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ScienceDirect

Ceramics International 38 (2012) 871–874

CERAMICS INTERNATIONAL

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Short communication

Synthesis of aluminum nitride powder from δ-alumina nanopowders under a mixed gas flow of nitrogen and hydrogen

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Received 19 March 2011; received in revised form 4 July 2011; accepted 5 July 2011

Abstract

Aluminum nitride (AlN) was synthesized by calcining δ-alumina (δ-Al_2O_3) nanopowders under a mixed gas flow of nitrogen and hydrogen that was passed over a crucible containing activated charcoal. The conversion process of δ-Al_2O_3 to AlN was monitored by powder X-ray diffraction patterns and ^{27}Al magic-angle spinning nuclear magnetic resonance spectroscopy. δ-Al_2O_3 began to be converted to AlN at 1200 °C and the conversion was completed after 5 h at 1600 °C. The hydrogen cyanide (HCN) gas that evolved during the calcination reacted with alumina to form white AlN.

Keywords: D. Al_2O_3; Aluminum nitride; Hydrogen cyanide

1. Introduction

Aluminum nitride (AlN) has many attractive thermomechanical and electronic properties, such as excellent thermal conductivity, high electrical resistivity, high mechanical strength, and high melting point [1]. It has therefore attracted extensive interest for applications as an electrical packaging material and a component in structural composites. The carbothermal reduction and nitridation (CRN) method is currently one of two synthesis methods used in the commercial production of AlN powders [2]. The CRN reaction is expressed by the equation:

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2AlN(s) + 3CO(g) \qquad (1)$$

In the CRN method, Al_2O_3 is intimately mixed with carbon and the excess carbon is burned, which may lead to oxygen contamination and degradation of the thermal conductivity of AlN [3]. Therefore, an alternative method which prevents oxygen contamination by avoiding any mixing of Al_2O_3 with carbon must be developed. Ammonia can be used as a nitrogen source for preparing AlN from Al_2O_3 that has not been mixed with carbon. For example, Zhang and Gao synthesized AlN by nitridation of nanosized δ-Al_2O_3 powders under a flow of ammonia at a high flow rate of 1 L/min and achieved complete conversion of the powders into AlN at 1350–1400 °C within 5 h [4]. However, no method has yet been determined for preparing AlN powder by calcining Al_2O_3 powder without mixing it with carbon under a flow of nitrogen.

In this study, therefore, we synthesized AlN powder by calcining δ-Al_2O_3 nanopowders that had not been mixed with any carbon source under a mixed gas flow of nitrogen and hydrogen. The conversion process of Al_2O_3 to AlN was monitored by powder X-ray diffraction (XRD) patterns and high-resolution ^{27}Al magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The gases evolved during the calcination were analyzed by infrared (IR) spectroscopy.

2. Experimental procedure

The δ-Al_2O_3 nanopowders (<50 nm, Sigma–Aldrich) were used as a precursor. The precursor powder in a graphite crucible was placed in an alumina tube with an inner diameter of 34 mm and calcined for 5 h under a flow of mixed gas of N_2 and H_2 (5 vol%) (hereafter, 5 vol% H_2/N_2) in the temperature range of 1200–1600 °C. An activated charcoal (Wako Pure Chemical Co)-containing crucible was placed upstream and adjacent to a precursor-containing graphite crucible. The sample was taken

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doi:10.1016/j.ceramint.2011.07.002

from the furnace after it had cooled to room temperature. The gas flow and ramping rates were 200 ml/min and 5 °C/min, respectively. The product powders were characterized by powder XRD with a PANalytical X'Pert PRO MPD X-ray diffractometer with Cu Kα radiation operating at 40 kV and 30 mA and by high-resolution ^{27}Al MAS NMR spectroscopy. The NMR spectra were measured at ambient temperature with a radio frequency of 156.3 MHz (Unity INOVA 600 spectrometer, Varian Inc., USA). The samples were spun at 20 kHz, with an excitation pulse length of 0.5 μs and a pulse delay time of 3 s. The chemical shifts (δ) were referenced to 1 M aqueous $AlCl_3$ solution. IR absorption spectra were measured using a Bio-Rad FTS-3000 MX Fourier transform IR spectrophotometer. The element content in the sample was determined by a CHN elemental analyzer (Flash 1112, Thermo Fischer Scientific). The morphology of the product powders was investigated by transmission electron microscopy (TEM, Philips CM 200 STEM).

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples obtained by calcining δ-Al_2O_3 nanopowders at various temperatures for 5 h. The XRD pattern of the precursor, shown in Fig. 1(a), matched that (JCPDS Card No. 46-1131) of δ-Al_2O_3. The XRD pattern (Fig. 1(b)) of the sample obtained at 1200 °C showed that most of the δ-Al_2O_3 was transformed into α-Al_2O_3 (JCPDS Card No. 46-1212) without being nitridated to AlN. In the sample (Fig. 1(c)) calcined at 1300 °C for 5 h, weak diffraction peaks corresponding to AlN (JCPDS Card No. 25-1133) were detected together with the diffraction peaks of α-Al_2O_3. The intensities of the former peaks increased as the temperature was increased from 1300 to 1600 °C. The sample obtained at 1600 °C did not exhibit any detectable peaks other than those assigned to AlN, as shown in Fig. 1(f).

The conversion process of δ-Al_2O_3 to AlN was also monitored by ^{27}Al MAS NMR spectroscopy, as shown in Fig. 2. The ^{27}Al MAS NMR spectrum (Fig. 2(a)) of the precursor exhibited two peaks at δ 9 and 68 ppm, which were assigned to the AlO_6 and AlO_4 sites in δ-Al_2O_3, respectively [5]. The NMR spectrum (Fig. 2(b)) of the sample obtained at 1200 °C showed a weak peak (at δ 114 ppm), assigned to AlN [5], together with the peak (at δ 14 ppm) assigned to α-Al_2O_3, even though its XRD pattern (Fig. 1(b)) showed no diffraction peaks corresponding to AlN. The intensity of the former peak increased as the temperature was increased from 1300 to 1600 °C. The NMR spectrum (Fig. 2(f)) of the sample obtained at 1600 °C showed only the peak assigned to AlN.

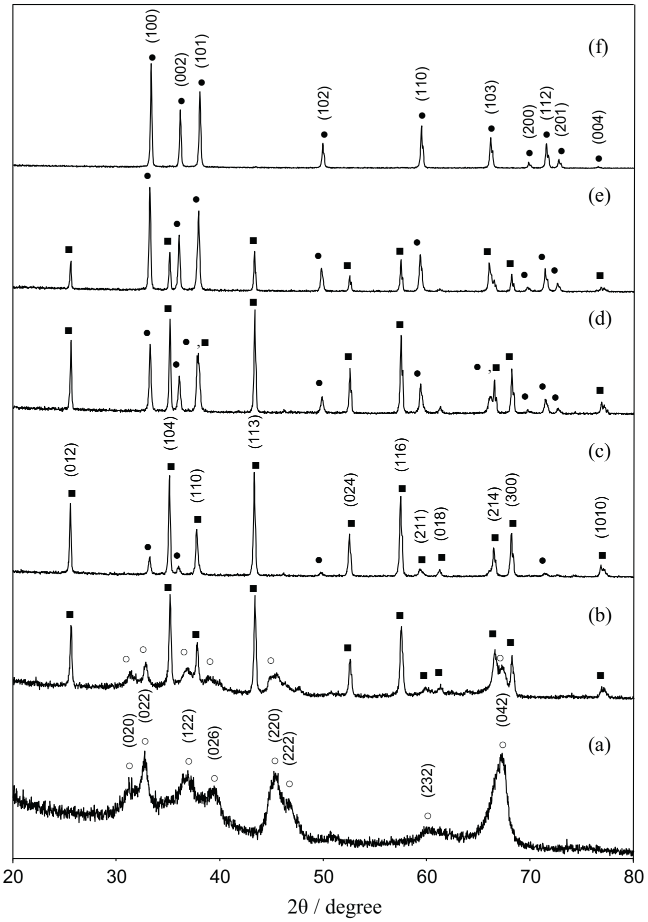

Fig. 1. XRD patterns of samples obtained by calcination of (a) δ-Al_2O_3 under a flow of 5 vol% H_2/N_2 at (b) 1200 °C for 5 h, (c) 1300 °C for 5 h, (d) 1400 °C for 5 h, (e) 1500 °C for 5 h, and (f) 1600 °C for 5 h. (●) AlN, (■) α-Al_2O_3, (○) δ-Al_2O_3.

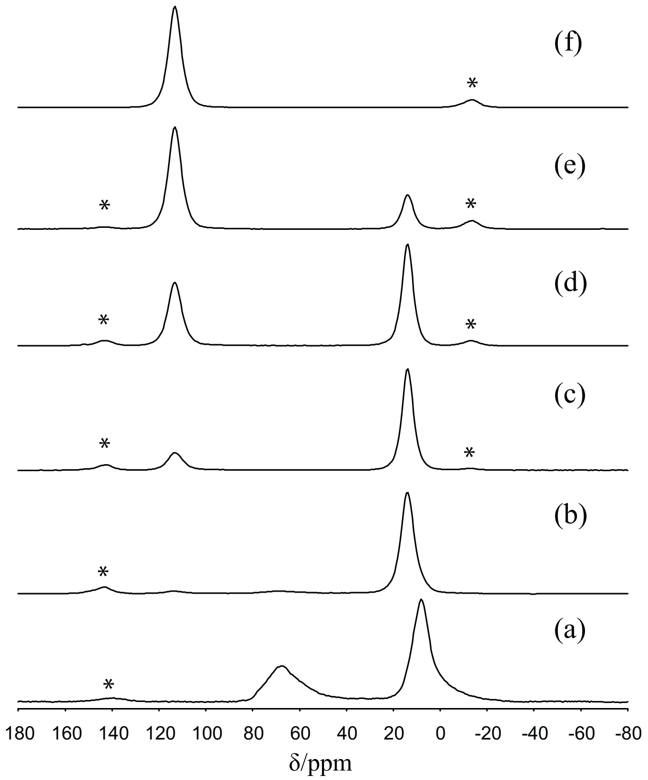

Fig. 2. ^{27}Al MAS NMR spectra of samples obtained by calcination of (a) δ-Al_2O_3 under a flow of 5 vol% H_2/N_2 at (b) 1200 °C for 5 h, (c) 1300 °C for 5 h, (d) 1400 °C for 5 h, (e) 1500 °C for 5 h, and (f) 1600 °C for 5 h. The spinning side bands are marked by asterisks.

The calcination of δ-Al_2O_3 nanopowders under a flow of 5 vol% H_2/N_2 did not yield AlN if the mixed gas was not passed over an activated charcoal-containing crucible. Therefore, the reactant involved in the nitridation of δ-Al_2O_3 must have been some product gas formed by the reaction of carbon with a mixed gas of N_2 and H_2. In order to identify the gas involved in the nitridation of δ-Al_2O_3, the gas evolved during the reaction was analyzed by IR spectroscopy using a 10-cm demountable IR gas cell with KRS-5 windows. Fig. 3 shows the change in the IR spectra of the gas evolved as the temperature was increased from 1000 to 1600 °C. The IR spectrum at 1000 °C exhibited only two bands at 1303 and 3016 cm^{-1}, which were assigned to ν_4 and ν_3 vibrations of CH_4, respectively [6]. The two bands became weaker with increasing temperature and diminished at temperatures $\geq$1300 °C. Two bands at 2118 and 2173 cm^{-1}, which were assigned to the stretching mode of CO, appeared at 1100 °C and their intensities increased with increasing temperature, indicating that the nitridation rate of δ-Al_2O_3 was increased at elevated temperatures. Two bands centered at 712 and 3312 cm^{-1}, which were due to ν_2 (bending) and ν_3 (C–H stretching) vibrations of hydrogen cyanide (HCN), respectively [6], were observed at temperatures $\geq$1200 °C. The HCN is presumed to have been formed by the reaction of carbon with the mixed gas of N_2 and H_2. The lowest temperature at which HCN was detected was approximately consistent to that at which AlN commenced to form, indicating that the reaction of HCN with Al_2O_3 produces AlN as follows:

$$Al_2O_3(s) + 3HCN(g) \rightarrow 2AlN(s) + 3CO(g) + (3/2)H_2(g) + (1/2)N_2(g) \quad (2)$$

The reaction (2) has been suggested by several investigators [7–9]. The detailed mechanism of AlN formation in this study remains unconfirmed. The nitrile group, which plays double roles as both deoxygenizing and nitridating agents, has been used for the nitridation of metal oxides to metal nitrides. For example, Buha et al. prepared AlN by the reaction of nanosized γ-Al_2O_3 with cyanamide at 900 °C for 6 h under a flow of N_2 [10].

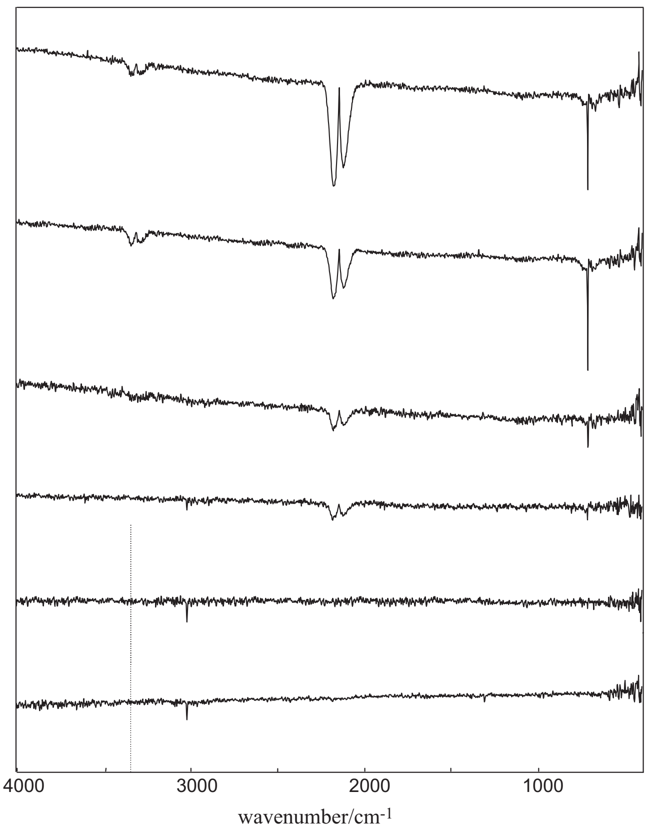

Fig. 3. IR spectra of the gas evolved at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1500 °C, and (f) 1600 °C in the calcination of δ-Al_2O_3 under a flow of 5 vol% H_2/N_2.

The morphology of the AlN powder obtained by calcination of δ-Al_2O_3 at 1600 °C for 5 h was observed by TEM. As shown in Fig. 4, the morphology of the AlN particles was almost spherical, with a diameter range of 220–340 nm, which was considerably different from that of the precursor (δ-Al_2O_3) particles. The AlN powder obtained at 1600 °C was white because of its very low carbon content (0.03 wt%). The nitrogen content was 30.26 wt%, which was slightly lower than the theoretical value (34.15 wt%) for AlN.

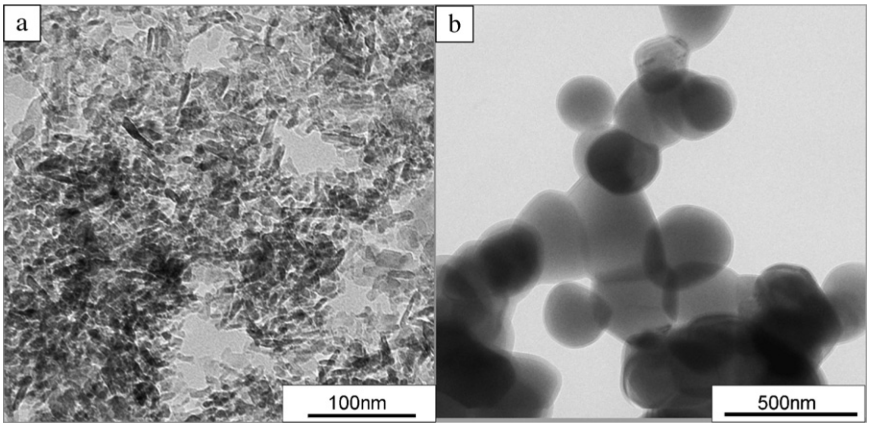

Fig. 4. TEM images of (a) δ-Al_2O_3 precursor and (b) AlN powders obtained by calcination of the precursor under a flow of 5 vol% H_2/N_2 at 1600 °C for 5 h.

4. Conclusions

AlN powders were synthesized by calcining δ-Al_2O_3 nanopowders under a flow of 5 vol% H_2/N_2. The conversion process of δ-Al_2O_3 to AlN was monitored by powder XRD patterns and ^{27}Al MAS NMR spectroscopy. δ-Al_2O_3 began to be converted to AlN at 1200 °C and the conversion was complete after 5 h at 1600 °C. The HCN gas, which is presumed to have been formed by the reaction of carbon with the mixed gas of N_2 and H_2, reacted with alumina, resulting in the formation of white AlN with very low carbon content. The synthesis method presented in this study for obtaining AlN powder is superior to the CRN method in that it is not necessary to mix Al_2O_3 with carbon, or to burn up the excess carbon.

Acknowledgements

This work was supported by the Human Resources Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No. 20104010100580) funded by the Korean Ministry of Knowledge Economy. The ^{27}Al MAS NMR spectra were recorded at the Analysis Research Division, Daegu Center, Korea Basic Science Institute.

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