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^{27}Al MAS NMR spectroscopic identification of reaction intermediates in the carbothermal reduction and nitridation of alumina

Woo-Sik Jung[a,*], Seen-Ae Chae[b]

[a] School of Display and Chemical Engineering, College of Engineering, Yeungnam University, Daedong 214-1, Gyongsan 712-749, Republic of Korea
[b] Korea Basic Science Institute Daegu Branch, Daegu 702-701, Republic of Korea

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ABSTRACT

The reaction intermediates in the carbothermal reduction and nitridation (CRN) reaction of γ-Al_2O_3 were identified by ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. This identification ruled out the possibility of a reaction mechanism involving the gaseous reaction intermediates. In the CRN reaction of γ-Al_2O_3, AlO_4 units were converted to AlN stepwise via AlN_xO_{4-x} ($x = 1, 2, 3$) intermediates, while AlO_6 units were more slowly converted to AlN than AlO_4 units and the NMR peaks of partially nitridated AlO_6 units were not detected. The NMR peak intensities of partially nitridated AlO_4 units became weaker with increasing reaction temperature.

1. Introduction

Aluminum nitride (AlN), which has a wurtzite-type structure composed of AlN_4 units in a hexagonal lattice, has many attractive thermomechanical and electronic properties, such as excellent thermal conductivity, high electrical resistivity, high mechanical strength, and high melting point [1]. Thus, it has attracted extensive interest for applications as electrical packaging materials and as components in structural composites. The carbothermal reduction and nitridation (CRN) method is the currently favored large-scale production method for high-quality AlN powders [2]. The CRN reaction is expressed by the equation:

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

Despite the apparent simplicity of the overall reaction, the mechanism involved is not simple and remains controversial. The CRN reaction is presumed to proceed via several steps through reaction intermediates than in a single step. In order to elucidate this mechanism, it is necessary to identify the reaction intermediates by spectroscopic or other analytical methods. The intermediates proposed so far can be classified into two types: gaseous reaction intermediates [3,4], including Al vapor and volatile aluminum suboxides, and solid-state reaction intermediates of AlO_xN_y [5]. The former intermediates are assumed to be formed by the thermal decomposition of Al_2O_3 [3] or reduction of Al_2O_3 by carbon [4]. Up to now, however, no conclusive evidence has been provided on the existence of the intermediates. The elucidation of the CRN mechanism would provide a clue as to how the AlN vapor is formed in the growth of AlN nanostructures by the CRN reaction [6–8].

If the intermediates are solid-state rather than gaseous, their identity may be determined by ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy because it can distinguish local structural units in ceramics by their chemical shifts [9]. It has been used to identify AlN_4 (with chemical shifts of 110–117 ppm), AlO_4 (with chemical shifts of 50–80 ppm), AlO_5 (with chemical shifts of 30–40 ppm), and AlO_6 (with chemical shifts of −10 to 15 ppm) units in aluminum oxides and aluminum oxynitrides [9]. In our previous work, we did not observe any peaks assigned to some reaction intermediates in 7.0 T (78.2 MHz) ^{27}Al MAS NMR spectra of the samples obtained by calcination of the (hydroxo)(succinato)Al(III) (hereafter referred to as AS) complex in the temperature range 1100–1500 °C for 2 h under a flow of N_2 [5]. The AS complex was converted into a homogeneous mixture of γ-Al_2O_3 and carbon and nitridated to AlN without mixing any carbon source under a flow of N_2 [10].

In this study we investigated the potential of 14.1 T (156.3 MHz) ^{27}Al MAS NMR spectroscopy as a tool for identifying the reaction intermediates in the CRN reaction of γ-Al_2O_3. The AS complex powder was calcined at various temperatures for 5 h under a flow of N_2 and the products were characterized by X-ray diffraction (XRD) and ^{27}Al MAS NMR spectroscopy.

2. Experimental

The method for synthesizing the AS complex has been described in a previous paper [10]. The precursor powder in an alumina crucible was placed in an alumina

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[*] Corresponding author. Tel.: +82 53 810 2528; fax: +82 53 810 4631.
E-mail address: wsjung@yu.ac.kr (W.-S. Jung).

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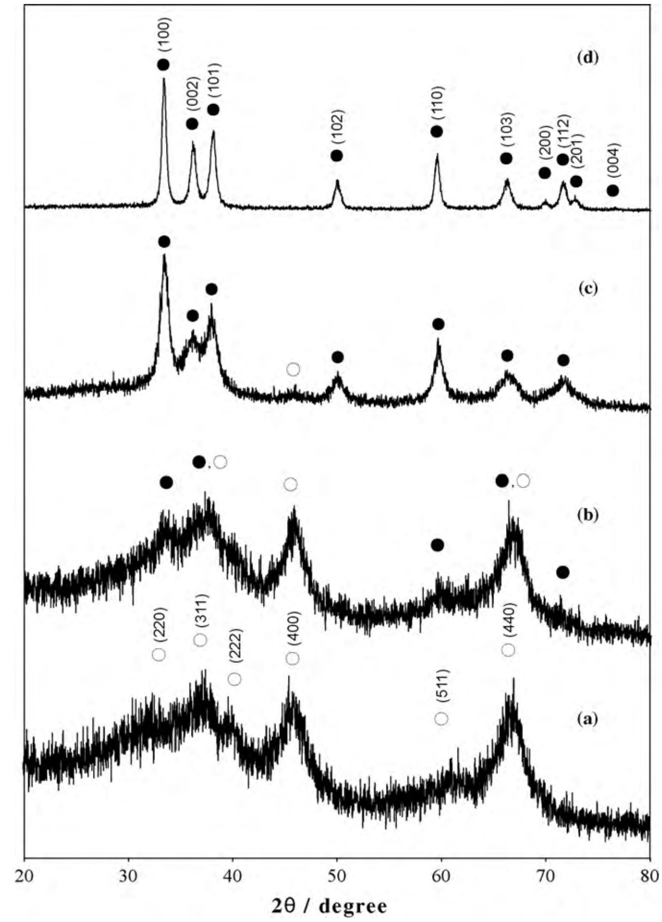

Fig. 1. XRD patterns of samples obtained by calcination of (hydroxo)(succinato)aluminum(III) complex at (a) 1100 °C, (b) 1150 °C, (c) 1200 °C, and (d) 1300 °C for 5 h under a flow of N_2. (●) AlN and (○) γ-Al_2O_3.

tube with an inner diameter of 36 mm and heated under a flow of N_2 in the temperature range of 1100–1300 °C for 5 h. The AS complex was also calcined at 1050 °C for 5 h under a flow of ammonia, at 1300 °C for 5 h under a mixed gas flow of 3 vol% CO/N_2, and at 1400 °C for 5 h under a mixed gas flow of 9 vol% CO/N_2. The flow rates of the gases were 200 ml min^{-1}. The sample was taken from the furnace after it had cooled to room temperature and then characterized by XRD with a PANalytical X'Pert PRO MPD X-ray diffractometer with Cu-Kα radiation operating at 40 kV and 30 mA and by ^{27}Al MAS NMR with a Unity INOVA 600 spectrometer. High-resolution ^{27}Al MAS NMR spectra were acquired at ambient temperature with a radio frequency of 156.3 MHz. The samples were spun at 23 kHz, and an excitation pulse length of 0.4 μs and a pulse delay times of 2 s were used. The chemical shifts (δ) were referenced to 1 M aqueous $AlCl_3$ solution.

3. Results and discussion

Fig. 1 shows XRD patterns of samples obtained by calcining the AS complex for at various temperatures for 5 h. As shown in Fig. 1(a), the sample obtained at 1100 °C exhibited only the peaks assigned to γ-Al_2O_3 (JCPDS No. 10-0425). In the sample calcined at 1150 °C, weak diffraction peaks assigned to AlN (JCPDS No. 25-1133) were detected together with those assigned to γ-Al_2O_3. The sample obtained at 1200 °C exhibited intense peaks assigned to AlN together with a weak (4 0 0) peak of unreacted γ-Al_2O_3. The sample calcined at 1300 °C contained no detectable peaks other than those assigned to AlN, as shown in Fig. 1(d). All XRD patterns in Fig. 1 exhibited no detectable peaks other than peaks assigned to γ-Al_2O_3 and AlN.

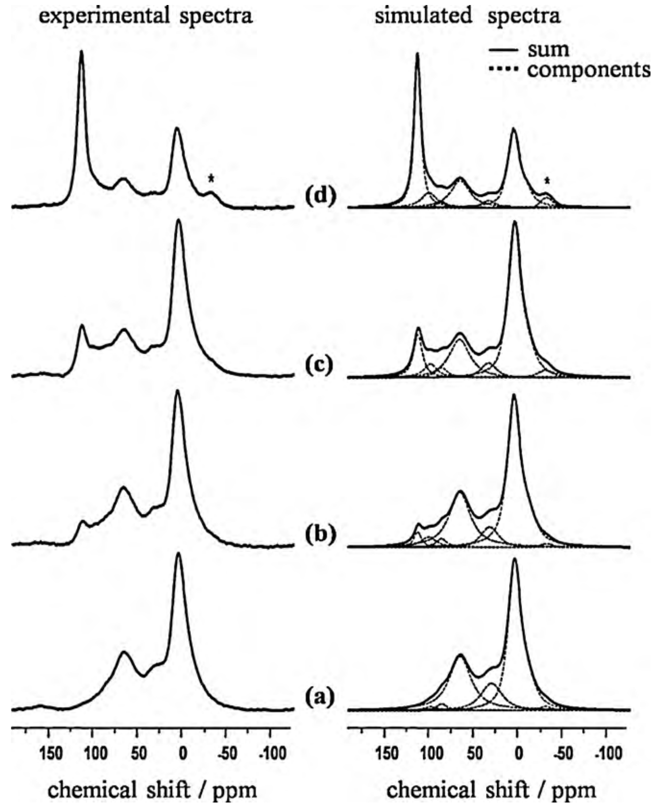

Fig. 2. Experimental (left column) and simulated (right column) ^{27}Al MAS NMR spectra of samples obtained by calcining (hydroxo)(succinato)aluminum(III) at various temperatures for 5 h under a flow of N_2. (a) 1100 °C, (b) 1130 °C, (c) 1150 °C, and (d) 1200 °C. The spinning side bands, which were assigned by varying the spinning rate, are marked by asterisks.

Fig. 2(a)–(d) (in the left column of Fig. 2) shows the ^{27}Al MAS NMR spectra of the samples obtained by calcination of the AS complex in the temperature range of 1100–1200 °C. The experimental NMR spectrum (Fig. 2(a)) of the sample calcined at 1100 °C exhibited three main peaks at δ 66, 31, and 6 ppm, which were assigned to AlO_4, AlO_5, and AlO_6 units in γ-Al_2O_3, respectively [9]. In the NMR spectrum (Fig. 2(b)) of the sample calcined at 1130 °C, a weak AlN peak was detected at δ 113 ppm [9], together with the three peaks corresponding to γ-Al_2O_3. The intensity of the AlN peak increased gradually with increasing reaction temperature but then abruptly increased at 1200 °C. Besides the aforementioned four peaks, some overlapping resonances between AlN_4 and AlO_4 peaks

Table 1
Simulated parameters for the ^{27}Al MAS NMR spectrum of the sample obtained by calcination of (hydroxo)(succinato)aluminum(III) at 1150 °C for 5 h under a flow of nitrogen.

Peak no.	^{27}Al chemical shift (ppm)	Unit	Linewidth (Hz)	Relative population (%)
1	112.6	AlN_4	12.0	10.2
2	98.7	AlN_3O	16.6	4.3
3	86.5	AlN_2O_2 and $AlNO_3$	15.7	3.1
4	66.4	AlO_4	27.9	21.4
5	34.1	AlO_5	20.9	6.1
6	6.0	AlO_6	16.6	55
7	−28.7	Spinning side band	18.3	0