$ molar ratios of 0.4, 0.33, 0.31 and 0.28 (corresponding to ratios of 1 mole Al_2O_3 / 2.5, 3, 3.15 and 3.5 mole C). The compositions corresponding to the $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.33 therefore represents the stoichiometric requirement for reaction (1) above.

The homogeneity of the mixture was checked by elemental analysis using a field emission scanning electron microscope (JSM-7100F, Jeol Ltd., Japan) with EDS (energy dispersive spectroscopy) attachment.

To conduct the test, a sample of 200 g of the mixed raw material (at different $\text{Al}_2\text{O}_3/\text{C}$ molar ratio) was first charged into a graphite crucible, and N_2 (99.999% purity) gas was flowed through the CRN reactor at different flow rates (75-300 mL/min). Other parameters tested include temperature in the range 1550-1750 °C and holding time in the range 0.5-4 hrs. Residual carbon and oxygen of the synthesized AlN powder was then removed by holding the sample for 0.5-4 hrs in an electric furnace at a temperature of 650-900 °C.

The crystalline phases of products were determined using an X-ray diffractometer (Ultima-IV, Rigaku Co, Japan) with $\text{CuK}\alpha$ radiation, and AlN conversion fraction was determined based on XRD peak intensity of the plane (100) for AlN and (311) for AlON. The carbon content of the AlN samples was measured using a carbon analyser (G4 ICARUS HF, Bruker Co, Germany) and oxygen was measured using an oxygen analyzer (TC-600, Leco Co, USA). The sample specific surface area

was measured using a surface area analyzer (BELSORP-mini II, BEL Co, Japan) whereas the particle morphology was observed using a field-emission scanning electron microscope (JSM-7100F, Jeol Ltd, Japan).

Results and Discussion

The intimate contact between particles involved in the synthesis is critical in determining the complete conversion of reagent mixes to AlN. To ensure this the feed materials were mixed for 24 hrs at 95 °C with samples taken every now and then checked for homogeneity using EDS analysis. These mixes were then subjected to different synthesis conditions to produce AlN powders. The experimental results were also compared to those predicted from thermodynamic modelling using HSC software [20].

Thermodynamic modelling

The thermodynamics of the synthesis system was modelled using HSC software [20], simulating the outcome of various synthesis conditions in the temperature range 1000-2200 °C. At stoichiometric molar ratio of $\text{Al}_2\text{O}_3/\text{C}/\text{N}_2$ of 1 : 3 : 1, as shown in reaction (1) a complete conversion to AlN could only be achieved at a temperature around 1950 °C. An excess of nitrogen (at $\text{Al}_2\text{O}_3/\text{C}/\text{N}_2$ of 1 : 3 : 2) would ensure complete conversion at a temperature below 1700 °C as shown in Fig. 1. Minute quantities of Al_2O or Al gases were detected at all conditions unless excess nitrogen is used. The experimental program was therefore conducted based on these modelling results.

Effect of nitrogen

The use of excess nitrogen would ensure the full conversion of AlN at a lower temperature as predicted by HSC modelling (Fig. 1). The effect of nitrogen is confirmed as shown in Fig. 2.

There is a continual decrease in carbon and oxygen content in the AlN product in the range of nitrogen flowrate 75-300 ml/min. A further increase of nitrogen

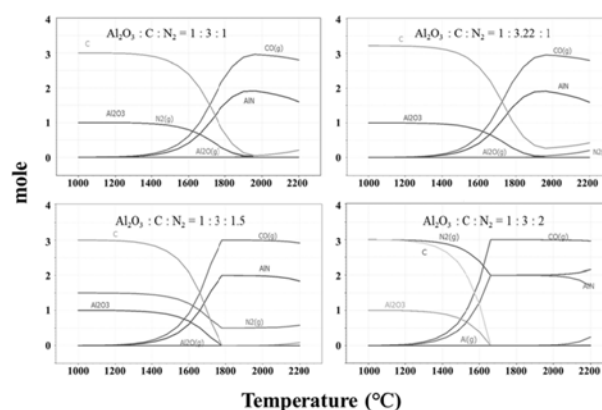


Fig. 1. HSC modelling of the thermodynamics of AlN synthesis in the range 1000-2200 °C at different molar ratios of $\text{Al}_2\text{O}_3/\text{C}/\text{N}_2$.

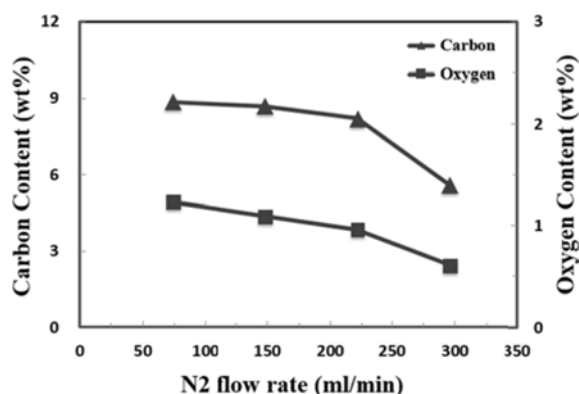


Fig. 2. Carbon and oxygen contents of AlN synthesized at 1700 °C for 4 hrs at different N₂ flow rates. (Al₂O₃/C molar ratio of 0.31, at 5% excess of C).

was not conducted as this would cool down the furnace below the set temperature. All experiments were therefore conducted at 300 ml/min nitrogen flowrate.

Crystalline phases after synthesis

Fig. 3 shows X-ray diffraction patterns of AlN powders prepared at different temperatures and holding times using the raw material mix at Al₂O₃/C molar ratio of 0.31. This molar ratio represents 5% excess carbon in the mix.

Alumina phase was observed in specimens synthesized at 1550 °C for 4 hrs. Evidence of excess carbon black present in this sample was also detected in the diffraction patterns. The formation of AlN is clearly shown at temperatures of 1600 °C or higher. Fig. 1(a) shows that full conversion to AlN was obtained if the reaction time was held for at least 2 hrs. At 1700 °C, for the sample tested at 200 g, a holding time of 0.5 hrs is not enough for full conversion to AlN. Holding time at 1 hr or longer shows complete disappearance of Al₂O₃ but remnants of excess carbon black still exists in the AlN product (Fig. 3(b)).

Effect of Al₂O₃/C molar ratio on the formation of AlON

Fig. 4 shows the AlN powders synthesized using mixes at different Al₂O₃/C molar ratio molar ratios.

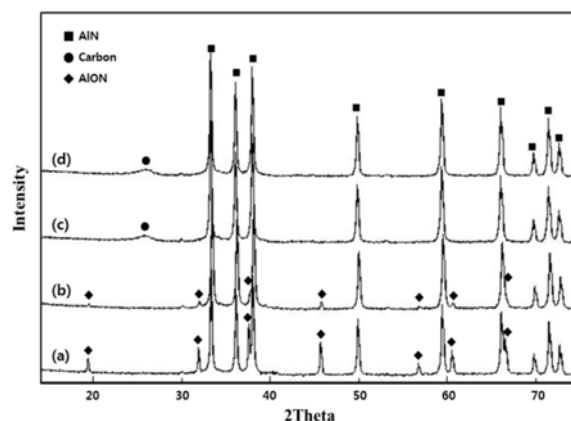


Fig. 4. Crystalline phase of AlN synthesized at 1700 °C for 4 hrs at different Al₂O₃/C molar ratio of (a) 0.40, (b) 0.33, (c) 0.31, (d) 0.28.

Only at Al₂O₃/C molar ratio of 0.28 (16.6% excess carbon black) or at 0.31 (5% excess carbon black) that AlN was formed with remnant carbon existing in the AlN product (Fig. 4(c,d)). Oxynitride (AlON) phase was detected at Al₂O₃/C molar ratio 0.40 and 0.33 (stoichiometric requirement) indicating full conversion of alumina into AlN could not be achieved under these conditions.

AlON was confirmed by few researchers as the main specie containing oxygen produced during the CRN process [1]. Therefore, excess carbon more than the stoichiometric requirement is required to convert this intermediate to AlN.

Carbon and oxygen contents of AlN powder after synthesis

The carbon and oxygen contents of AlN powders prepared at various synthesis temperatures and holding times are shown in Fig. 5. AlN powders synthesised at 1700-1750 °C had a lowest oxygen at <1.0 wt% O₂ whereas C still remained in the AlN samples at 6 wt% C. These carbon and oxygen levels in the AlN powders prepared at different synthesis times reached steady state after 3 hrs (for carbon) and 2 hrs (for oxygen), respectively. As a result, the synthesis temperature for full conversion to AlN should be above 1650 °C and the holding time should be at least 3 hrs.

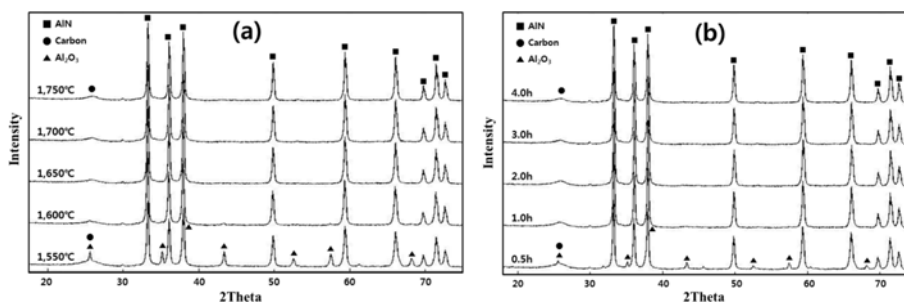


Fig. 3. XRD patterns of AlN synthesised at different temperatures and holding times, 1550-1750 °C, 4 hrs (b) 1700 °C, 0.5-4 hrs, Both are at Al₂O₃/C molar ratio 0.31, 5% excess carbon black).

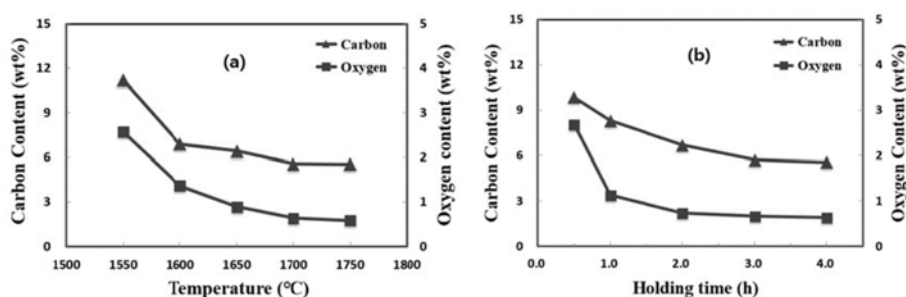


Fig. 5. Carbon and oxygen contents of AlN synthesised using an $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31 (5% excess C) at (a) 1550-1750 °C, 4 hrs (b) 1700 °C, 0.5-4 hrs.

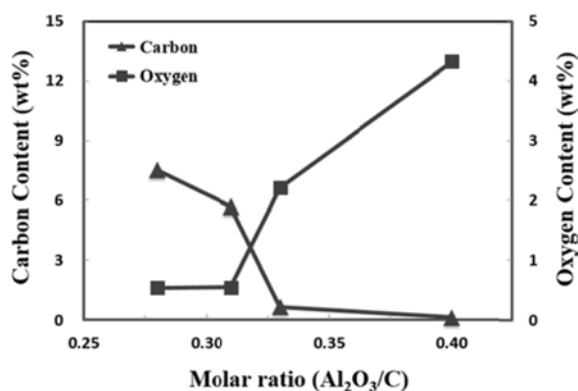


Fig. 6. Carbon and oxygen contents of AlN synthesized at 1700 °C for 3 hrs with different mixed molar ratio of 0.40, 0.33, 0.31, 0.28.

Table 1. Conversion of AlN synthesized at 1700 °C for 3 hrs at different $\text{Al}_2\text{O}_3/\text{C}$ molar ratios.

Molar ratio ($\text{Al}_2\text{O}_3/\text{C}$)	Conversion to AlN (%)	Crystalline phase
0.40	81.7	AlN, AlON
0.33	91.6	AlN, AlON
0.31	100	AlN, Residual C
0.28	100	AlN, Residual C

Fig. 6 shows the carbon and oxygen contents of AlN powder after synthesis using various $\text{Al}_2\text{O}_3/\text{C}$ molar ratios of raw materials. The lower the mix molar ratio (carbon black in excess), the higher the carbon content was as expected. The oxygen content was the highest at 4.32 wt % O_2 at the mix molar ratio of 0.40 and ~0.54 wt % O_2 at the mix molar ratio in the range 0.28

and 0.31 where carbon black is in excess.

Conditions for optimizing and minimizing carbon and oxygen levels in the final AlN are therefore opposite. Oxygen could be effectively removed only when excess carbon black was used in the mix. Without excess carbon black the AlON phases were also formed in the AlN product. As shown in Table 1, full conversion to AlN can be confirmed at $\text{Al}_2\text{O}_3/\text{C}$ molar ratios of 0.31 and 0.28.

Carbon and oxygen contents after decarbonization

Fig. 7 shows the oxygen and carbon contents after decarbonization of AlN powders synthesised from mixes at $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31 at various temperatures and holding times. The carbon and oxygen contents were ~385 ppm C and 0.65-0.71 wt % O_2 , respectively at 700-800 °C (Fig. 7(a)). At 900 °C, the contents of carbon and oxygen were 147 ppm C and 1.91% O_2 , respectively. At a temperature higher than 800 °C, surface oxidation of AlN took place, and the oxygen content increased accordingly. The optimum annealing temperature for removing residual carbon of synthesized AlN powder should be in the range 700-800 °C. The optimized time for decarbonization of AlN powders is 2 hr, as longer treatment at 750 °C would not further remove any residual carbon or oxygen from the samples.

Under the CRN synthesis conditions of temperature at 1700 °C in nitrogen atmosphere for 4 hrs with $\text{Al}_2\text{O}_3/\text{C}$ molar ratio varying in the range 0.28-0.40 and decarbonization at 750 °C in 2 hrs, the observed carbon and oxygen content from yielded products are shown in

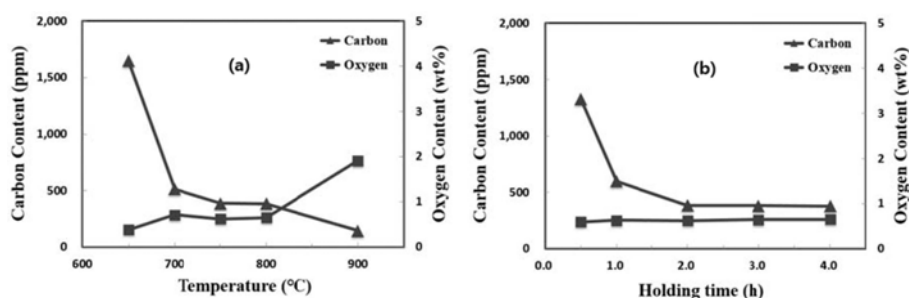


Fig. 7. Carbon and oxygen contents of AlN decarbonised at (a) 650-900 °C in 2 hrs (b) 750 °C in 0.5-4.0 hrs. (Synthesized at 1700 °C for 4 hrs with $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31).

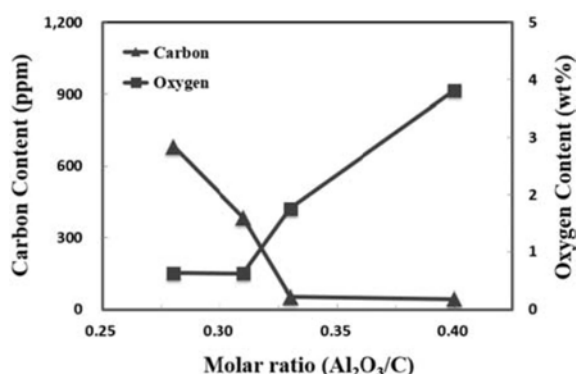


Fig. 8. Carbon and Oxygen contents of AlN decarbonized at 750 °C in 2 hrs at different $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.40-0.28.

Fig. 8. At stoichiometric requirement of alumina and carbon ($\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.33) the residual oxygen is still close to 2 wt% O_2 . Only in excess of carbon in the raw material mix ($\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31 and 0.28) that the residual oxygen reached less than 1 wt % target for the final product. The optimum $\text{Al}_2\text{O}_3/\text{C}$ molar ratio was 0.31 where carbon was maintained at ~380 ppm C and oxygen was at ~0.6 wt% O_2 .

Optimum conditions for synthesizing AlN from pure alumina powder and carbon black are therefore 1700 °C roasting within 3-4 hrs using a mixture of alumina and carbon black at a $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31 (5% excess of carbon black), followed by decarbonization at 750 °C within 2 hrs.

AlN product properties

Scanning electron microscopy was used to evaluate the morphology of different materials produced at different stages in this study. Fig. 9(a) shows an image of a raw material mix (at $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31 or 5% excess carbon black) with carbon black appearing as fine specs among the alumina particles of sizes < 2 mm. Carbon black specs still existed in the preliminary AlN product after roasting to 1700 °C after 4 hrs (Fig. 9(b)) whereas carbon was hardly detected after decarbonization at 750 °C in 2 hrs (Fig. 9(c)).

The final products synthesized using the developed techniques have a mean particle size of 1.6 mm, compatible to commercial products from several companies as shown in Table 2. The surface area was 1.5 m^2/g whereas

Table 2. Comparison of AlN powder (specimen synthesized at 1700 °C for 4 hrs with $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31 and decarbonised at 750 °C in 2 hrs) from this study to other commercial products.

AlN powder	Mean particle size (μm)	Specific surface area (m^2/g)	Impurities		Manufacturing process
			O_2 (wt%)	C (ppm)	
AlN specimen	1.6	1.5	0.62	385	Carbothermal reduction - nitridation
H-Grade	1.7	2.3 ~ 2.9	≤ 1.0	≤ 700	
JC-Grade	1.2	3.0	≤ 1.2	≤ 600	
SA-Grade	1.2	2.5	≤ 0.8	≤ 1000	Direct nitridation
B-Grade	2.0 ~ 4.5	2.0 ~ 4.0	≤ 1.5	≤ 1000	

H-Grade: Tokuyama soda Co. (Japan), JC-Grade: Toyo Aluminium K.K (Japan).

SA-Grade: Denka Co. Ltd. (Japan), B-Grade: H.C. Starck (Germany).

impurities of oxygen and carbon exist at much lower levels compared to commercial products.

Conclusions

A study was conducted to determine the optimized conditions for the synthesis of aluminum nitride (AlN) using the carbothermal reduction-nitridation (CRN) techniques in nitrogen and carbonization in air to produce high quality AlN powders. HSC modelling of the synthesis system shows the critical factors (which minimize the contamination of the final products with residual carbon and oxygen) as $\text{Al}_2\text{O}_3/\text{C}$ molar ratio, excess nitrogen and roasting temperature. The reaction time is also critical during the synthesis, as determined from the experiments. From the conditions tested including $\text{Al}_2\text{O}_3/\text{C}$ molar ratio (0.28-0.40), temperature (1550-1750 °C), 1.1 atm nitrogen (75-300 mL/min) in 0.5-4 hrs, and annealing (decarbonization) in air at 600-900 °C in 0.5-4 hrs, optimum conditions were determined as roasting at 1700 °C in a nitrogen atmosphere (300 mL/min) within 3-4 hrs and annealing in air at 750 °C in 2 hrs. The best AlN powders produced from this study contain 0.6 wt % O_2 and 385 ppm C, lower than for current commercial products.

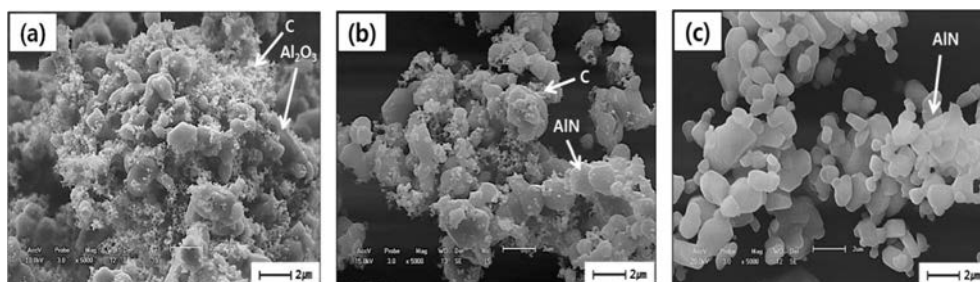


Fig. 9. SEM images of AlN specimens (a) mixed raw materials with $\text{Al}_2\text{O}_3/\text{C}$ molar ratio of 0.31, (b) synthesised AlN powder at 1700 °C, 4 hrs, (c) decarbonised AlN at 750 °C in air for 2 hrs.

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References

1. V.S. Kudyyakova, R.A. Shishkin, A.A. Elagin, M.V. Baranov, A.R. Beketov, Soc. J. Eur. Ceram. 37 (2017) 1143-1156.
2. E. Polycarp, A.B. Rehmat, S.B. Jalaluddin, G. Baba, in: Proceeding of 19th IASTEM (Int. Adv. Sci. Eng. and Tech.) 4[2] Spl. Issue 3 (2016).
3. P. Wei, Q. Yang, J. Cai, Thermochemica Acta 325 (1999) 89-93.
4. A.C. Da Cruz, R.J. Munz, IEEE Trans. on Plasma Sci. 25 (1997) 1008-1016.
5. S.B. Qadri, E.P. Gorzkowski, B.B. Rath, C.R. Feng, R. Amarasinghe, Journal of Alloys and Compounds 708 (2017) 67-72.
6. S. Kume, M. Tasuoka, S.K. Lee, A. Kan, H. Ogawa, K. Watari, J. Eur. Ceram. Soc. 27 (2007), 2967-2971.
7. Q. Wang, Y. Ge, J. Kuang, P. Jiang, W. Liu, W. Cao, J. of Alloys and Compounds 696 (2017) 220-225.
8. Y. Xiong, Z.Y. Fu, H. Wang, Y.C. Wang, Q.J. Zhang, Materials Science and Engineering B 123 (2005) 57-62.
9. A.M. Hundere, M.A. & Einarsrudl, J. of the Eur. Ceram. Soc. 17 (1997) 873-878.
10. T. Ide, K. Komeya, T. Meguro, J. Tatami, J. Am. Ceram. Soc. 82 (1999) 2993-98.
11. Tokuyama Soda product information, Accessed on 11 August 2017: http://www.tokuyama.co.jp/eng/products/specialty/shapal/aln_powder_granules.html
12. Toyo Aluminum K.K. product information: Accessed on 11 August 2017: http://www.toyal.co.jp/eng/products/powder/pw_al_nitro.html
13. H.C. Starck product information, Accessed on: https://www.hcstarck.com/aluminum_nitride
14. M. Qin, X. Du, J. Wang, I.S. Humail, X. Qu, J. of the Euro. Ceram. Soc. 29 (2009) 795-799.
15. W. Nakao, H. Fukuyama, K. Nagata, J. Am. Ceram. Soc. 85 (2002) 889-96.
16. H. Fukuyama, S. Kusunoki, A. Hakomori, K. Hiraga, J. of App. Phys. 100 (2006) 024905.
17. H. Fukuyama, K. Hiramatsu, Jap. J. of Appl. Phys. 55 (2016) 05FL02.
18. C.C. Chen, H.S. Yang, J.S. Lin, Atlas J. of Mater. Sci. 1(2014) 30-37.
19. J.C. Kuang, C.R. Zhang, X.G. Zhou, Q.C. Liu, Ye C., Mater. Letters 59 (2005) 2006-2010.
20. Outotec HSC Chemistry software, available from: <http://www.chemistry-software.com/index.html>