JOURNAL OF MATERIALS SCIENCE 30 (1995) 3888–3892

Preparation of Si_3N_4 whiskers by reaction of wheat husks with NH_3

S. MOTOJIMA, Y. HORI
Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu 501-11, Japan

S. GAKEI
Cotec Ltd, 1-121 Yatsuya-cho, Nakagawa-ku, Nagoya 454, Japan

H. IWANAGA
Faculty of Liberal Arts, Nagasaki University, Nagasaki 852, Japan

α-Si_3N_4 whiskers that are 1–10 mm long and 0.5–1.1 μm thick were obtained by the reaction of wheat husks with NH_3 at 1250–1450 °C. A maximum whisker yield of about 30% was obtained at 1450 °C with the addition of an iron impurity. Whiskers with 1.3–2.2 μm thickness (average 1.6 μm) were obtained by the addition of an H_2S impurity. Thin whiskers with periodic thick and thin diameters were also obtained.

1. Introduction

A large amount of rice and wheat husks is produced every year as agricultural waste products. The husks contain very fine and active silica, and are thus very useful as a source of silicon-based ceramics, such as SiC and Si_3N_4.

The original research for the preparation of SiC whiskers from rice husks was carried out by Cutler *et al.* [1]. Many other investigators have since obtained SiC whiskers using rice husks as the source material [2–17]. However, other source materials, such as wheat husks or straw, have not been used. Recently, we have obtained SiC whiskers from grasses such as wheat straw, Japanese pampas grass and field horsetail [18].

Mansour *et al.* [3, 8] and Kaneko *et al.* [19, 20] obtained Si_3N_4 whiskers by the reaction of rice husks with NH_3 at 1200–1400 °C. However, the growth conditions have never been examined in detail.

In this work, Si_3N_4 whiskers were obtained by the reaction of wheat husks with NH_3 in the temperature range 1200–1500 °C. Growth conditions, impurity effects and the growth mechanism of the Si_3N_4 whiskers were examined in some detail.

2. Experimental procedure

A sample of dried and pulverized wheat husks weighing 0.24 g was mixed with 15 mg Fe powder (75 μm average diameter), which was then dispersed in an alumina boat located in the central part of a reaction tube (alumina tube, 30 mm i.d.). The amount of wheat husk ash used was about 10 wt %, and the ash contained 96.9 wt % Si, 2.1 wt % Cu, 0.8 wt % S and 0.2 wt % Fe. The wheat husks were heated under a nitrogen atmosphere at a rate of 15 °C min^{-1} to a given reaction temperature, followed by Si_3N_4 whisker growth under a gas mixture of NH_3 and H_2. The growth conditions of the whiskers were fixed as follows, unless otherwise noted: reaction temperature 1400 °C, reaction time 1 h, NH_3 flow rate 175 standard cm^3min^{-1}, hydrogen flow rate 35 standard cm^3min^{-1}. The yield of the whiskers was estimated from the ratio of the amounts of source silicon and that of the obtained whiskers.

3. Results and discussion

Whiskers grew on the inner wall of the alumina boat and/or on the wheat husks. The obtained whiskers were white and wool-like consisting of α-Si_3N_4 phase. No growth of SiC or SiO_2 whiskers was observed at any of the reaction conditions used in this work.

3.1. Effects of reaction temperature and time

The effect of reaction temperature on the average length and average diameter of the whiskers after a 1 h reaction time is shown in Fig. 1. A small amount of whiskers was obtained at 1250 °C which is 50 °C higher than the lowest eutectic temperature of the Fe–Si system (1200 °C). Whiskers having a length of 3.5–8 mm (average 6 mm) and 4–10 mm (average 8 mm) were obtained at 1350 and 1450 °C, respectively. These lengths are much larger than that reported by Kaneko *et al.* [19], who obtained 0.03–1.8 mm long Si_3N_4 whiskers from rice husks at 1400 °C after 10 h.

The effect of reaction temperature on the yield of whiskers is shown in Fig. 2. The yield increased with increasing reaction temperatures and attained a maximum (about 32%) at 1450 °C. A steep decrease in yield above this temperature was observed. This

0022–2461

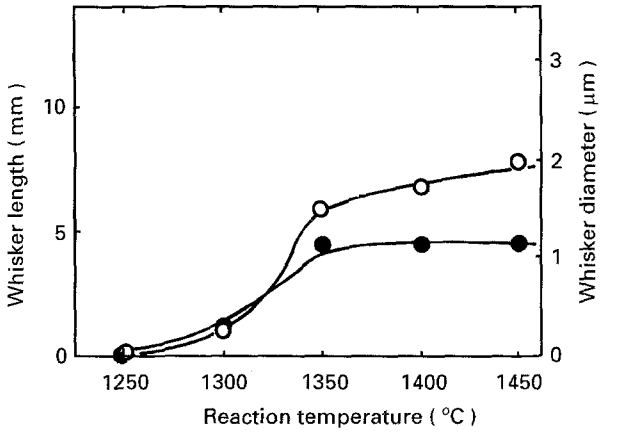

Figure 1 Effect of reaction temperature on the average length and average diameter of the Si_3N_4 whiskers. Reaction time 1 h. (○) Whisker length, (●) whisker diameter.

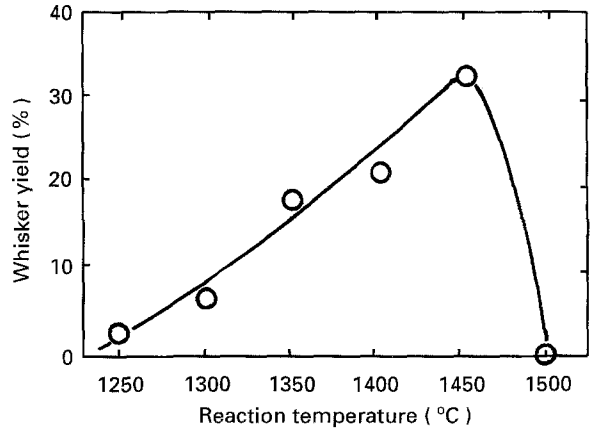

Figure 2 Effect of reaction temperature on the yield of Si_3N_4 whiskers. Reaction time 1 h.

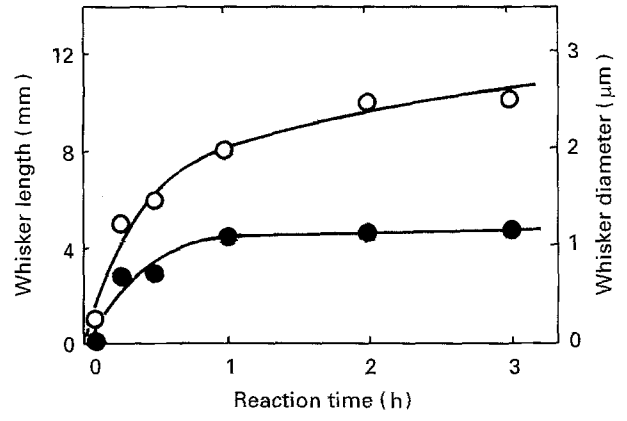

Figure 3 Effect of reaction time on the average length and average diameter of the Si_3N_4 whiskers. Reaction temperature 1400 °C. (○) Whisker length, (●) whisker diameter.

maximum yield is much higher than that for SiC whiskers obtained at the same temperature from rice husks [13].

The effect of reaction time on the length and diameter of the whiskers is shown in Fig. 3. The length increased steeply with increasing reaction time up to 30 min, followed by decreasing length after this time. Whiskers 10 mm (average 8 mm) long and 5–12 mm

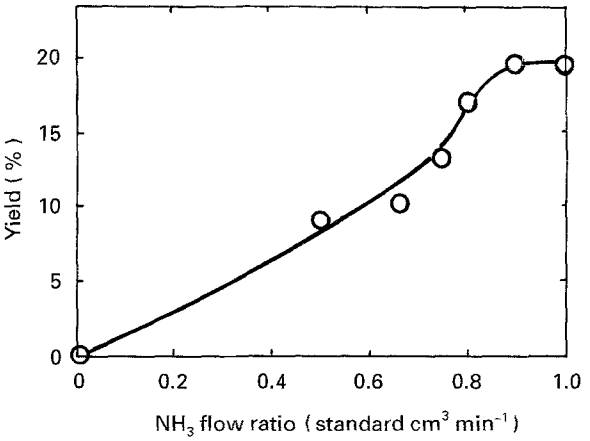

Figure 4 Effect of NH_3 flow ratio in total flow on the whisker yield. Reaction temperature 1400 °C, reaction time 30 min, total flow rate ($NH_3 + H_2$) 210 standard $cm^3 min^{-1}$.

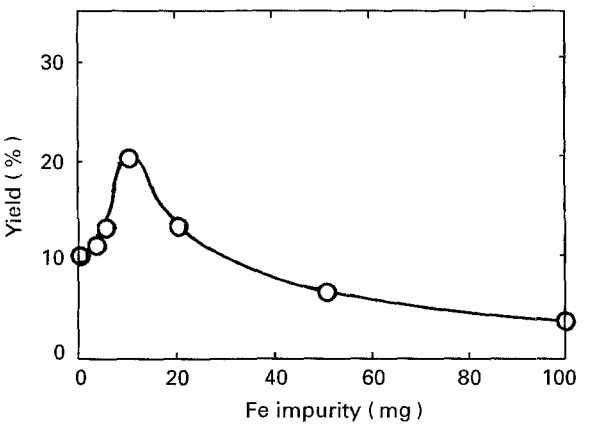

Figure 5 Effect of iron impurity on the whisker yield. Reaction temperature 1400 °C, reaction time 30 min.

(average 10 mm) long were obtained after a 1 and 2 h reaction time, respectively. On the other hand, the whisker diameters reached at a constant length of 0.4–2.2 μm (average 1.1 μm) after a 1h reaction time.

3.2. Effect of gas ratio

The effect of the NH_3 ratio in the total gas flow ($NH_3 + H_2$) on the whisker yield is shown in Fig. 4. The yield increased with increasing NH_3 flow ratio and attained a constant of 20% above the 0.9 ratio. The length and diameter of the whiskers were not affected by the NH_3 flow ratio.

3.3. Effect of impurities

The dried wheat husks contain about 0.04 wt % Fe, and this iron impurity may act as a liquid-forming agent for vapour–liquid–solid (VLS) growth of the whiskers. However, the iron amounts originally present in the source wheat husks was too low to obtain whiskers in high yield. Accordingly, in this work, an iron impurity was added to the source wheat husks to activate the growth of the whiskers. Fig. 5 shows the effect adding different amounts of an iron impurity on the whisker yield in which the reaction time was fixed at 30 min. Without an additional iron impurity, the

TABLE I Effect of the kind of impurity metals on whisker growth. Reaction temperature 1450 °C, reaction time 30 min

Impurity metals	Yield (%)	Average length (mm)	Average diameter (μm)
Fe	32.5[a]	8.0[b]	1.1[b]
Ni	15.5	6.0	0.8
Co	12.5	6.0	0.8
Mn	13.0	6.0	0.8
Ti	2.7	2.6	0.8
Cr	7.7	4.8	0.5
Mo	1.7	3.2	0.5
Cu	1.7	2.8	0.5

[a] Reaction time 1 h.
[b] Reaction temperature 1400 °C, reaction time 1 h.

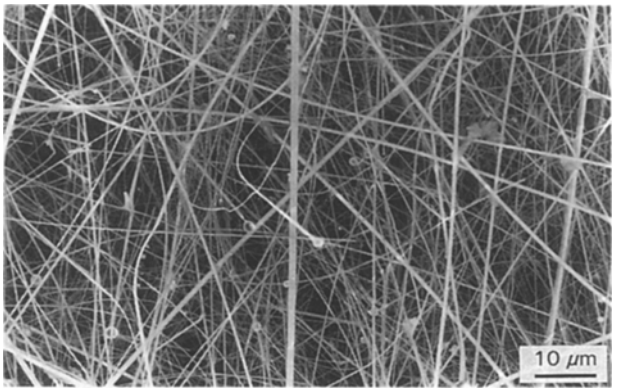

Figure 6 Representative morphology of Si_3N_4 whiskers obtained using iron impurity.

whisker yield was only 10%. The yield increased with an increase in the iron impurity, and the maximum yield of 20% was obtained with a 15 mg Fe addition followed by a decreased yield above this amount. The average length of the whiskers was about 6 mm for an iron addition under 0–50 mg, and about 2 mm for a 100 mg Fe addition.

Table I shows the effect of various kinds of metal impurities on the yield, length and diameter of the whiskers, in which 15 mg metal powder was added to the source wheat husks. Of the metal impurities used, the iron impurity has the most significant effect on the growth of the whiskers. Nickel, cobalt and manganese had some effect on the growth of the whiskers and yields of 12%–15% were obtained.

An H_2S impurity of 0.04–0.13 standard $cm^3\,min^{-1}$ was added to the growth atmosphere. We found that the diameter of the whiskers increased to 1.3–2.2 μm (average 1.6 μm) with the addition of H_2S, while the length and yield of the whiskers decreased. Maeda *et al.* [21] reported that the fracture toughness of a 20 vol % SiC whisker-reinforced Al_2O_3 ceramic was $K_{1c} = 3.0$ and $4.95\,MPa\,m^{1/2}$ for diameters of 0.3–0.5 and 1.83 μm, respectively. Thick Si_3N_4 whiskers may also be expected to increase further the fracture toughness of composites compared to using thin whiskers.

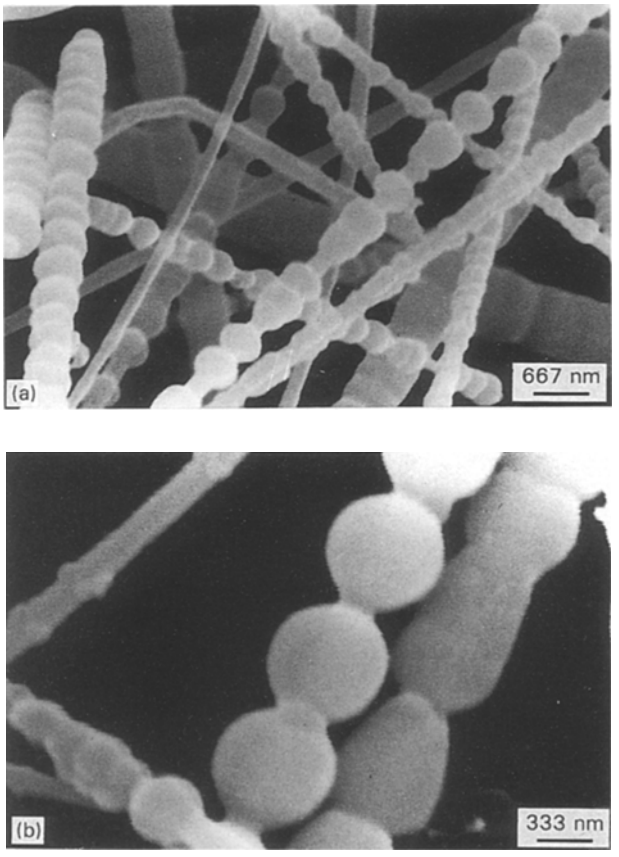

Figure 7 Enlarged view of thin Si_3N_4 whiskers.

3.4. Morphology and growth mechanism

The obtained whiskers were generally white and wool-like. Representative whiskers obtained at 1400 °C after 30 min are shown in Fig. 6. The whiskers have a diameter of 0.3–1.3 μm (average 0.7 μm). Enlarged views of the thin whiskers are shown in Fig. 7. Many thin whiskers have a periodically changing thickness. Fig. 7b shows the whiskers as a string of beads. On the other hand, thick whiskers having a 1 μm diameter generally have a uniform thickness. It may be supposed that very thin whiskers grew during the first stage by a VLS mechanism followed by periodic nucleation on the surface to thicken that part, thus forming the whiskers with the interesting morphology shown in Fig. 7. With thickening diameter, the surface of the whiskers may be levelled to decrease the surface energy and form a uniform thickness.

A droplet-like deposit was usually observed on the tip of the whiskers as shown in Figs 8 and 9. The ratio of the diameter of the droplet to that of the whisker was usually 0.5–3.0 (Fig. 8). A thin whisker sometimes has a large droplet compared with the whisker diameter and has the ratio of 5–8 (Fig. 9). Fig. 9b shows an interesting flower-like droplet, which contained a large amount of iron as well as silicon, suggesting an iron impurity-activated VLS growth. Usually a droplet is a single ball. Multi-ball-like droplets, as shown in Fig. 10, were rarely observed on the tip. A brightened part contained large amounts of iron impurity. It is also very interesting to observe that another short whisker (arrow) grew from the tip. It is reasonable to consider that the presence of a droplet on the tip of a whisker is evidence of the tip of VLS growth.

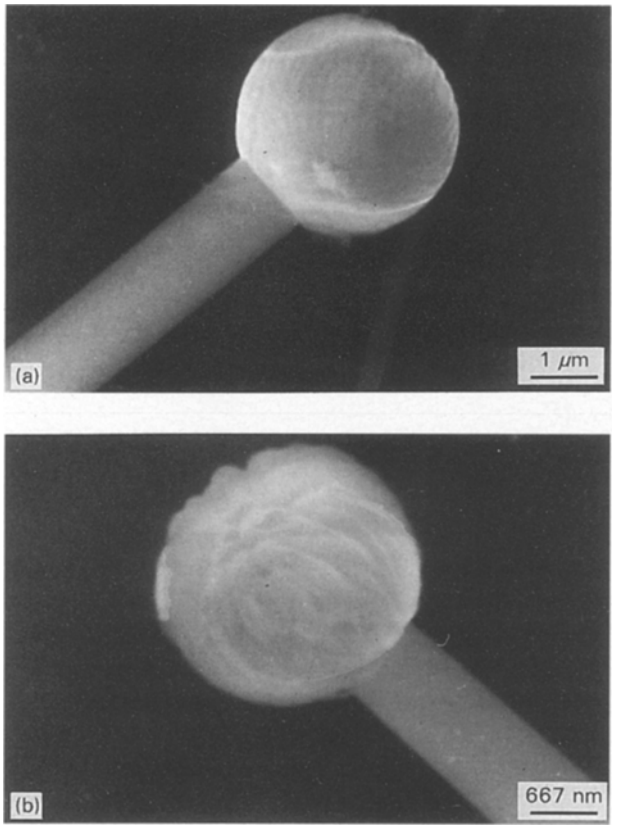

Figure 8 The tip of a thick Si_3N_4 whisker.

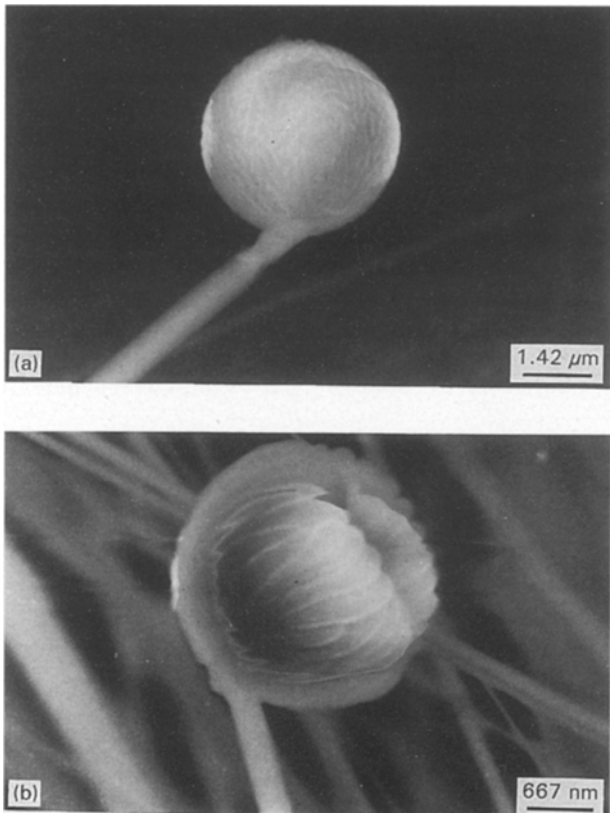

Figure 9 The tip of a thin Si_3N_4 whisker.

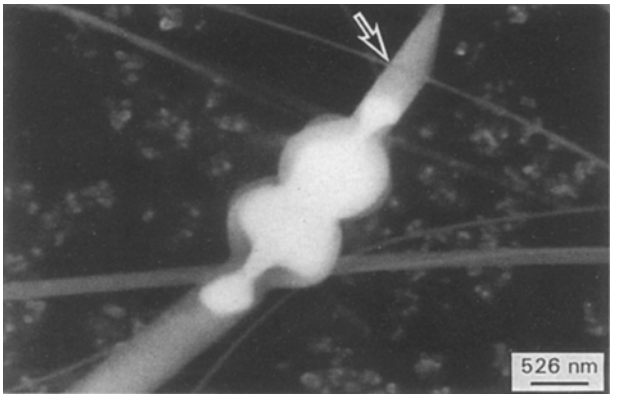

Figure 10 Interesting morphology of the tip.

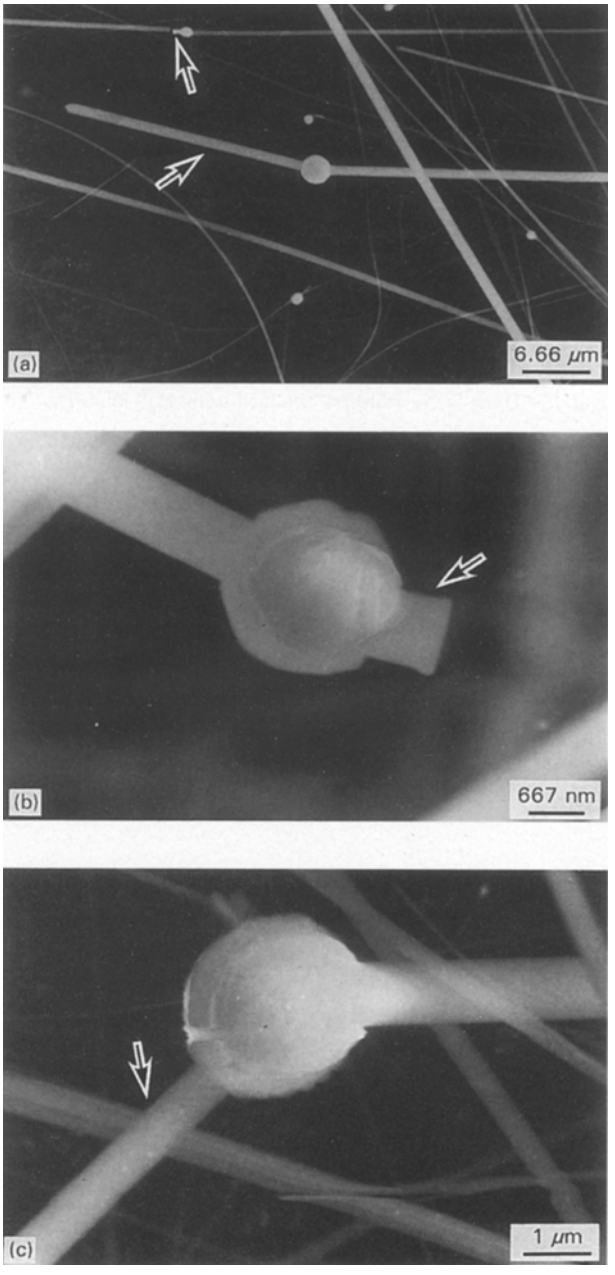

Figure 11 A secondarily grown whisker (arrow) from a droplet.

Fig. 11 shows interesting morphology of the tip from which another short whisker (arrow) had grown. The whiskers grown secondarily from the droplet are only 1.5–30 μm in length and thinner than the originally grown whisker. It may be considered that these short whiskers observed on the droplet are secondarily grown by a bottom VLS mechanism. Fig. 12 shows the Si_3N_4 whiskers obtained using a nickel impurity. The whiskers have a wide thickness range of 0.05–1.1 μm. Fig. 13 shows the thick whiskers

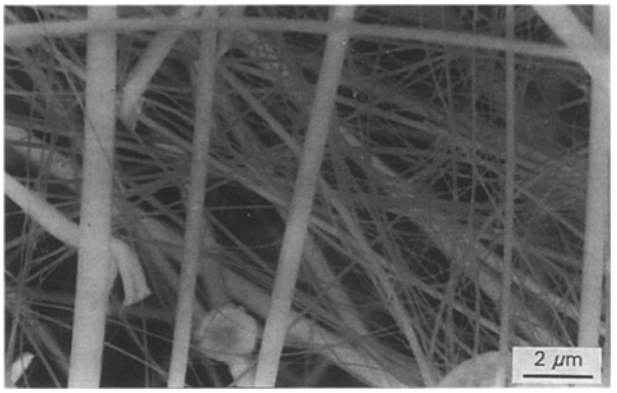

Figure 12 Si_3N_4 whiskers obtained using nickel impurity.

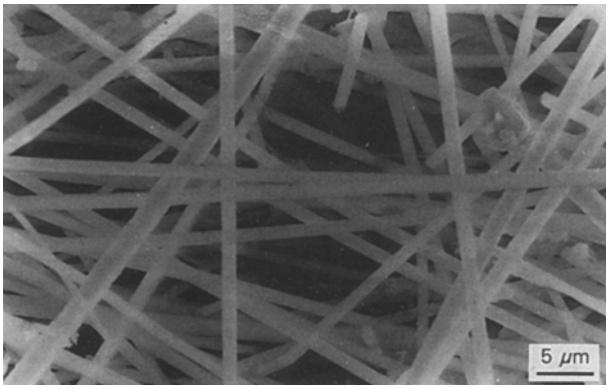

Figure 13 Thick Si_3N_4 whiskers obtained using H_2S impurity.

obtained by the addition of H_2S impurity. The whiskers have a relatively uniform thickness of 1.3–2.2 μm, while thin whiskers below 1 μm were rarely observed.

References

1. I. B. CUTLER, US Pat. 3754 076 (1973).
2. J.-G. LEE and I. B. CUTLER, *Am. Ceram. Soc. Bull.* **54** (1975) 195.
3. N. A. L. MANSOUR and S. B. ANNA, *Trans. J. Br. Ceram. Soc.* **78**(6) (1979) 132.
4. B. C. BECHTOLD, R. L. BEATTY and J. L. LOOK, *Prog. Sci. Eng. Compos.* **1** (1982) 113.
5. R. V. KRISHNARAO and M. M. GODKHINDI, *Ceram. Int.* **18** (1982) 185.
6. N. K. SHARMA, W. S. WILLIAMS and A. ZANGVIL, *J. Am. Ceram. Soc.* **67** (1984) 715.
7. J. V. MILEWSKI, F. D. GAC, J. J. PETROVIC and S. R. SHAGGO, *J. Mater. Sci.* **20** (1985) 1160.
8. S. B. ANNA, N. A. L. MANSOUR, A. S. TAHA and H. M. A. ABDALLAH, *Br. Ceram. Trans. J.* **84**(1) (1985) 18.
9. M. PATER and A. KARERA, *Interceram.* **38**(3) (1989) 17.
10. S. R. NATT, *J. Am. Ceram. Soc.* **71**(3) (1989) 149.
11. M. PATER and A. KARERA, *J. Mater. Sci. Lett.* **8** (1989) 955.
12. R. V. KRISHNARAO, M. M. GODKHINDI, P. G. MUKUNDA and M. CHAKRABORTY, *J. Am. Ceram. Soc.* **74** (1991) 2869.
13. A. K. RAY, G. MAHANTY and A. GHOSE, *J. Mater. Sci. Lett.* **10** (1991) 227.
14. M. PATEL and A. KARERA, *Powder Metall. Int.* **23**(1) (1991) 30.
15. R. V. KRISHNARAO and M. M. GODKHINDI, *Ceram. Int.* **18** (1992) 35.
16. K. SHIMOKAWA, I. SEKIGUCHI, Y. SUZUKI and Y. UEDA, *J. Ceram. Soc. Jpn* **100** (1992) 1127.
17. R. V. KRISHNARAO, M. M. GODKHINDI and M. CHAKRABORTY, *J. Mater. Sci.* **27** (1992) 1127.
18. S. MOTOJIMA, I. HASEGAWA, T. IKAWA and H. IWANAGA, *J. Chem. Vapor Deposition* **1** (1992) 181.
19. Y. KANEKO, K. AMEYAMA and H. IWASAKI, *Zairyo* **37**(412) (1988) 65.
20. *Idem, Kona* **7** (1989) 83.
21. E. MAEDA, T. FUNAHASHI and R. UCHIMURA, *Kawasaki Seitetsu Giho* **21** (1989) 294.

Received 16 December 1993
and accepted 3 February 1994