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Microstructure of Si_3N_4 Whisker Prepared from Diatomaceous Earth

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Abstract

Silicon nitride whiskers were prepared by carbothermal reduction and nitridation of diatomaceous earth at temperature of 1350°C under the presence of nitrogen and ammonia. Scanning and transmission electron microscopy (SEM), electron probe microanalysis (TEM) and X-ray diffraction were used to characterize the microstructure. SEM studies indicated that the whiskers were quite straight and hexagonal in cross-section. The whiskers were found to be highly crystalline, as determined by TEM analysis.

Siliciumnitridwhisker wurden durch carbothermale Reduktion und Nitrierung von Diatomeenerde bei 1350°C in Gegenwart von Stickstoff und Ammoniak hergestellt. Raster- und Transmissionselektronenmikroskopie, Mikrosondenanalyse (REM and TEM) und Röntgendiffraktometrie wurden angewandt, um die Mikrostruktur zu charakterisieren. REM Untersuchungen deuteten darauf hin, daß die Whisker sehr gerade waren und einen hexagonalen Querschnitt hatten. Die Whisker stellten sich bei der TEM-Analyse als sehr kristallin heraus.

Des trichites de nitrure de silicium ont été préparés par carboréduction et nitruration de terres à diatomées à une température de 1350°C en présence d'azote et d'ammoniac. La microscopie électronique à transmission et à balayage (MET), la microsonde électronique (MEB) et la diffraction des rayons X ont été utilisées pour caractérise la microstructure. Les études par MEB indiquent que les whiskers sont droits et présentent une section hexagonale. Comme le montre l'analyse par MET, les trichites sont parfaitement cristallisés.

1 Introduction

Silicon nitride whiskers have many excellent engineering and chemical properties, such as high strength, good thermal shock resistance, and high tensile strength. Si_3N_4 powder has been prepared from a number of silicon sources;[1] however, studies of Si_3N_4 whisker formation are very limited. Saito and coworkers[2,3] studied the vapor phase growth of Si_3N_4 whiskers by the nitridation of the SiO_2–C–Na_3AlF_6 system in flowing N_2 gas at 1350–1450°C. They reported that the addition of fluorides accelerated the carbothermal reduction of SiO_2.

Motojima *et al.*[4] obtained whiskers and regularly coiled spring-like fibers of Si_3N_4 from a gas mixture of Si_2Cl_6, NH_3 and H_2 on a quartz or graphite substrate at 1200°C. The whiskers were α-Si_3N_4 accompanied by a small amount of β-Si_3N_4, but the spring-like fibers were amorphous Si_3N_4. They suggested that the whiskers grew by the vapor–liquid–solid (VLS) mechanism.[5] However, Si_3N_4 whiskers, obtained from these methods, are likely to be relatively expensive, because they require pure or very expensive raw materials.

In the authors' previous work,[6] it was reported that fiber-like Si_3N_4 was produced by the carbothermal reduction and nitridation of diatomaceous earth at 1350°C in the presence of carbon. It was the first work of its kind; preparation of Si_3N_4 fibers from crude materials such as diatomaceous earth. Moreover, it was revealed that Fe contained in the

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diatomaceous earth was beneficial to the growth of Si_3N_4 fibers. The purpose of this study is to characterize the structural and chemical properties of the Si_3N_4 whiskers, which were produced from diatomaceous earth.

2 Experimental

The diatomaceous earth, produced in Oita prefecture, is composed of 82·5 wt% SiO_2, 5·69 wt% Al_2O_3, and very small amounts of metal oxides (Table 1). The diatomaceous earth was calcined at 1000–1200°C in a stream of air to remove organic impurities.

The authors used the same apparatus as in their previous experiment, shown schematically in Fig. 1. A mixture of high purity NH_3 and N_2 (99·99%), obtained commercially, was introduced directly into the reaction zone without further purification. A 0·5 g sample of diatomaceous earth was charged on a carbon plate and was reduced and nitrided in a stream of N_2 (8·8 cm min^{-1}) and NH_3 (26·4 cm min^{-1}) at 1350°C for 24 h. After the completion of the reaction, the remaining carbon in Si_3N_4 was oxidized in air at 700°C.

Structural properties of the products and their weight fractions of α- and β-Si_3N_4 were determined by X-ray powder diffractometry (Model CN 2013, Rigaku Ltd, Tokyo, Japan) with CuK_α radiation using the method of Gazzara & Messier.[7] The

Table 1. Chemical properties of the diatomaceous earth produced in Oita prefecture

	Untreated	*Calcined*[a]
Surface area ($m^2 g^{-1}$)	37·2	7·1
Chemical composition (wt%)		
SiO_2	82·5	89·2
Al_2O_3	5·69	5·70
Fe_2O_3	1·17	1·76
MnO	0·016	0·011
MgO	0·23	0·20
CaO	0·97	0·87
TiO_2	0·24	0·25
Na_2O	0·51	0·46
K_2O	0·31	0·23
Ignition loss	5·86	0·28

[a] At 1000–1200°C in air.

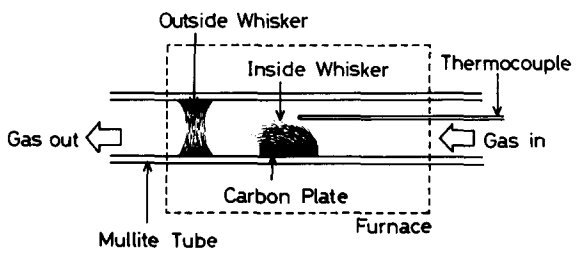

Fig. 1. Schematic diagram of the apparatus and regions of Si_3N_4 whisker and powder product.

morphology and composition of the Si_3N_4 whiskers were investigated by scanning electron microscopy (SEM; Model H900, Hitachi Ltd, Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDX; Model TN 5500, Tracor Northern, Middleton, WI, USA). Specimens were prepared by mounting the whiskers onto a sample stage, followed by Au or carbon coating. Transmission electron microscopy (TEM; Model JEM 2000 FX, Jeol Ltd, Tokyo, Japan) specimens were prepared by dipping the grid into an ultrasonically dispersed mixture of whiskers and ethanol. Whiskers were observed using bright-field imaging. Selected area diffraction was used to determine crystallographic orientation by stereographic techniques.[8] Surface area of the samples was measured by the BET technique using N_2.

3 Results and Discussion

Si_3N_4 powder was obtained on the original carbon plate. Short needle-like Si_3N_4 whiskers (inside whiskers) covered the Si_3N_4 powder, and wool-like whiskers formed on the wall of the mullite tube at the lower reach of the N_2–NH_3 flow (outside whiskers) (Fig. 1). In this method, the total yield of Si_3N_4 formed reached 83%, and 0·139 g whiskers was obtained from 1·0 g diatomaceous earth. All of the nitridation products were α-phase-rich Si_3N_4. Figure 2 shows the X-ray diffraction patterns of the products obtained from carbothermal reduction and nitridation of diatomaceous earth. The phase composition of α- and β-Si_3N_4 in each product depends strongly on the nitridation temperature and deposit position,[6] and the $\alpha/(\alpha+\beta)$ ratio was 0·7–*c.* 1·0. No diffraction peaks from Si, SiO_2 or Si_2ON_2 were detected in these patterns.

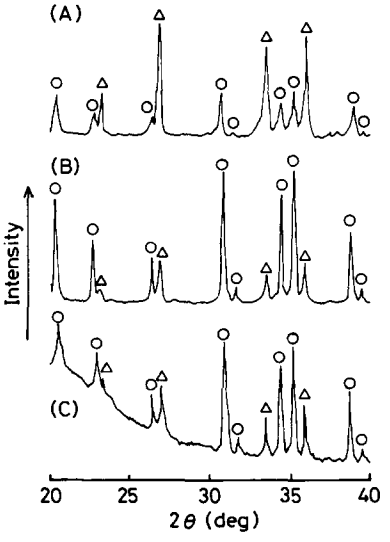

Fig. 2. X-Ray diffraction patterns of the products obtained from carbothermal reduction and nitridation of diatomaceous earth at 1350°C. (A) Si_3N_4 powder, (B) inside whisker and (C) outside whisker; ○, α-Si_3N_4; △, β-Si_3N_4.

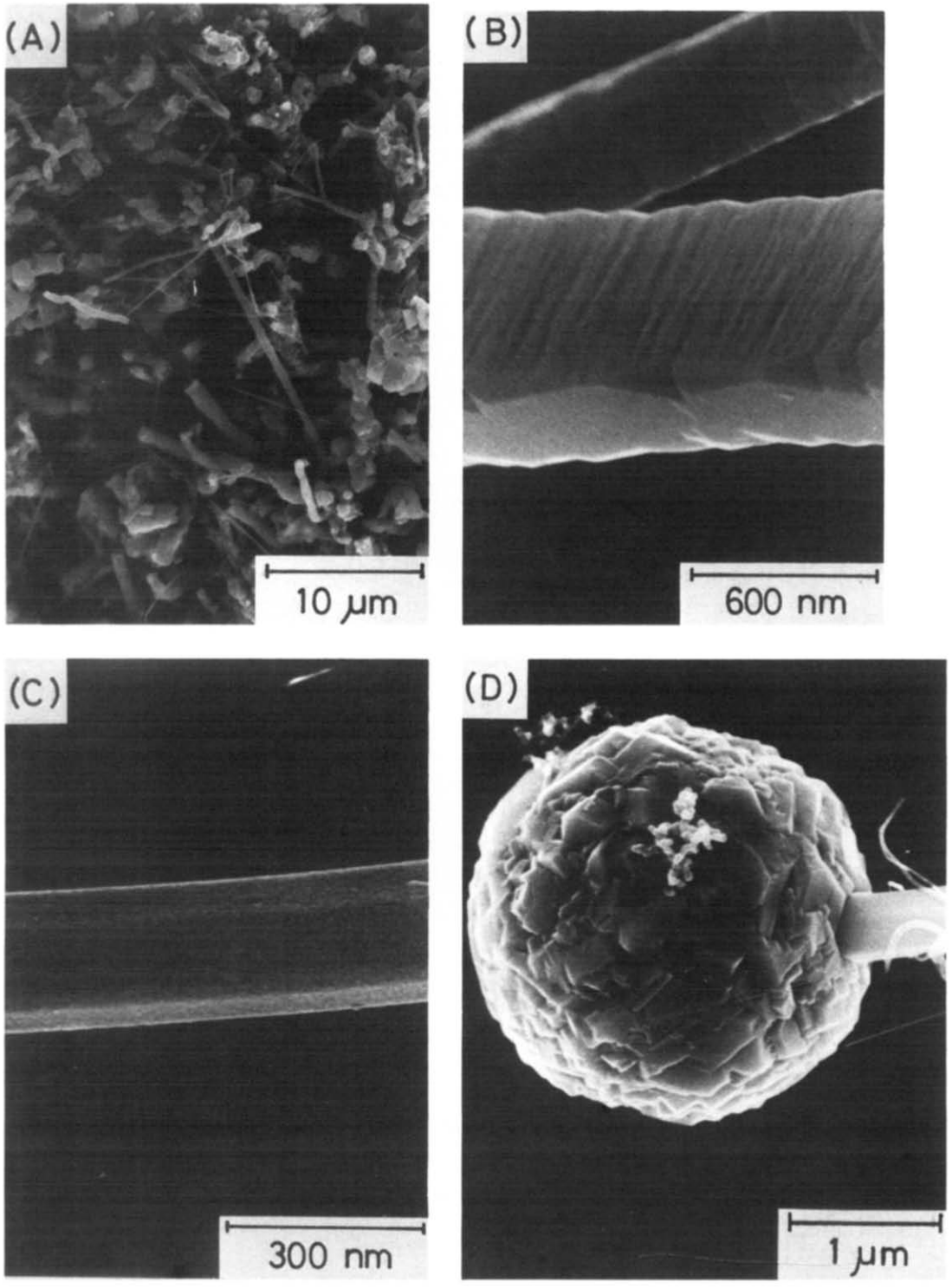

Fig. 3. Scanning electron micrographs of the products obtained from carbothermal reduction and nitridation of diatomaceous earth. (A) Powder, (B) inside whisker, (C) outside whisker and (D) droplet on the outside whisker.

As can be seen from the scanning electron micrographs of nitrided products, shown in Fig. 3(A), Si_3N_4 powder consisted of spherical particles with a uniform distribution of around 1·0 μm. A few fiber-like Si_3N_4 particles were also formed, of the order of 10 μm in length. The dimensions of the inside whiskers were distributed widely, and were typically 10 μm in diameter and 0·5–1·0 mm in length. As illustrated in Fig. 3(B), the inside whiskers were quite rectilinear in shape and the cross-sectional view was rectangular. Most inside whiskers had a dentate edge, some of them branched out. On the other hand, no droplets were ever observed on the inside whiskers. These facts suggest that the inside whiskers were formed by direct deposition of SiO through the vapor–solid (VS) mechanism.[9] The outside whiskers were 0·2–2·0 μm in diameter and 10 mm in length with hexagonal cross-section (Fig. 3(C)), and they had relatively smooth surfaces without the dentate edge observed in the inside whiskers. A few whiskers had droplets on top. In addition, the droplet was observed as an aggregate

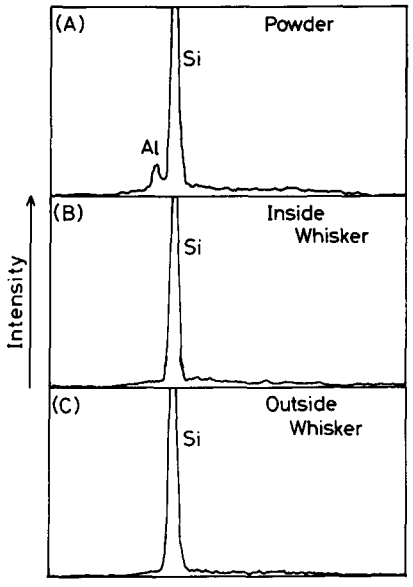

Fig. 4. EDX analysis results of the products obtained from carbothermal reduction and nitridation of diatomaceous earth. (A) Powder, (B) inside whisker and (C) outside whisker.

of small tips by high resolution scanning electron microscopy (Fig. 3(D)).

Energy dispersive X-ray spectroscopy showed that the droplets contained Fe,[6] and both inside and outside whiskers contained Si only (Fig. 4(B), (C)). Furthermore, X-ray diffraction patterns supported the conclusion that inside and outside whiskers did not form solid solutions by substitution of Al for Si, because the peaks of β-Si_3N_4 in both whiskers were not shifted in the patterns.[10] Thus, it was considered that other metal impurities, contained in the original diatomaceous earth, were preserved in the powder, which the EDX results supported (Fig. 4(A)). Judging from these results, the outside whiskers are thought to have grown at the vapor (SiO, N_2, NH_3, CO), liquid (Fe droplet) and solid (Si_3N_4 whisker) interface. It is known that Fe promotes whisker growth.[11] Hence, outside whisker growth is activated by Fe impurities contained in the original diatomaceous earth.

Two examples of the microstructures found at the whisker surfaces are illustrated by the bright-field

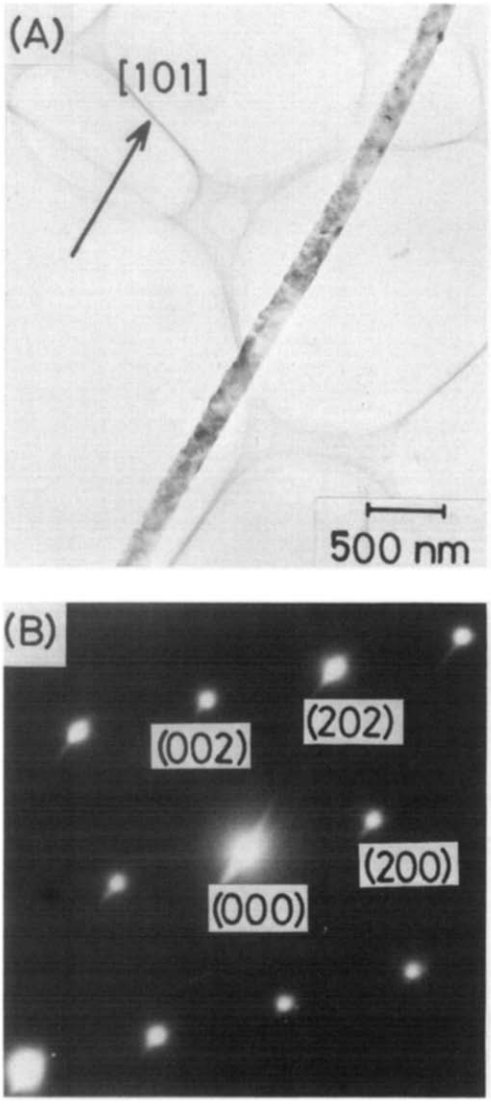

Fig. 5. Bright-field TEM image (A) and electron diffraction patterns (B) of inside whisker, beam direction along [010].

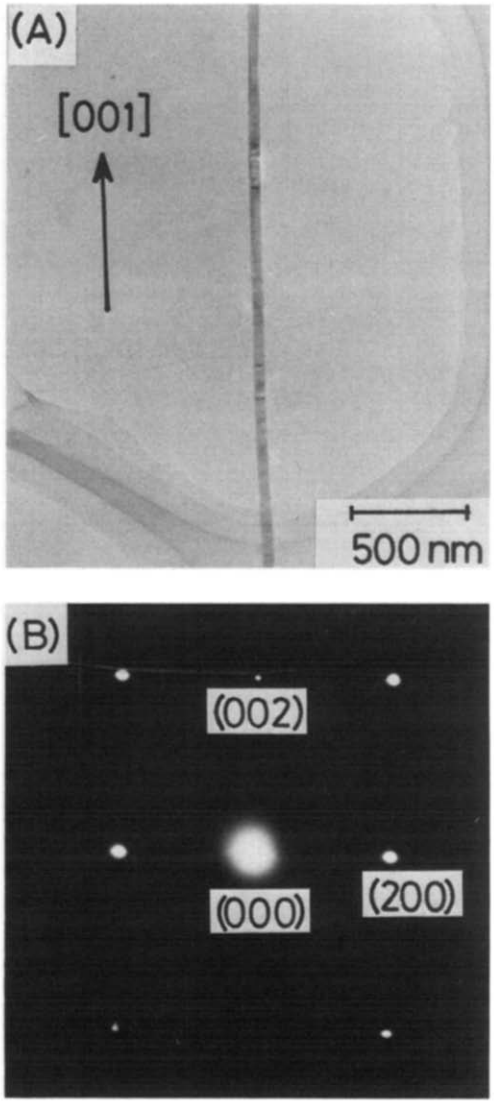

Fig. 6. Bright-field TEM image (A) and electron diffraction patterns (B) of outside whisker, beam direction along [010].

TEM micrographs shown in Fig. 5(A) and Fig. 6(A). At the same time, two types of whiskers were also analyzed by electron diffraction. The figures show two electron diffraction patterns taken for a beam direction along [010] from an inside (Fig. 5(B)), and an outside whisker (Fig. 6(B)). Both (002) and (200) reflections appeared. Single crystals examined in this study were shown to be only α-Si_3N_4. Moreover, transitions from α-Si_3N_4 to β-Si_3N_4 were not observed via bright-field TEM micrographs. These patterns indicated that whiskers were α-Si_3N_4, and completely single crystals of a hexagonal unit. Furthermore, micrographs revealed that the inside and outside whiskers have preferentially grown along the directions of [101] and [001] respectively.

Figure 7 shows high-resolution transmission electron micrographs (HRTEM) of the inside and outside whiskers. No dislocations, stacking faults or other defects were noted in the inside and outside whiskers. The inside whiskers have saw teeth edges, and the angle between the edge and the (200) plane of the inside whisker was determined to be 36° (Fig. 7(A)). On the other hand, the edge face of the outside whiskers was parallel to the (200) plane (Fig. 7(B)), which was observed as a striped pattern with the interplane spacing of 0·336 nm. These observations agree well with the results of the electron diffraction of the whiskers. At the same time, the lattice parameter of this outside whisker was calculated to be $a_0 = 0{\cdot}776$ nm. This compares favorably with the accepted values of $a_0 = 0{\cdot}7758$ nm (ASTM Card No. 9-250, α-Si_3N_4).

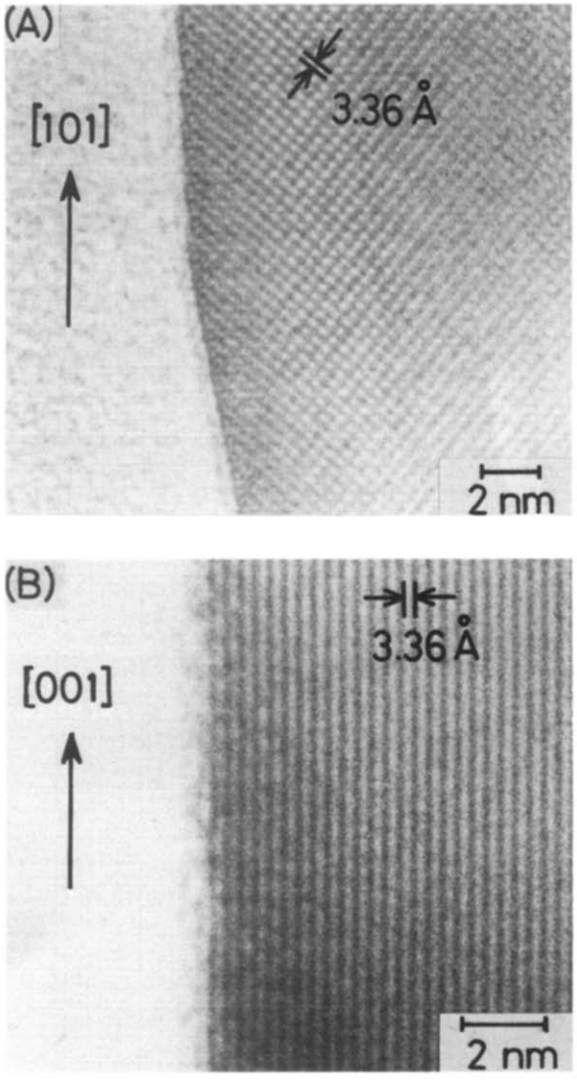

Fig. 7. HRTEM image of the Si_3N_4 whiskers. The electron beam is parallel to [010] of (A) inside and (B) outside whisker.

4 Conclusion

Two types of silicon nitride whiskers, which were prepared from diatomaceous earth, were successfully observed through high-resolution SEM and TEM imaging techniques. These observations revealed that the individual whiskers were single crystals of extreme perfection. Stereographic analysis indicated that the [101] crystallographic direction coincided with the inside whisker axis, the other [001] with outside whisker axis.

Acknowledgements

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References

1. Vanedenede, V., Leriche, A., Cambier, F., Pickup, H. & Brook, R. J., Sinterability of silicon nitride powders and characterization of sintered material. In *Non-oxide Technical and Engineering Ceramics*, ed. S. Hampshire. Elsevier, London, 1986, pp. 53–67.
2. Saito, H., Hayashi, T. & Miura, K., Effect of fluorides on vapor phase growth of silicon nitride whiskers. *Nippon Kagaku Kaishi*, **1982** (1982) 401–7.
3. Hayashi, T., Kawabe, S. & Saito, H., Vapor phase growth of β-sialon whisker by nitridation of the system SiO_2–C–Na_3AlF_6. *Yogyo Kyokaishi*, **94** (1986) 19–25.
4. Motojima, S., Ueno, S., Hattori, T. & Iwanaga, H., Preparation of whiskers and spring-like fibers of Si_3N_4 by impurity-activated chemical vapor deposition. *J. Cryst. Growth*, **96** (1989) 383–9.
5. Messier, D. R. & Wong, P., Kinetics of nitridation of Si powder compacts. *J. Am. Ceram. Soc.*, **56** (1973) 480–5.
6. Mizuhara, Y., Noguchi, M., Ishihara, T., Satoh, A., Hiramatsu, K. & Takita, Y., Preparation of fiber-like silicon nitride from diatomaceous earth. *J. Am. Ceram. Soc.*, **74** (1991) 846–8.

7. Gazzara, C. P. & Messier, D. R., Determination of phase content of Si_3N_4 by X-ray diffraction analysis. *Am. Ceram. Soc. Bull.*, **56** (1973) 777–80.
8. Johari, O. & Thomas, G., *Techniques of Metals Research*, Vol. IIA, *The Stereographic Projection and Its Applications*. Interscience, New York, 1969.
9. Kato, A. & Tamari, N., Some common aspects of the growth of titanium nitride, zirconium nitride, titanium carbide and zirconium carbide whiskers in chemical vapor. *J. Cryst. Growth*, **49** (1989) 199–203.
10. Gauckler, L. J., Prietzel, S., Bodemer, G. & Petzow, G., Some properties of β-$Si_{6-x}Al_xO_xN_{8-x}$. In *Nitrogen Ceramics*, ed. F. L. Riley. Noordhoff International, Leyden, The Netherlands, 1977, pp. 529–38.
11. Shaw, J., The combined effects of Fe and H_2 on the nitridation of silicon. *J. Mater. Sci. Lett.*, **1** (1982) 337–40.