

Preparation of Ca- α SiAlON powder by reduction-nitridation in a gas mixture of C₃H₈ and NH₃

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Ca- α SiAlON powders were synthesized from a SiO₂–Al₂O₃–CaCO₃ powder mixture by reduction-nitridation with C₃H₈–NH₃ gas. Ca- α SiAlON with small amounts of AlN and β -SiAlON phases was produced at 1450°C for 120 min. Angular particles and agglomerated and bonded particles with irregular shapes were formed. In the product prepared at 1450°C without any holding time, Si₂N₂O was detected as an intermediate phase, in addition to the Ca- α SiAlON, β -SiAlON and AlN phases. A large number of agglomerated and bonded particles were observed.

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SiAlON ceramics possess high hardness and excellent oxidation and corrosion resistance.^{1)–4)} α -SiAlON is a solid solution having a α -Si₃N₄ crystal structure, with some Al and O substituted for Si and N and some metal cations incorporated as a stabilizer. The general formula for α -SiAlON is M_{m/v}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}, where v is the valency of the stabilizing cation M. M can be Li, Mg, Ca, Y, or most rare-earth elements.⁵⁾ α -SiAlON powders have been prepared by carbothermal reduction-nitridation (CRN) of the SiO₂–Al₂O₃–M_xO_y system mixed with carbon powder as a reducing agent under flowing N₂ gas.^{6)–12)} In our previous study, Ca- α SiAlON powders were prepared from mixtures of SiO₂, Al₂O₃, CaCO₃ and carbon powders by CRN.^{13)–16)} The powders prepared had hollow spheres composed of nanosized particles.¹³⁾ Solid spherical particles that consisted of a liquid phase containing Si, Al, Ca, O were generated at the initial stage of the CRN process. As the reaction proceeded from the liquid phase to the crystalline Ca- α SiAlON, the solid spheres changed into hollow spheres.^{14),15)}

High-purity and fine-grained AlN powders were obtained by gas reduction-nitridation (GRN) of fine-grained Al₂O₃ using a gas mixture of C₃H₈ and NH₃ as a reduction-nitridation agent.^{17),18)} This indicated that the resultant particles retained the morphology of the starting powders because of a gas-solid reaction between Al₂O₃ and NH₃, and that the use of a hydrocarbon gas as reducing agent promoted more reduction-nitridation compared to the case of CRN with carbon powder.

In the present work, Ca- α SiAlON powders were prepared through GRN of a mixture of SiO₂, Al₂O₃, and CaCO₃ powders using a C₃H₈–NH₃ gas mixture, and the crystalline phases and particle morphology of the products were investigated. The effect of hydrocarbon gas as a reducing agent on the particle morphology of the products was also discussed.

As starting materials, SiO₂ (QS-102, Tokuyama Co., particle size: 0.005–0.05 μ m), Al₂O₃ (AKP-50, Sumitomo Chemical Co., Ltd., 0.21 μ m) and CaCO₃ (Junsei Chemical Co., Ltd., 1.0 μ m) powders were used. The proportions of these powders were adjusted so as to obtain a nominal composition of Ca_{1.0}Si_{9.0}Al_{3.0}O_{1.0}N_{15.0} [i.e. Ca_xSi_{12-3x}Al_{3x}O_xN_{16-x} ($x = m/v = n$) with $x = 1.0$], which was the maximum content of Ca- α SiAlON phase in the products obtained by CRN of SiO₂–Al₂O₃–CaCO₃ powder mixtures with x varying from 0.3 to 1.4.¹³⁾ The starting powders were mixed with a small amount of ethanol. The mixture was dried, sieved, placed in an Al₂O₃ boat, and heated in a horizontal electric furnace under a flowing gas mixture of C₃H₈ (20 mL/min) and NH₃ (4 L/min) at a rate of 10°C/min up to 1450°C, for holding times of 0 to 120 min. The crystalline phases that appeared in the specimens were identified by X-ray diffractometry (XRD). The content of the Ca- α SiAlON phase was calculated from the XRD peak intensities.¹⁵⁾ Scanning electron microscopy (SEM) was used to characterize the particle morphology of the specimens.

Figure 1 shows the XRD pattern of the specimen prepared at 1450°C for 120 min by GRN. Ca- α SiAlON was detected as the major phase, and AlN and β -SiAlON as minor phases, the relative amounts being 80, 15 and 5%, respectively. In our previous study, CRN of SiO₂–Al₂O₃–CaCO₃ powder mixtures yielded no β -SiAlON. Instead, 85–90% Ca- α SiAlON and 10–15% AlN were found in the specimens prepared at 1450°C for 120 min at the composition $x = 1.0$ and a carbon content 1.2 to 2.0 times the stoichiometric value.^{13),16)} Moreover, in the specimen prepared at the stoichiometric carbon content, the intermediate phases of Si₂N₂O, SiAl₇O₂N₇ and AlN were generated.¹⁶⁾ In the present study, the β -SiAlON phase presumably formed as a result of the difference in the evaporation rate of SiO gas from SiO₂ by using carbon powder versus a hydrocarbon gas as reducing agent. A flow of 20 mL/min C₃H₈ and 4 L/min NH₃ was sufficient to produce Ca- α SiAlON through GRN of the SiO₂–Al₂O₃–CaCO₃ powder mixture.

Figure 2 shows the SEM micrographs of the specimens prepared at 1450°C for 120 min by GRN. Angular particles with

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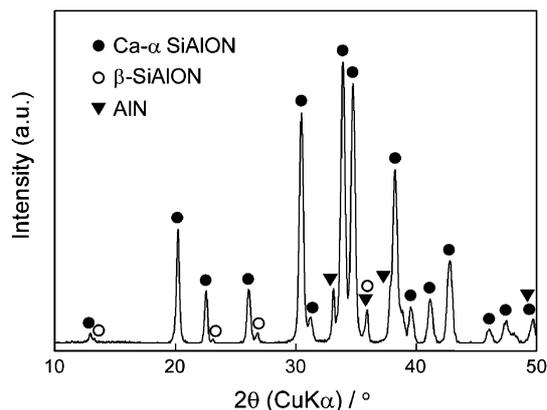


Fig. 1. XRD pattern of the specimen prepared by GRN at 1450°C for 120 min.

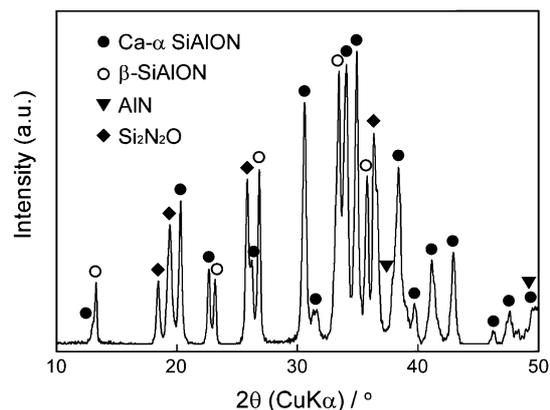


Fig. 3. XRD pattern of the specimen prepared by GRN at 1450°C without any holding time.

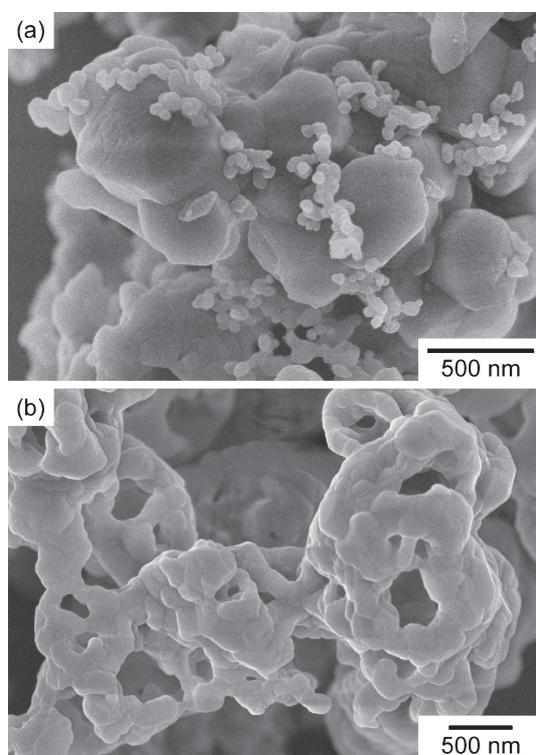


Fig. 2. SEM micrographs of the specimen prepared by GRN at 1450°C for 120 min.

a diameter of around 0.5 μm [Fig. 2(a)], and agglomerated and bonded particles with irregular shapes [Fig. 2(b)] were observed. Fine particles with diameters of less than 100 nm were also present [Fig. 2(a)]. Hollow spherical particles, obtained by CRN of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaCO}_3$ powder mixtures in our previous study, were hardly observed.^{13),15)}

In order to analyze the formation process of Ca- α SiAlON through GRN of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaCO}_3$ powder mixture in $C_3H_8\text{-NH}_3$ gas, the powder mixture was heated to 1450°C, but not held at this temperature, and the resulting crystalline phases and microstructure were characterized. **Figure 3** shows the XRD pattern of the specimen prepared by GRN at 1450°C without any holding time. The $\text{Si}_2\text{N}_2\text{O}$ phase was identified, in addition to Ca- α SiAlON, β -SiAlON and AlN. In our previous work, $\text{Si}_2\text{N}_2\text{O}$ was also confirmed as an intermediate phase in the

formation of Ca- α SiAlON through CRN of SiO_2 , Al_2O_3 and CaCO_3 powders mixed with carbon powder under flowing N_2 .^{14),15)} The β -SiAlON to Ca- α SiAlON XRD peak intensity ratio was higher in the specimens prepared at 1450°C without any holding time than in that prepared with a 120-min holding time, indicating the higher proportion of β -SiAlON in the former specimen. In the specimens prepared by CRN at 1450°C without any holding time, an amorphous shoulder was observed at low 2θ values in the XRD patterns,^{14),15)} while no amorphous shoulder was detected in specimens prepared by GRN. The XRD peaks of the crystalline phases in the specimens prepared by GRN at 1450°C without any holding time were higher and sharper than those obtained in the case of CRN.^{14),15)} Thus, the reduction-nitridation of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaCO}_3$ mixture to Ca- α SiAlON via GRN with $C_3H_8\text{-NH}_3$ gas presumably proceeded faster than that by CRN with carbon powder and N_2 gas. Furthermore, the XRD peaks of Ca- α SiAlON in the specimen prepared at 1450°C without any holding time shifted to higher 2θ values compared to those obtained in the case of the reaction at 1450°C with a 120-min holding time. This would suggest that the Ca, Al and O content of the Ca- α SiAlON increased as the holding time was increased from 0 to 120 min, because the lattice constant was increased by incorporation of Ca into the α -SiAlON structure, and substitution of Al and O for Si and N.

Figure 4 shows the SEM micrographs of the specimen prepared by GRN at 1450°C without any holding time. Agglomerated and bonded particles, composed of a large number of particles with a diameter of less than 0.5 μm , can be observed. In the case of CRN, solid spherical particles were seen in specimens prepared at 1450°C without any holding time.^{14),15)} The XRD pattern in Fig. 3 suggests that the formation process of Ca- α SiAlON powder from a $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaCO}_3$ mixture is nearly the same both in GRN and CRN. The difference in particle morphology between the specimens prepared at 1450°C for 120 min by GRN versus CRN may be attributable to the different reducing agents used in the two cases. In the case of CRN with carbon powder as the reducing agent, spheres consisting of a Si-Al-Ca-O liquid phase were formed during the initial stage of the reaction, because of the poor wettability between the liquid and carbon. The solid spheres subsequently changed into hollow spheres as the reduction-nitridation reaction proceeded.¹⁴⁾ In the case of GRN with C_3H_8 gas, on the other hand, the Si-Al-Ca-O liquid phase did not lead to the formation of spheres, because the hydrocarbon gas was not conducive to the formation of spherical particles. Hence, agglomerated and bonded particles would be

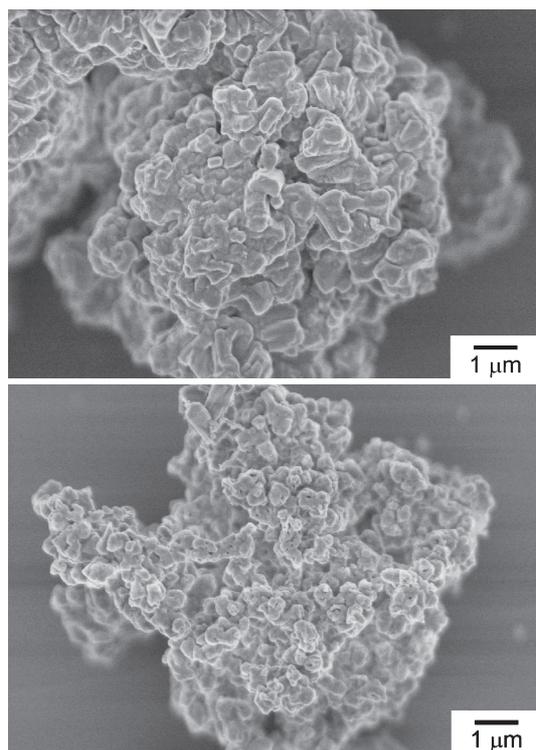


Fig. 4. SEM micrographs of the specimen prepared by GRN at 1450°C without any holding time.

generated in the initial stage of the GRN process, and Ca- α SiAlON would be produced while maintaining the particle morphology (Figs. 2 and 4).

In summary, Ca- α SiAlON powders were prepared through GRN of a SiO₂-Al₂O₃-CaCO₃ powder mixture under flowing C₃H₈-NH₃, and the crystalline phases and microstructure of the products were studied. Ca- α SiAlON, AlN and β -SiAlON phases were found in the specimens prepared at 1450°C for 120 min. The Ca- α SiAlON content was 80%. Angular particles, and agglomerated and bonded particles were observed in the final product. In the specimen prepared at 1450°C without any holding time, Si₂N₂O was detected as an intermediate phase.

Agglomerated and bonded particles were observed in the product. The spherical particles generated by CRN of SiO₂-Al₂O₃-CaCO₃ powders mixed with carbon powder under flowing N₂ were largely absent in the specimens prepared by GRN.

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