Effect of gaseous carbon on the carbothermal reduction and nitridation of alumina under a flow of nitrogen

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The carbothermal reduction and nitridation (CRN) of α -alumina (α -Al₂O₃) to aluminum nitride (AlN) with gaseous carbon under a flow of nitrogen was investigated by X-ray diffraction and ²⁷Al magic-angle spinning nuclear magnetic resonance (NMR) spectroscopy. The mixture of α -Al₂O₃ and gaseous carbon was obtained by the reaction of aluminum sulfide (Al₂S₃) with carbon monoxide (CO). The AlN formation commenced at 1100°C, which is the lowest temperature reported for AlN formation by the CRN reaction. The involvement of gaseous carbon in the CRN reaction, which has not previously been reported in the CRN reaction, greatly reduced the nitridation temperature of α -Al₂O₃.

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1. Introduction

The AlN has many attractive thermomechanical and electronic properties, such as excellent thermal conductivity, high electrical resistivity, high mechanical strength, and high melting point.¹⁾ The carbothermal reduction and nitridation (CRN) method is one of the most useful methods to synthesize AlN powders.²⁾ The CRN reaction is expressed as follows:

Until now, all carbon sources used in the CRN method have been solid-state.³⁾ In our previous paper,⁴⁾ we showed that the reaction of Al₂S₃ with CO afforded a mixture of α -Al₂O₃ and graphene sheets. The formation of the graphene sheets indicated that gaseous carbon was evolved during the reaction of Al₂S₃ with CO. If the gaseous carbon acts as a carbon source in Eq. (1), the nitridation temperature of Al₂O₃ will be greatly lowered. In this report, we investigated the effect of the gaseous carbon on the CRN reaction of Al₂O₃ through calcination of Al₂S₃ under a mixed gas flow of CO and N₂.

2. Experimental procedure

The compound Al₂S₃ powder used in this study is commercially available as granules (Aldrich Chemical, 98%) and was ground to obtain a fine powder with a diameter of ≤ 0.125 mm (~ 120 mesh) before its calcination. The powders in an alumina crucible were set in an alumina tube with an inner diameter of 36 mm and heated at a rate of 5°C/min to the reaction temperature (1000–1300°C) in a flowing gas mixture (200 ml/min) of CO and N₂. The duration time, unless otherwise stated, was 10 h. The as-synthesized products were characterized by powder X-ray diffraction (XRD) with a PANalytical X'Pert PRO MPD X-ray diffractometer with Cu K α radiation operating at 40 kV and 30 mA and by ²⁷Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) with a Unity INOVA 600 spectrometer (Varian Inc.). High-resolution ²⁷Al MAS NMR spectra were acquired at ambient temperature with a radio frequency of

156.3 MHz. The samples were spun at 18 kHz, and excitation pulse lengths of 0.5 μ s and pulse delay times of 3 s were used. The chemical shifts (δ) were referenced to 1 M aqueous AlCl₃ solution. A transmission electron microscopy (TEM) image was recorded on a Philips CM 200 STEM (working at 200 kV) equipped with energy dispersive X-ray spectroscopy (EDXS).

3. Results and discussion

The compound Al₂S₃ is known to form four polymorphs: a hexagonal α -form, a related hexagonal β -form that has a defect wurtzite-type structure, a γ -form having the corundum-type structure, and a high-pressure tetragonal polymorph with a defect spinel structure.⁵⁾ The coordination of Al in the α - and β -forms is tetrahedral, while it is octahedral in the corundum type. The XRD pattern of the Al₂S₃ powder used in this work showed that it is a mixture of α - and γ -Al₂S₃. The Al₂S₃ powders were calcined at the temperature range 1000–1300°C under a mixed gas flow of 1 vol% CO/N₂ and the products were characterized by XRD patterns. The XRD pattern (Fig. 1(a)) of the powder calcined at 1000°C contained no peaks other than those assigned to α -Al₂O₃ (JCPDS No. 46-1212) and α -Al₂S₃ (JCPDS No. 47-1313). In the sample calcined at 1100°C, the peaks assigned to AlN (JCPDS No. 25-1133), α -Al₂O₃, and α -Al₂S₃, were detected, as shown in Fig. 1(b). With increasing the calcination temperature, the peaks assigned to α -Al₂S₃ became weaker and completely disappeared for the samples obtained at temperatures $\geq 1250^\circ\text{C}$. On the other hand, the intensities of the peaks assigned to AlN gradually increased as the calcination temperature was increased from 1100 to 1300°C. As shown in Fig. 1(f), the sample calcined at 1300°C was a mixture of AlN and α -Al₂O₃.

MAS NMR spectroscopy is a powerful probe to characterize solid-state materials, particularly when complex phase mixtures of crystalline and amorphous components are present. The XRD pattern-based assignments of the samples, which were calcined at different reaction temperatures for 10 h under a flow of 1 vol% CO/N₂, were confirmed by ²⁷Al MAS NMR spectroscopy. The NMR spectrum (Fig. 2(a)) of the Al₂S₃ precursor, which was quite different from that⁶⁾ measured at the magnetic field of 6.9 T

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Fig. 1. XRD patterns of samples obtained by calcination of Al_2S_3 powder under a flow of 1 vol% CO/N_2 at various temperatures for 10 h; (a) 1000°C, (b) 1100°C, (c) 1150°C, (d) 1200°C, (e) 1250°C and (f) 1300°C. (●) AlN, (■) $\alpha\text{-Al}_2\text{O}_3$, (○) $\alpha\text{-Al}_2\text{S}_3$.

Fig. 2. ^{27}Al MAS NMR spectra of Al_2S_3 powders (a) before and after calcination at (b) 1000, (c) 1150, (d) 1200 and (e) 1300°C for 10 h under a flow of 1 vol% CO/N_2 . The spinning side bands are marked by asterisks.

and spinning rate of 5 kHz, exhibited two powder-patterned peaks centered at ca. δ 50 and 110 ppm, each of which is assigned to six-coordinated (AlS_6) and four-coordinated (AlS_4) aluminum sites, respectively, considering that the coordination of Al in the γ - and $\alpha\text{-Al}_2\text{S}_3$ is octahedral and tetrahedral, respec-

Fig. 3. XRD patterns of samples obtained by calcination of Al_2S_3 powder at 1300°C for 10 h under a flow of 10 vol% CO/N_2 (a) before and after further calcination at (b) 1300, (c) 1400 and (d) 1500°C for 5 h under a flow of N_2 . (●) AlN, (■) $\alpha\text{-Al}_2\text{O}_3$, (△) $\gamma\text{-AlON}$, (☆) graphene sheets.

tively. In the sample calcined at 1000°C an intense peak (at δ 15 ppm) assigned to $\alpha\text{-Al}_2\text{O}_3$ was detected together with a weak powder-patterned peak of $\alpha\text{-Al}_2\text{S}_3$. The peak at δ 114 ppm observed in Figs. 2(c) to (e) is assigned to AlN.⁷⁾ With increasing the calcination temperature, the peak assigned to $\alpha\text{-Al}_2\text{S}_3$ became weaker. As shown in Fig. 2(e), the peak assigned to $\alpha\text{-Al}_2\text{S}_3$ completely disappeared for the sample calcined at 1300°C.

As aforementioned, the AlN formation by the CRN reaction of $\alpha\text{-Al}_2\text{O}_3$ commenced at 1100°C, which is the lowest temperature reported for AlN formation by the CRN reaction. In our previous paper⁴⁾ we showed that the reaction of Al_2S_3 with CO afforded a mixture of $\alpha\text{-Al}_2\text{O}_3$ and graphene sheets and that not all evolved gaseous carbon crystallized in the graphene sheets. The formation of the graphene sheets indicated that gaseous carbon was evolved during the reaction of Al_2S_3 with CO. The reduced AlN formation temperature was attributed to the involvement of the gaseous carbon in the CRN reaction of Eq. (1). It might be proposed, therefore, that the formation reaction of AlN by calcining Al_2S_3 under a mixed gas flow of CO and N_2 consists of the following two consecutive reactions I and II:

The proposed reaction mechanism is supported by the following findings. First, the calcination of Al_2S_3 under a mixed gas flow of CO and argon afforded graphene sheets (corresponding to C(s) in reaction I) and $\alpha\text{-Al}_2\text{O}_3$ ⁴⁾ but did not afford AlN because of

Fig. 4. (a) TEM image of the sample obtained by calcination of Al_2S_3 powder at 1300°C for 10 h under a flow of 10 vol% CO/N_2 and (b) EDX spectrum of the portion designated by the dotted circle in Fig. 4(a).

no occurrence of reaction II. Second, a part of the gaseous sulfur liberated in reaction I was deposited on the inner wall of the downstream end of the alumina tube. Third, the calcination of Al_2S_3 under a flow of N_2 did not afford AlN because of no occurrence of reaction I.

The possibility that $\alpha\text{-Al}_2\text{O}_3$ reacted with solid-state carbon (graphene sheets) at the temperatures $\leq 1300^\circ\text{C}$ can be ruled out by the following findings. We prepared the sample obtained by calcining Al_2S_3 powder at 1300°C for 10 h under a mixed gas flow of 10 vol% CO/N_2 and measured its XRD pattern and TEM image. The XRD pattern (Fig. 3(a)), showing that the sample was a mixture of $\alpha\text{-Al}_2\text{O}_3$, AlN , graphene sheets, and $\gamma\text{-AlON}$ (JCPDS No. 80-2173), was considerably different from that (Fig. 1(f)) of the sample calcined at 1300°C for 10 h under a flow of 1 vol% CO/N_2 because of the retardation effect of CO in reaction II. The CRN reaction became more retarded with increasing CO content in the mixed gas.⁸⁾ The $\gamma\text{-AlON}$ phase was formed by the reaction of AlN with $\alpha\text{-Al}_2\text{O}_3$ and its formation temperature was ca. 300°C lower than that in the modified CRN reaction.⁹⁾ The TEM image (Fig. 4(a)) of the sample showed rippled graphene sheets and nanosized ceramic particles. The sample's energy dispersive X-ray (EDX) spectrum (Fig. 4(b)) exhibited the existence of elements such as carbon, aluminum, nitrogen, and oxygen. The high atomic% of carbon strongly supported the existence of graphene sheets in the sample. The sample calcined at 1300°C for 10 h under a flow of 10 vol% CO/N_2 was further calcined at 1200, 1300, 1400, and 1500°C for 5 h under a flow of N_2 . The XRD patterns of the samples obtained are shown in Figs. 3(b)–(d). The XRD patterns of the samples calcined at 1200 and 1300°C were the same as that (Fig. 3(a)) before the further calcination, indicating that $\alpha\text{-Al}_2\text{O}_3$ did not react with the graphene sheets at 1200 and 1300°C . As shown in Fig. 3(c), the calcination at 1400°C afforded a mixture of $\alpha\text{-Al}_2\text{O}_3$ and AlN . The peaks assigned to AlN in Fig. 3(c) were more intense than those in Fig. 3(a) and the peaks assigned to graphene sheets disappeared, indicating that $\alpha\text{-Al}_2\text{O}_3$ reacted with graphene sheets at 1400°C . The nitridation temperature of 1400°C was at least 100°C lower than that^{2),3)} in the conventional CRN method in which $\alpha\text{-Al}_2\text{O}_3$ powder is mechanically mixed with carbon sources. This is caused by the mixing homogeneity of $\alpha\text{-Al}_2\text{O}_3$ and carbon (graphene sheets). The XRD pattern (Fig. 3(d)) of the sample calcined at 1500°C was almost the same as that of Fig. 3(c). These results lead to the conclusion that $\alpha\text{-Al}_2\text{O}_3$ did not

react with the graphene sheets at the temperatures $\leq 1300^\circ\text{C}$. Therefore, the AlN formation at the temperatures $\leq 1300^\circ\text{C}$ under a flow of 1 vol% CO/N_2 was caused by the CRN reaction of $\alpha\text{-Al}_2\text{O}_3$ with gaseous carbon. This is the first report of the involvement of gaseous carbon in the CRN reaction of Eq. (1). The incomplete conversion of Al_2S_3 to AlN under a flow of 1 vol% CO/N_2 was caused by the partial exhaust of gaseous carbon evolved in reaction I.

If gaseous carbon is used instead of solid-state carbon in the CRN reaction, the nitridation reaction temperature will be much lowered and the processes such as the intimate mixing of Al_2O_3 with carbon and removal of unreacted carbon will be unnecessary.

4. Conclusion

The gaseous carbon, which was produced by the reaction of Al_2S_3 with CO , reacted with $\alpha\text{-Al}_2\text{O}_3$ under a flow of N_2 to afford AlN . The AlN formation commenced at 1100°C , which is the lowest temperature reported for AlN formation by the CRN reaction. This is the first report of the involvement of gaseous carbon in the CRN reaction. This work has demonstrated that the use of gaseous carbon in the CRN reaction greatly lowers the nitridation temperature of Al_2O_3 .

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