Synthesis of β -SiAlON from a zeolite by reduction nitridation in a mixture of NH_3 - C_3H_8

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Gas reduction-nitridation (GRN), which uses a mixture of NH_3 and carbohydrate as a reactant gas, has been proposed a synthetic technique for producing high-purity nitride powders. In this study, β -SiAlON powder was produced from zeolite using GRN. Zeolite was used directly as the raw material without previous preparation or handling. It was found that high purity β -SiAlON nanopowder was synthesized at 1400°C for 60 min. Furthermore, pure β -SiAlON was successfully produced, containing no minor phases, by the optimization of nitridation, that is, of concentration of C_3H_8 and the timing of its introduction.

Key-words : β -SiAlON, Zeolite, Gas reduction-nitridation, Nano powder

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1. Introduction

SiAlON ceramics are promising engineering materials because of their excellent properties, e.g. high fracture toughness, high strength and corrosion resistance close to β - Si_3N_4 . β -SiAlON is a solid solution of β - Si_3N_4 in which some Si and N are replaced by Al and O. Its stoichiometric composition depends on the solid solubility limit. The chemical formula is as follows;

β -SiAlON ceramics are commonly produced by the reaction sintering of mixtures of Si_3N_4 , AlN, and Al_2O_3 over at 1500°C . As its corrosion resistance lowers with the formation of its glassy phase in the sintered body, the preparation of β -SiAlON powder and its sintering using spark plasma sintering (SPS)¹⁾ has received considerable attention as it avoids the formation of glassy phase in the grain boundary.

β -SiAlON powder is mostly synthesized from mixtures of SiO_2 and Al_2O_3 by carbothermal reduction-nitridation (CRN) over at 1400°C . The suitability of various minerals as raw materials for this process has been widely investigated. These include such as kaolinite,²⁾⁻⁶⁾ halloysite,^{6),7)} montmorillonite⁸⁾ and bentonite.⁹⁾ These minerals are mainly composed of Si and Al, and contain them uniformly on an atomic scale; however, due to the effects of the contamination and the difficulty of controlling the compositions, for example the Si/Al ratio, in the raw materials, products synthesized using these minerals consequently contain AlN, mullite and 15R polytype as impurity phases. The work presented here focuses on using a zeolite as a raw material to avoid these problems. Zeolites are hydrated, crystalline, tectoaluminosilicates constructed from TO_4 tetrahedra (where T=tetrahedral atom, e.g. Si and Al).¹⁰⁾⁻¹²⁾ They contain well-ordered, nanometer-sized void spaces (ca. 0.3–1.5 nm) in their structures. Furthermore, it is possible to control the Si/Al ratio of zeolites by controlling the starting composition. It is also easy to incorporate charge compensation cations (e.g. Na^+ , Ca^{2+} and H^+) uniformly in zeolite struc-

tures by ion exchange since the structure contains many anionic Al sites. Sugahara et al.¹³⁾ synthesized β -SiAlON from compounds containing zeolite-polyacrylonitrile by the CRN process; they showed the suitability of zeolite as a raw material, but the formation of high-purity β -SiAlON could not be performed by the technique discussed. In a previous study,¹⁴⁾ high-purity β -SiAlON was synthesized from a mixture of zeolite and carbon by the CRN process; however, the resultant products had a large distribution in z value since the composition of the glassy phase became inhomogeneous due to the formation of mullite during firing.

In recent years, gas reduction-nitridation (GRN), which uses a mixture of NH_3 and carbohydrate as a reactant gas, has been proposed a synthetic technique for producing high-purity nitride powders.¹⁵⁾⁻¹⁹⁾ The GRN process is quite a simple process since it does not require mixing, milling or a decarburization process. Moreover, the GRN process is generally performed at lower temperatures and with less solid solution of carbon in the products than the CRN process. In this paper, β -SiAlON powder is synthesized from a zeolite by the GRN process, producing highly-pure β -SiAlON composed nanoparticles (<100 nm).

2. Experimental

Zeolite Y (HSZ-330HUA, Toso Chem. Co., Tokyo) was used as a starting material since zeolite Y is one of the most representative zeolites and is able to be synthesized with wide range of Si/Al ratio (from 1.5 to ∞). The main characteristics of the raw powder are listed in **Table 1**. The raw powder was weighed into an alumina boat, placed in an electric furnace with a high-purity alumina work tube, and then fired to 700°C at a heating rate of $5^\circ\text{C}/\text{min}$. The powder was heated in Ar gas (99.999% purity) in order to eliminate oxygen in the system and remove the absorption water in the zeolite. It was confirmed that the structure of the zeolite did not change during the pre-heating process up to 700°C . Heating was continued in a flowing gas mixture (4 l/min) of NH_3 (99.999% purity) and C_3H_8 (99.99% purity, 0.5 vol%). The

Table 1. Characteristics of the Raw Powder

Characteristics	Value
Zeolite type	Y-type
Si/Al (mol/mol)	3 ($z=1.5$)
Mean particle size (μm)	0.6 μm
Specific surface area (m^2g^{-1})	550

※ As provided by the supplier.

sample was heated to the reaction temperature of 1200–1400°C at a rate of 8°C/min and held for 0–60 min before being cooled in NH_3 . Note that in some cases, the effect of the timing of the introduction of C_3H_8 was investigated and in others C_3H_8 was introduced at 1200°C, 1300°C and 1400°C, respectively.

For comparison, the CRN process was performed using the same zeolite as a raw material.¹⁴⁾ At first, zeolite was mixed with carbon (650B, Mitsubishi Chemical Co., Ltd.). The carbon content was fixed at 1.2 times the required stoichiometric value. The mixture was milled without solvent for 36 h, and was subsequently ground and passed through a sieve with 50-mesh holes. 1.0 g of the sample was placed on a carbon boat and was fired in a furnace at 1450°C for 120 min in N_2 flow (0.5 l/min). The heating rate was set at approximately 12°C/min. The residual carbon was removed by burning the resultant powders at 700°C for 120 min in atmospheric conditions. Further, a mixture of SiO_2 (QS-102 Tokuyama Co., Ltd.) and Al_2O_3 (Boehmite, AD220P, Tomita Pharmaceutical Co. Ltd), with the same composition as raw zeolite, was also prepared²⁰⁾ and nitrided by GRN process.

The phases present in the products were identified by X-ray diffractometry (RINT2500, Rigaku, Tokyo) using $\text{CuK}\alpha$ radiation operated at 50 kV and 300 mA. Changes in the morphologies were observed by transmission electron microscope (JEM-2000FX, JEOL, Tokyo). The specific surface areas of the products were measured by single-point of Brunauer-Ematt-Teller method (BET; Quantasorb, Quantachrome, Boynton Beach, FL).

3. Results and discussion

Figure 1 shows XRD patterns of the products synthesized at 1200°C for 0 min, 1400°C for 0 min and 1400°C for 60 min from raw zeolite, the product synthesized by the CRN process from raw zeolite and the product synthesized from SiO_2 - Al_2O_3 mixture by the GRN process. It was found that raw zeolite was transformed into its amorphous phase at 1200°C (Fig. 1b) and α '-SiAlON and X' -SiAlON as intermediate phases were confirmed in the sample synthesized at 1400°C for 0 min (Fig. 1c), matching results reported in a previous study.⁶⁾ Finally, high-purity β -SiAlON was obtained by the heat treatment at 1400°C for 60 min as shown in Fig. 1d. Figure 1e shows the XRD pattern of the sample prepared by the CRN process. It is found that high purity β -SiAlON can also be synthesized by the CRN process; however the peak of β -SiAlON is broadened as indicated in the arrow in Fig. 1e; indicating that the resultant products have a large distribution of z values because of the formation of a Si rich amorphous phase and Al rich mullite phase in products formed during firing and subsequent

Fig. 1. XRD patterns of (a) raw zeolite, (b) the product synthesized at 1200°C for 0 min, (c) 1400°C for 0 min and (d) 1400°C for 60 min. For comparison, XRD patterns of (e) the product synthesized by the CRN process and (f) the product synthesized from SiO_2 - Al_2O_3 mixture by the GRN process are shown. The arrow indicates the product has a large distribution of z values.

crystallization to β -SiAlON.²¹⁾ Figure 1f shows the XRD pattern of the product prepared from SiO_2 - Al_2O_3 mixture. It was found that α - Si_3N_4 represents a considerable impurity phase when compared to using zeolite as a raw material (Fig. 1d). This result can be ascribed to inhomogeneous distributions of Si and Al atoms in the SiO_2 - Al_2O_3 mixture. It is known that SiO gas is formed in a reducing atmosphere around 1400°C.^{22)–24)} Because the Si and Al atoms are not distributed uniformly on an atomic scale in the SiO_2 - Al_2O_3 mixture, SiO gas is easily formed and reacts with NH_3 . As a result, a larger volume of α - Si_3N_4 is formed as indicated in the following equations.

On the other hand, since Si and Al atoms are mixed uniformly on an atomic scale in zeolite, it is thought that formation of SiO gas is prevented by well-dispersed Al atoms in the amorphous phase, suppressing α - Si_3N_4 formation. The vapor pressure of AlO gas is extremely low compared with SiO gas. We think that the vapor pressure of SiO decreases by the vapor pressure depression because a lot of Al atom exists.²⁵⁾ It can be concluded that high purity β -SiAlON with sharper z value distribution than that obtained by the CRN process was successfully synthesized from zeolite Y by the GRN process.

TEM photographs of the products synthesized at 1200°C for 0 min, 1400°C for 0 min and 1400°C for 60 min, together with a photograph of raw material are shown in Fig. 2. It was found that well-faceted zeolite particles were changed to a beadlike morphology at 1400°C for 0 min. TEM image,

Fig. 2. TEM photographs of raw material (a) and the products synthesized at 1200°C for 0 min (b), 1400°C for 0 min (c) and 1400°C for 120 min (d).

Fig. 3. Specific surface areas of the products synthesized at various reaction temperatures at 1200–1400°C for 0–120 min.

as shown in Fig. 2b, of particle morphologies of the resulting powders at 1400°C for 60 min shows that generated particles exhibited hollow spheres approximately 200–500 nm in diameter, these being produced mainly from ultrafine initial particles of 50–100 nm. In previous research, similar morphology has been confirmed in the synthesis of Ca α -SiAlON.^{26),27)} It is thought that hollow spheres are formed by the nucleation of β -SiAlON and intermediate phases on the surface of each particle and the subsequent mass transfer due to crystal growth and/or by the generation of H₂O and CO gas during nitridation. **Figure 3** shows the specific surface areas of the products synthesized at 1200, 1300 and 1400°C without holding time, and at 1400°C with 30 and 60 min holding. It was obtained that the specific surface area of

Fig. 4. Effect of concentration of C₃H₈ on the phase compositions of the products by GRN process fired at 1400°C for 30 min. (a) 0.25, (b) 0.05 and (c) 0.025 vol%.

a raw material was drastically decreased by introducing amorphization. However, it was found that the specific surface area was increased from 9.1 up to 19.4 m²/g during the GRN process. Therefore it is concluded that the specific surface area increases with the production of β -SiAlON. This conclusion agrees with those obtained by XRD and TEM as shown in Figs. 1 and 2, respectively. **Figure 4** shows the effect of C₃H₈ concentration on the phase compositions of the materials produced by the GRN process fired at 1400°C for 30 min. The presence of O'-SiAlON and X'-SiAlON was confirmed in conditions with lower C₃H₈ concentrations. As the concentration of C₃H₈ increased, phase contents of O'-SiAlON and X'-SiAlON decreased and formation of α -Si₃N₄ was confirmed. C₃H₈ plays the role of reducing agent, promoting nitridation, that is, the formation of N-T(-T) (-T) bonds from T-O-T bonds (T = Si and Al). In conditions with lower C₃H₈ concentrations, O'-SiAlON and X'-SiAlON, which are stable phases at lower temperatures, still remain in the samples since nitridation of the aluminosilicate amorphous phase is not greatly promoted. On the other hand, reduction nitridation of the aluminosilicate amorphous phase is promoted in conditions with higher C₃H₈ concentrations as indicated in the following equation.

The SiO gas formed reacts with NH₃ to form α -Si₃N₄ as follows.

It appears, therefore, that formation of α -Si₃N₄ as a minor phase is promoted in conditions with higher C₃H₈ concentrations.

Figure 5 shows the effect of C₃H₈ injection timing on the phase compositions of the materials produced by the GRN process fired at 1400°C for 30 min. C₃H₈ was introduced at 1200, 1300 and 1400°C before the holding period. It was found that when the introduction of C₃H₈ was delayed to 1300 and 1400°C, nitridation did not complete and as a result O'-SiAlON and X'-SiAlON were formed. On the other hand, pure β -SiAlON was successfully obtained when C₃H₈ was introduced at 1200°C. We think that the generation of the SiO gas is suppressed due to the rapid nitridation reaction influenced by the introduced C₃H₈ gas at the low

Fig. 5. Effect of C_3H_8 injection timing on phase compositions of the products by GRN process fired at 1400°C for 30 min. C_3H_8 was introduced at (a) 1200°C , (b) 1300°C and (c) 1400°C before the holding period.

temperature. Whereas at high temperatures of 1300°C and 1400°C , we think that $\alpha\text{-Si}_3\text{N}_4$ has already nucleated before passing the C_3H_8 . It is thought that crystallization of $\alpha\text{-Si}_3\text{N}_4$ is promoted even if the reaction time is long. It may be that formation of $\alpha\text{-Si}_3\text{N}_4$ has relation with a heat treatment time. These was concluded, therefore, that it is possible to produce pure $\beta\text{-SiAlON}$ without any minor phases by the optimization of nitridation; that is, optimizing both the concentration, and timing, of introduction of C_3H_8 .

4. Conclusions

High purity $\beta\text{-SiAlON}$ powder was produced from zeolite using gas-reduction-nitridation. Zeolite was used directly as the raw material without previous preparation or handling. It was found that high purity $\beta\text{-SiAlON}$ nanopowder was synthesized at 1400°C for 60 min, and that the powder was comprised of hollow spheres which formed from the initial particles with diameters of about 30–50 nm. Furthermore, pure $\beta\text{-SiAlON}$ was successfully produced, containing no minor phases, by the optimization of nitridation, that is, of concentration of C_3H_8 and the timing of its introduction.

References

- Q Li, K. Komeya, J. Tatami, T. Meguro and L. Gao, *Key Eng. Mater.*, 247, 75–78 (2006).
- H.-L. Lee, H.-J Lim, S. Kim and H.-B. Lee, *J. Am. Ceram. Soc.*, 72, 1458–1461 (1989).
- M. Vlasova, V. B. Vinokurov, O. N. Grigo'ev, A. D. Panasyuk, N. D. Bega, M. Kakazey, J. G. G.-Rodriguez, G. D.-Patiño and M. D.-Patiño, *Mat. Sci. Eng.*, A366, 325–331 (2004).
- Y. W. Cho and J. A. Charles, *Mater. Sci. Eng.*, 7, 399–406 (1991).
- X.-J. Liu, X. W. Sun, J. J. Zhang, X. P. Pu, Q. M. Ge and L. P. Huang, *Mater. Res. Bull.*, 38, 1939–48 (2003).
- K. J. D. Mackenzie, R. H. Meinhold, G. V. White and C. M. Sheppard, *J. Mater. Sci.*, 29, 2611–2619 (1994).
- M. E. Bowden, K. J. D. MacKenzie and J. H. Johnston, *Material Sci. Forum.*, 34–36, 599–603 (1988).
- Y. Sugahara, K. Kuroda and C. Kato, *J. Am. Ceram. Soc.*, 72, C247–248 (1984).
- A. D. Mazzoni and E. F. Aglietti, *Appl. Clay. Sci.*, 17, 127–140 (2000).
- R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1982.
- C. S. Cundy and P. A. Cox, *Chem. Rev.*, 103, 663 (2003).
- T. Wakihara and T. Okubo, *Chem. Lett.*, 34, 276–281 (2005).
- Y. Sugahara, H. Hiraiwa, K. Kuroda and C. Kato, *J. Mat. Sci.*, 23, 3181–3186 (1988).
- F. J. Li, J. Tatami, T. Meguro and K. Komeya, *Key. Eng. Mater.*, 247, 109–112 (2003).
- T. Yamakawa, T. Wakihara, J. Tatami, K. Komeya and T. Meguro, *Ceram. Trans.*, 190, 3–8 (2006).
- T. Suehiro, J. Tatami, T. Meguro, S. Matsuo and K. Komeya, *J. Eur. Ceram. Soc.*, 85, 715–717 (2002).
- T. Yamakawa, J. Tatami, T. Wakihara, T. Meguro, K. Komeya, K. J. D. MacKenzie, S. Takagi and M. Yokouchi, *J. Am. Ceram. Soc.*, 89[1], 171–175 (2006).
- T. Yamakawa, J. Tatami, T. Wakihara, T. Meguro, K. Komeya and K. J. D. MacKenzie, *Key Eng. Mater.*, 317–18, 215–218 (2006).
- T. Yamakawa, J. Tatami, K. Komeya and T. Meguro, *J. Eur. Ceram. Soc.*, 26(12), 2413–2418 (2006).
- Q. Li, C. Zhang, K. Komeya, J. Tatami, T. Meguro and L. Gao, *Key. Eng. Mater.*, 237, 117–122 (2003).
- F. J. Li, T. Wakihara, J. Tatami, T. Meguro, K. Komeya and K. J. D. MacKenzie, *J. Am. Ceram. Soc.*, 90, 1541–1544 (2007).
- A. Hendry and K. H. Jack, *Special Ceramics*, 6, 199–208, Ed. P. Popper (1975).
- S.-C. Zhang and W. R. Cannon, *J. Am. Ceram. Soc.*, 67[10], 691–695 (2006).
- S. A. Siddipi and A. Hendry, *J. Mater. Sci.*, 20, 3230–3238 (1985).
- S. I. Shornikov, I. Yu. Archakov, M. M. Shultz and N. V. Borisova, *Doklady Chemistry.*, 383(1–3), 82–85 (2002).
- K. Komeya, C. Zhang, M. Hotta, J. Tatami, T. Meguro and Y.-B. Cheng, *J. Am. Ceram. Soc.*, 83, 995–997 (2000).
- J. Tatami, M. Iguchi, M. Hotta, C. Zhang, K. Komeya, T. Meguro, M. Omori, T. Hirai, M. E. Brito and Y.-B. Cheng, *Key. Eng. Mater.*, 237, 105–110 (2003).