Effect of nitrogen gas pressure during heat treatment on the morphology of silicon nitride fibers synthesized by carbothermal nitridation

Sotaro Baba, Tomoyo Goto, Sung Hun Cho and Tohru Sekino

The Institute of Scientific and Industrial Research (ISIR), Osaka University, Ibaraki, Osaka, Japan

ABSTRACT
The effects of \( N_2 \) gas pressure on the diameter and morphology of \( \text{Si}_3\text{N}_4 \) fibers obtained via carbothermal nitridation were investigated. Sol-gel-derived precursors containing a silica and carbon mixture were placed in an \( \text{Al}_2\text{O}_3 \) crucible and heat-treated under various \( N_2 \) pressures from 0.1 to 0.5 MPa at 1500ºC. The heat-treated samples were characterized by X-ray diffraction (XRD), a scanning electron microscope (SEM) coupled with an energy dispersion X-ray (EDX) spectrometer, and transmission electron microscopy (TEM). Various nitride fibers with \( \alpha \) - and \( \beta \)-phase \( \text{Si}_3\text{N}_4 \) were formed. The fiber diameter decreased with increases in \( N_2 \) pressure, and nanometer-scale fibers of around 200 nm in diameter were obtained at a \( N_2 \) pressure of 0.5 MPa. It was found that silicon oxynitride \( \text{Si}_3\text{N}_4\text{O} \) or its Al-doped form, \( \text{O}^{+}\text{SiAlON} \), was produced due to high \( N_2 \) pressure and doping with Al originating from the \( \text{Al}_2\text{O}_3 \) crucible. This oxynitride was considered to act as a template for \( \text{Si}_3\text{N}_4 \) fiber growth by the direct phase transformation mechanism. It was shown that the diameter of the \( \text{Si}_3\text{N}_4 \) fibers decreased for two reasons: decreased partial pressure of \( \text{SiO} \) gas due to high \( N_2 \) pressure and increased formation of the silicon oxynitride templates.

1. Introduction
Silicon nitride (\( \text{Si}_3\text{N}_4 \)) ceramics have high strength, high toughness, low density, excellent high-temperature strength and a low dielectric constant. \( \text{Si}_3\text{N}_4 \) is therefore widely used as a structural material in turbocharger rotors, ball bearings, cutting tools, etc. On the other hand, one-dimensional silicon nitride nanomaterials such as fibers and whiskers have many special applications. They are used as reinforcing fibers in various matrices such as resins, metals and ceramics, for example, to improve their mechanical and thermal properties. Hirao et al. [1] produced an oriented \( \text{Si}_3\text{N}_4 \) whisker-reinforced composite \( \text{Si}_3\text{N}_4 \) matrix combining high strength and toughness. Kusunose et al. [2] produced an epoxy/\( \text{Si}_3\text{N}_4 \) nanowire composite that improved thermal conductivity. To develop higher-performance materials using silicon nitride fibers, it is necessary to control the structure of the bulk materials precisely; thus, morphology and crystalline phase control of the silicon nitride fibers is very important.

Carbothermal reduction and nitridation is a method of synthesizing \( \text{Si}_3\text{N}_4 \) through reduction and nitridation heat treatment of silica (\( \text{SiO}_2 \)) with carbon (C) in a nitrogen (\( N_2 \)) atmosphere. The reaction is as follows:

\[
3\text{SiO}_2 + 6\text{C(s)} + 2\text{N}_2(g) = \text{Si}_3\text{N}_4(s) + 6\text{CO(g)} \tag{1}
\]

This reaction starts at around 1300ºC. The carbothermal reduction and nitridation method is useful due to the simple process required to fabricate fibers. It should be noted, however, that different mechanisms for the formation of \( \text{Si}_3\text{N}_4 \) fibers have been proposed. Zhang et al. [3] synthesized \( \text{Si}_3\text{N}_4 \) nanowires from Si powder or a Si/\( \text{SiO}_2 \) powder mixture under nitrogen or ammonium gas, with or without Fe or Ni powders. Chaudhuri et al. [4] synthesized \( \text{Si}_3\text{N}_4 \) nanowires from silica gel with ultrafine excess carbon. \( \text{Si}_3\text{N}_4 \) fibers are known to employ one of two growth mechanisms: vapor–liquid–solid (VLS) or vapor–solid–solid (VSS). VLS growth occurs when a metal catalyst is added to a precursor. The nuclei of a fiber are a liquid metal catalyst droplet above the eutectic temperature. The precursor gases are dissolved into the droplet and the fiber grows from within the supersaturated liquid droplet. It is a feature of the product that droplets of metal catalyst remain at the end of the produced fibers [2,5]. On the other hand, the VSS mechanism begins with supersaturated solid particles below the melting temperature, in which both the matrix and growing phase remain as solids. The important feature here is that the solid particles provide a template for growth and may control the diameter of the fibers. Nevertheless, the catalysts always remain in the synthesized fibers, and their removal in post-treatment is required to obtain pure \( \text{Si}_3\text{N}_4 \) fibers.
Previous researchers have focused their studies mainly on the type of precursor silica, thermodynamic analysis, crystal phase and so on [2–6]. It should be noted that the crystalline phase obtained by these methods was mainly α-type Si3N4 because the carbothermal synthetic method was carried out at around atmospheric pressure via the vapor-phase growth route, which allows the formation of a thermodynamically stable α-phase. Chen et al. [7] reported synthesis of β-Si3N4 nanofibers by the combustion synthetic route, but they used a high N2 pressure of 10 MPa. Kusunose et al. [2] also synthesized β-fibers, but at a high temperature and gas pressure (above 160°C and 0.5 ~ 0.98 MPa, respectively) and by use of a Co catalyst.

It is well known that β-type Si3N4 is widely used in sintered ceramics, and anisotropic-shaped β-Si3N4 is regarded as a strengthening filler or seed crystal for controlling the grain-morphology of sintered silicon nitride ceramics. Therefore, a means of achieving facile and reproductive synthesis of β-Si3N4 fibers, including nano-sized fibers, under moderate conditions such as a lower temperature and/or gas pressure is required. In this study, we have focused on the morphology and crystalline phase of Si3N4 synthesized by the carbothermal nitridation process using sol–gel-derived precursor powder. Special emphasis has been placed on clarifying the effect of N2 gas pressure on the formation, crystalline phase and morphology of the Si3N4 fibers.

2. Experimental procedures

The sol–gel technique was used for synthesis of the precursors in this study. Tetraethyl orthosilicate (TEOS, Si(OC2H5)4) was used as the precursor for the silicon source, and polyvinyl alcohol (PVA) was used as the precursor for the carbon source and to accelerate gelation.

First, 7.62 mL of TEOS (Wako Pure Chemical Ind. Ltd., Tokyo, Japan) and 30 mL of ethanol (Wako Pure Chemical Ind. Ltd., Tokyo, Japan) were added to a solution of 30 mL ultra-pure water at 80°C with 3 g of PVA (Wako Pure Chemical Ind. Ltd., Tokyo, Japan) having a degree of polymerization of 500. Subsequently, nitric acid (HNO3; Wako Pure Chemical Ind. Ltd., Tokyo, Japan) was added until the pH reached 3. The obtained solution was kept at 60°C to form a gel. After 72 h, a transparent gel was obtained. The gel was heated at 200°C for 5 h to completely remove the solvent. Finally, a dried precursor powder was obtained by grinding the product using an alumina mortar.

The precursor powder was placed in an alumina crucible and then heat-treated for carbothermal reduction and nitridation using a multipurpose high-temperature furnace (High multi 5000, Fujidempa Kogyo, Osaka, Japan). The sample was heated to 1500°C at 10°C·min⁻¹ and then held for 5 h under a N2 atmosphere. The carbothermal reduction and nitridation were carried out at 0.1, 0.3, 0.4, and 0.5 MPa of N2 pressure, respectively.

The crystalline phases of the samples were determined by X-ray diffraction (XRD; D8 Advance, Bruker AXS Co. Ltd., Tokyo, Japan) with Cu Kα radiation. The β-ratio was calculated from the X-ray peak areas of α-Si3N4 and β-Si3N4 according to the following equation [8]:

\[
\frac{\beta}{\alpha + \beta} = \frac{\beta(101) + \beta(210)}{\alpha(210) + \alpha(201) + \beta(101) + \beta(210)}.
\]

The sample morphology was observed by ultra-high-resolution field-emission scanning electron microscopy (FE-SEM; SU9000, Hitachi High-Technologies Co., Tokyo Japan) and a transmission electron microscope (TEM; JEOL-2010, JEOL Ltd., Tokyo, Japan). The elemental analysis of samples was performed by energy-dispersive X-ray spectroscopy using an X-ray spectrocope (EDS; EMAX Evolution Xmax, HORIBA Ltd., Kyoto Japan) equipped with FE-SEM.

3. Results

The precursor powders were successfully obtained by the sol–gel process. Images of the powders formed in the crucible by carbothermal heat treatment at 1500°C and at different N2 pressures are shown in Figure 1. At low N2 pressures, a small amount of fibrous product was found at the edge of the crucible, and many black residual particles were seen in the bottom of the crucible. With increases in N2 pressure, the amount of white fibrous product increased and a large number of fibers could be obtained at 0.5 MPa.

Figure 2 shows the XRD patterns of the obtained samples after heat treatment. The samples extracted from the crucible were placed directly on the XRD sample holder. The samples included both the white fibrous product and the black residual particles. A broad peak of the amorphous phase was shown in the low N2 pressure samples. By contrast, α-Si3N4 (JCPDF 9–250) and β-Si3N4 (JCPDF 33–1160) were detected in the sample produced at 0.5 MPa of N2 pressure. Additionally, as seen in Figure 2(d), a small amount of silicon oxynitride (Si3N2O; JCPDF 33–1162) was also detected. The β-ratio, which was calculated from the X-ray peak intensity of α- and β-type silicon nitride using the formula \(\beta/(\alpha + \beta)\), showed a relatively high value (45%) under these conditions.

The morphology of the fibrous samples was investigated by SEM. SEM images of the fibrous products formed at 0.1 to 0.4 MPa of N2 pressure are shown in Figure 3. The scattering of fibrous samples that
formed at the edges of the crucible was collected. The samples were wide ribbon-like fibers, which seemed to be further elongated as the N\textsubscript{2} pressure increased. Furthermore, SEM images of the fibers obtained at 0.5 MPa are shown in Figure 4. The SEM observation revealed two types of fibers: straight (area (a)) and rolled (area (b)).

A more detailed observation of the two types of fibers (straight and rolled) obtained at a N\textsubscript{2} pressure of 0.5 MPa and their elemental analyses are shown in Figure 5. The straight fibers had a smooth surface (see Figure 5(a)), and Si and N from silicon nitride were detected, but Al and O impurities were also detected in the fibers. On the other hand, the rolled fibers showed a uniquely rough surface (see Figure 5(b)), and Si, N, Al and O were detected in the fibers, much as in the case of the straight fibers.

Figure 6 shows the fiber diameter of the fibrous samples under each N\textsubscript{2} pressure, as measured by SEM observation. At 0.1 MPa, the fiber diameter of about 2.4 μm decreases with increasing N\textsubscript{2} pressure, and the fibers become nanofibers with a diameter of about 200 nm when prepared under an N\textsubscript{2} pressure of 0.5 MPa.

To determine the crystal structure and growth direction, the two forms of fiber obtained at a N\textsubscript{2} pressure of 0.5 MPa were investigated by TEM. Figure 7(a) shows the TEM image and Figure 7(b) the electron diffraction pattern of the fibers with a smooth surface. The smooth-surfaced fibers have a structure with a uniform texture and show d-spacing corresponding to the {110} and {202} planes of α-Si\textsubscript{3}N\textsubscript{4} (JCPDF 9−250). The longitudinal direction of the fibers was the <501> direction.

Figure 7(c) shows the TEM image and Figure 7(d) represents the electron diffraction image of the fibers with a rough surface. Grain boundaries and fine particles were found in the rough-surfaced fibers. The d spaces corresponding to {100}, {101}, {111} and {211} of β-Si\textsubscript{3}N\textsubscript{4} (JCPDF 33−1160) are identified and shown. The longitudinal direction of the fibers was the <211> direction. As a result, it is considered that the smooth-surfaced fibers obtained in this experiment were α-type single crystalline. On the other hand, the rough-surfaced fibers had a polycrystalline structure consisting mainly of β-type Si\textsubscript{3}N\textsubscript{4}. 

---

**Figure 1.** Optical micrograph images of heat-treated samples in alumina crucibles reduced at different N\textsubscript{2} pressures: (a) 0.1 MPa; (b) 0.3 MPa; (c) 0.4 MPa; and (d) 0.5 MPa.

**Figure 2.** Powder XRD patterns of samples synthesized under different N\textsubscript{2} pressures: (a) 0.1 MPa; (b) 0.3 MPa; (c) 0.4 MPa; and (d) 0.5 MPa.
4. Discussion

The results showed that the Si$_3$N$_4$ fiber diameter and its morphology were strongly affected by nitrogen pressure. One reason for the decreasing fiber diameter was considered to be the following: At high nitrogen gas pressure, the concentration of SiO gas, which is an intermediate gas species, would be low due to inhibition of SiO gas generation by the SiO$_2$ precursor solid by the high N$_2$ base, while consumption of SiO gas continued due to the reaction with C and higher pressure of N$_2$ gas. However, high N$_2$ pressure contributes to the nitridation reaction of oxide species that may act as a factor enhancing fiber growth. The fiber growth rate might be complexly affected by the dynamics and kinetics of the constituent species therefore, although a decrease in the diameter was found experimentally, as shown in Figure 7.

Another reason was considered based on the results of the study into the thermodynamic effects. EDS elemental analysis of the fibers showed that the fibers with complicated shapes contained aluminum in addition to Si and N (Figure 5). It is thought that this alumina derived from the alumina crucible used during heat treatment. The XRD results showed that silicon oxynitride (Si$_3$N$_2$O) was produced.

It is known that Si$_3$N$_2$O is produced under conditions of low P$_{O_2}$/P$_{N_2}$ [9]. As shown in Figure 8...
(a), Si$_2$N$_2$O [10] has a crystalline structure in which the nitrogen in β-Si$_3$N$_4$ (Figure 8(b)) is partially replaced with oxygen. In addition, when alumina is added to the Si$_2$N$_2$O, the O′-SiAlON (Si$_{2-x}$Al$_x$O$_{1+x}$N$_{2-x}$) phase was reported to be formed by replacing Si with Al, and hence part of the Si-N bonds in silicon nitride are changed to Al-O bonds at high temperatures [11]. It was also reported that Si$_2$N$_2$O (O′) was an intermediate phase when β-Si$_3$N$_4$ (β-SiAlON) is produced at high temperatures [4,12].

Figure 5. Magnified SEM images and EDS elemental mapping images of (a) straight fibers (region a in Figure 4) and (b) rolled fibers (region b in Figure 4) obtained at 0.5 MPa.

The Si$_2$N$_2$O and Si$_3$N$_4$ in this study were formed by the following chemical reactions, carbothermal reduction of sol–gel-derived SiO$_2$ and nitridation:

$$2\text{SiO}_2(s) + 3\text{C}(s) + \text{N}_2(g) = \text{Si}_2\text{N}_2\text{O}(s) + 3\text{CO}(g)$$

(2)

$$\text{Si}_2\text{N}_2\text{O}(s) + 3\text{C}(s) + \text{N}_2(g) = 2\text{Si}_3\text{N}_4(s) + 3\text{CO}(g)$$

(3)

Reaction (2) is considered to be divided into the following two reactions:

$$\text{SiO}_2(s) + \text{C}(s) = \text{SiO}(g) + \text{CO}(g)$$

(4)

$$2\text{SiO}(g) + \text{C}(s) + \text{N}_2(g) = \text{Si}_2\text{N}_2\text{O}(s) + \text{CO}(g)$$

(5)

For these reactions, the thermodynamic Gibbs’s free energy of formation was calculated based on the JANAF data and the data presented by Ekelund [13] for the standard conditions of various silicon nitride formation, i.e. the whole reaction of silica reduction nitridation (Equation (1)), the SiO$_2$ partial reduction reaction to form Si$_2$N$_2$O (Equation (2)), and the Si$_2$N$_2$O to Si$_3$N$_4$ formation reaction (Equation (3)); the calculated results are shown in Figure 9. It can be understood that the generation of Si$_2$N$_2$O (Equation (2)) is favored...
at low temperatures, while the formation of Si$_3$N$_4$ (Equation (1)) with the β-phase is favored when the temperatures are high. On the other hand, the formation of Si$_3$N$_4$ from Si$_2$N$_2$O (Equation (3)) is expected to be carried out at higher temperatures.

In this study, the Gibbs free energy $\Delta G$ under increased nitrogen pressure was also calculated based on a result obtained by Yamagishi et al. [14], showing that CO gas contained 0.3% at 0.1 MPa of N$_2$. Based on this result, Gibbs energies were calculated by assuming the partial pressure of CO gas to be 0.0003 MPa at 0.1 MPa and 0.0015 MPa at 0.5 MPa of N$_2$ gas pressure. The value of $\Delta G$ calculated by assuming increased N$_2$ pressure was negative at

---

**Figure 7.** TEM images and corresponding SAED patterns of fibers with smooth surfaces (a and b) and those for fibers with rough surfaces (c and d) found in samples at 0.5 MPa of N$_2$ pressure.

**Figure 8.** Crystal structure images of (a) Si$_2$N$_2$O and (b) β-Si$_3$N$_4$.

**Figure 9.** Standard Gibbs’s free energy of the nitride formation reaction calculated from Equations (1)–(3).
above 1500°C (1773K) for all the reactions, and it was speculated that all substances could be produced. In addition, Al was introduced from the alumina crucible in the present case, and thus the Si₃N₄O reaction in Equation (2) might occur most easily, and thus resulting in the conversion to O′-SiAlON.

Based on the above considerations, the reasons why Si₃N₄O (O′) was stably generated and the Si₃N₄ fiber diameter decreased under high N₂ pressure are discussed. In general, second phase particles, which are usually metal particles used as a catalyst, are found in fibers and/or nano-sized rods when they are synthesized via VLS or VSS mechanisms. The diameter of VLS- or VSS-grown fibers depends on the size of the metal catalyst particles, moreover, which act as templates [15]. In the present study, however, the presence of metal particles was not confirmed at the end of each fiber. Another mechanism should therefore be considered.

In the present study, the growth of β-Si₃N₄ fibers might be conducted through the formation of an intermediate Si₂N₂O (O′) phase, which acts as a template for the β-phase Si₃N₄. As mentioned earlier, Si₂N₂O crystallized under high N₂ pressure (0.5MPa, see Figure 2), and it was speculated based on the thermodynamic calculation that it would form at lower temperatures (Figure 9, Equation (2)). The fibers with a rough surface (Figure 5(b)) consisted of β-Si₃N₄ and contained a smaller amount of Al, moreover, as found by EDS (Al mapping in Figure 5(b)). These facts suggested the following: i) Si₂N₂O was formed first at a lower temperature by the reduction of amorphous SiO₂ via vapor-to-solid precipitation; ii) Al was then doped into the Si₂N₂O to form the O′-SiAlON phase; and iii) this phase might be a template for the β-Si₃N₄ or β-SiAlON phase for further growth at increased temperatures.

It should be noted again here that Si₂N₂O has the same crystalline structure as β-Si₃N₄, and that O′-SiAlON, which is the Al and O doped Si₂N₂O phase, also has the same structure as β-SiAlON. In addition, our preliminary investigation of synthesis of Si₃N₄ fibers through the same carbothermal reduction and nitridation process, except without the use of an alumina crucible, revealed that the obtained fibers were α-Si₃N₄ only, and that no β-phase was obtained. From these facts, it is easily assumed that the existence of Al as well as O plays an important role in the phase development of β-type nitride fibers.

Because the elemental Al was supplied from the alumina crucible via the vapor phase, the concentration of Al in the Si₂N₂O precursor might differ among the samples. This special distribution of different chemical compositions of the fibers might be one of the reasons that there were different types of nitride fibers, α-Si₃N₄ with smooth surfaces and β-Si₃N₄ with rough surfaces.

It was concluded in consideration of these facts that the complicated structure with many domains of rough-surfaced fibers (Figure 7) was due to the formation of the O′ phase, followed by conversion to the β-phase by phase transformation through nucleation and growth of the β-region at elevated temperatures, which might generate internal stress owing to the formation of phase boundaries.

Zhang et al. [3] studied the synthesis of α-Si₃N₄ and amorphous nanofibers by heat treating Si powder at 1200°C using an alumina crucible. It was considered that Si₂N₂O might not be formed under their experimental conditions because of the lower synthesis temperature than that of the present study. However, the amorphous fibers found in their report may crystallize to α-Si₃N₄ [4–6]. On the other hand, β-Si₃N₄ fibers were already reported, but most of them were prepared using a metal catalyst [2] that promoted VLS growth of the β-phase, or else they were synthesized under high pressure such as 10 MPa [7]. Unlike these previous reports, the present study demonstrated the synthesis of fine β-Si₃N₄ fibers at a lower N₂ pressure without using a metal catalyst.

5. Conclusions

The morphologies and crystalline phase of carbothermal synthesized Si₃N₄ fibers under various nitrogen pressures were studied. The results and findings are described below.

1. Sol–gel-derived SiO₂ precursor powder was subjected to carbothermal reduction and nitridation, and long silicon nitride fibers and ribbons with various shapes and morphologies were obtained.
2. The fiber diameter decreased with increasing N₂ pressure, and nanometer-sized fibers of approximately 200 nm in diameter were successfully obtained at a high N₂ pressure of 0.5 MPa.
3. Unique rough-surfaced nanofibers were discovered that consisted of β-type Si₃N₄ with a complicated polycrystalline-like fiber shape, whereas α-Si₃N₄ single crystalline fibers with smooth surfaces were also synthesized.
4. Silicon oxyynitride (Si₃N₄O), which was regarded as a template for further growth of the β-Si₃N₄ fibers, was found to form during the synthesis. This phase transformation resulted in the formation of β-phase fibers with complicated shapes and rough surfaces.
5. The elements oxygen and aluminum were found in the samples, which contributed to the formation of various crystalline phases and morphologies of the Si₃N₄ fibers, especially the β-type fibers with distorted shapes and resultant rough surface structures.
From the findings obtained in this study, it was suggested that control of the Si₃N₄ fiber diameter, morphology and crystalline phase without using a metal catalyst could be achieved by tuning the processing conditions of the fiber synthesis, especially the gas pressure and doping.

**Acknowledgments**

The authors are grateful to Prof. Dr. S. Seino for his support with the TEM investigation. The authors thank also Enago (www.enago.jp) for the English language review.

**Disclosure statement**

The authors reported no potential conflict of interest.

**Funding**

This work was supported by the MEXT, Japan [“Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials” in “Network Joint Research Center for Materials and Devices”] and partly by the Korea Institute of Industrial Technology [Joint Research Project].

**ORCID**

Sotaro Baba [http://orcid.org/0000-0003-0010-5403]
Tomoyo Goto [http://orcid.org/0000-0003-1362-6750]
Sung Hun Cho [http://orcid.org/0000-0002-6254-1094]
Tohru Sekino [http://orcid.org/0000-0002-6605-9166]

**References**

[1] Hirao K, Ohashi M, Brito ME, et al. Processing strategy for producing highly anisotropic silicon nitride. J Am Ceram Soc. 1995;78:1687–1690.

[2] Kusunose T, Yagi T, Firoz SH, et al. Fabrication of epoxy/silicon nitride nanowire composites and evaluation of their thermal conductivity. J Mater Chem A. 2013;1:3440–3445.

[3] Zhang Y, Wang N, He R, et al. A simple method to synthesize Si₃N₄ and SiO₂ nanowires from Si or Si/SiO₂ mixture. J Cryst Growth. 2001;233:803–808.

[4] Chaudhuri MG, Dey R, Mitra MK, et al. A novel method for synthesis of α-Si₃N₄ nanowires by sol-gel route. Sci Technol Adv Mater. 2008;9:015002.

[5] Wang F, Jin GQ, Guo XY. Formation mechanism of Si₃N₄ nanowires via carbothermal reduction of carbonaceous silica xerogels. J Phys Chem B. 2006;110:14546–14549.

[6] Li Y, Li D, Wang H, et al. Long silicon nitride nanowires synthesized in a simple route. Appl Phys Mater Sci Process. 2008;93:471–475.

[7] Chen H, Cao Y, Xiang X, et al. Fabrication of β-Si₃N₄ nano-fibers. J Alloys Compd. 2001;325:5–7.

[8] Gazzara CP, Messier DP. Determination of phase content of Si₃N₄ by X-ray diffraction analysis. Am Ceram Soc Bull. 1977;56:777–780.

[9] Japan society for promotion of Science. Advanced silicon nitride ceramics. Tokyo: Uchida Rokakuho Publishing; 2009. p. 38–39.

[10] Jack KH. Sialons and related nitrogen ceramics. J Mater Sci. 1976;11:1135–1158.

[11] Rouquié Y, Jones M. Influence of additives and compositions on the nitridation and formation of SiAlONs produced by reaction bonding and silicothermal reduction. J Asian Ceram Soc. 2013;1:53–64.

[12] Shimada K, Fukusugie Y, Hitara Y. Nitrides formed by reducing process of the shirasu glass with carbon. J Ceram Soc Japan. 1978;86:11–18.

[13] Ekelund M, Forslund B, Eriksson G, et al. Si-C-O-N high-pressure equilibria and ΔG_f for Si₂O₃N₂. J Am Ceram Soc. 1988;71:956–960.

[14] Yamagishi C, Miyata N, Hakoshima J, et al. Preparation of sialon powder by carbothermal reduction and nitridation(1) preparation of Z=0 sialon(Si₃N₄). J Japan Soc Powder Metall. 1993;40:1214–1217.

[15] Hansen TW, Wagner JB. Controlled atmosphere transmission electron microscopy. Switzerland: Springer International Publishing; 2016. p. 213–235.