Bull. Mater. Sci., Vol. 17, No. 2, April 1994, pp. 195–199. © Printed in India.

Novel synthesis of α-Si_3N_4 fibres[+]

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MS received 18 February 1994

Abstract. α-Si_3N_4 fibres have been synthesized by carbothermal reduction and nitridation of pre-oxidized $SiO_{1.7}$. The fibres were characterized using X-ray diffraction, infrared spectroscopy and electron microscopic techniques. The likely mechanism of reaction has been outlined.

Keywords. Carbothermal reduction; silicon nitride; ceramic fibres.

Ceramic fibres have the advantage of high strength, low density and good thermal shock resistance over other types of fibres. They are used as important reinforcing materials in composites. Silicon nitride (Si_3N_4) fibre is a potential candidate for use as reinforcements in turbine blades in high-temperature alloy matrices. While Si_3N_4 powders have been produced (Mazdiyasini and Cooke 1973; Moulson 1979; Zhang and Cannon 1984) in a number of ways, very few reports (Hanna *et al* 1985; Tanaka and Kawabe 1986; Motojima *et al* 1989; Mizurhara *et al* 1991) have appeared on the synthesis of Si_3N_4 fibres. Commercial production (Hendry and Jack 1975; Siddiqi and Hendry 1982; Cho and Charles 1991; Durham *et al* 1991) of Si_3N_4 powders is based on carbothermal reduction and nitridation (CTR/N) of pure silica. However, fibre formation is reported (Wang and Wada 1990) to be dependent on the presence of impurities in the reaction mixture. In this communication we report for the first time a simple method which gives a high yield of α-Si_3N_4 fibres by CTR/N reaction of pre-oxidized $SiO_{1.7}$ free of any metallic impurities. $SiO_{1.7}$ is an industrial byproduct. The yield of fibres in the present method is as high as 30 wt%.

Brownish flaky amorphous $SiO_x(1{\cdot}0 < x < 2{\cdot}0)$ was received from Metkem Silicon Limited, Mettur, India. The amorphous SiO_x powder is prone to slow oxidation after its removal even at low temperatures. Oxidation rate is significantly high at about 700 K. Using thermogravimetry, the oxygen content in SiO_x was determined. The as-received silicon oxide was amorphous and had the composition $SiO_{1.7}$. $SiO_{1.7}$ was monophasic (not a physical mixture of SiO_2 and Si). It contained no impurities except an occasional SiC particle. The monophasic nature of $SiO_{1.7}$ was confirmed by the method suggested by Brewer and Edwards (1954). Magic angle spinning NMR (MASNMR) of (SiO_2 + Si) mixture was different from that of $SiO_{1.7}$ in many details (Ramesh and Rao 1994) and the MASNMR of the $SiO_{1.7}$ powder agreed well with the published (Dupree *et al* 1984a) results. The optimum temperature for oxidation of brown amorphous $SiO_{1.7}$ to white amorphous SiO_2 was found to be 1273 K in oxygen. Above 1273 K SiO_2 crystallizes to cristoballite. Both amorphous $SiO_{1.7}$ and amorphous SiO_2 (pre-oxidized $SiO_{1.7}$) were subjected to CTR/N reaction separately.

Powders of $SiO_{1.7}$ and SiO_2 were separately pulverized with activated charcoal

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[+]Communication No. 224 from MRC

(99% pure) (in the ratio oxide:carbon as 1:5) in an agate ball mill for 3 h in acetone wetting medium. The particle sizes of $SiO_{1.7}$ and SiO_2 were $< 1\,\mu m$ and $< 3\,\mu m$ respectively. The particle size of activated charcoal was $< 5\,\mu m$. The resultant powders were dried and were placed in a perforated carbon boat of 45 mm length, 15 mm width, 8 mm height. The nitridation was carried out in a high-temperature furnace using ultra-high-purity nitrogen. Nitrogen gas was passed through Cu_2O/kieselguhr mixture (Brauer 1963) kept at 200°C in order to remove oxygen (theoretical partial pressure of oxygen is 10^{-20} atm) as completely as possible. A fibrous product was found to form at the top of the carbon boat which was carefully removed and characterized using X-ray diffraction (XRD) (Philips, Netherlands), Fourier-transform infrared spectroscopy (FTIR) (Biorad, Japan), scanning electron microscopy (SEM) (Cambridge, England), and high-resolution electron microscopy (HREM) (Jeol, Japan) techniques.

Fibres were not formed in CTR/N of as-received $SiO_{1.7}$. But CTR/N of SiO_2 from pre-oxidized $SiO_{1.7}$ gave rise to fibres even at 1573 K. The maximum yield of Si_3N_4 fibres was obtained at 1623 K by a 24 h reaction. Figure 1 shows a scanning electron micrograph of such fibres formed at the top of the carbon boat. Nearly 30% by weight of total products were in the form of fibres. Significant fibre formation can be observed after about 3 h of reaction. Fibre spirals were formed occasionally. The cross-section of these fibres was nearly rectangular rather than circular (figure 2).

The X-ray diffraction pattern (figure 3) confirmed that the fibres were α-Si_3N_4. No reflections corresponding to β-Si_3N_4 were observed. Also, electron diffraction experiments confirmed the phase structure (figure 2 inset). In the FTIR spectrum taken for fibrous material, all the peaks compared well with those reported (Wada *et al* 1981) for α-Si_3N_4. The average thickness and average length of fibres increased gradually with time (inset to figure 3). After 24 h reaction, the average length was about 2 cm and average thickness about 1 μm.

Fibre formation was observed only when a carbon boat was used. No fibres were formed when the reaction was carried out in alumina boats. While the top of the carbon boat was covered with a large mass of fibres, powdery products of both α- and β-Si_3N_4 and silicon carbide (SiC) remained at the bottom of the boat.

Three important observations with regard to fibre formation are (i) fibre formation occurs only with pre-oxidized $SiO_{1.7}$ (amorphous SiO_2 powder) and not with $SiO_{1.7}$, (ii) fibres are formed and observed only at the top portion of the carbon boat well separated from the reaction mixture, (iii) fibres were exclusively of α-Si_3N_4. Since the formation of fibres takes place only in carbon boats and fibres begin to grow from the wall well above the reaction mixture, we believe that formation of fibres involves two stages: (i) nucleation of α-Si_3N_4 by solid-state reaction at the carbon surface,

$$3SiO(s) + 2N_2(g) + 3C(s) \rightleftharpoons Si_3N_4(s) + 3CO(g),$$

(ii) growth of α-Si_3N_4 fibre occurring possibly through a vapour-phase reaction in which SiO is directly reduced and nitrided to α-Si_3N_4,

$$3SiO(s) + 3CO(g) + 2N_2(g) \rightleftharpoons Si_3N_4(s) + 3CO_2(g).$$

CO is formed from the reaction

$$SiO_2(s) + C(s) \rightleftharpoons SiO(g) + CO(g).$$

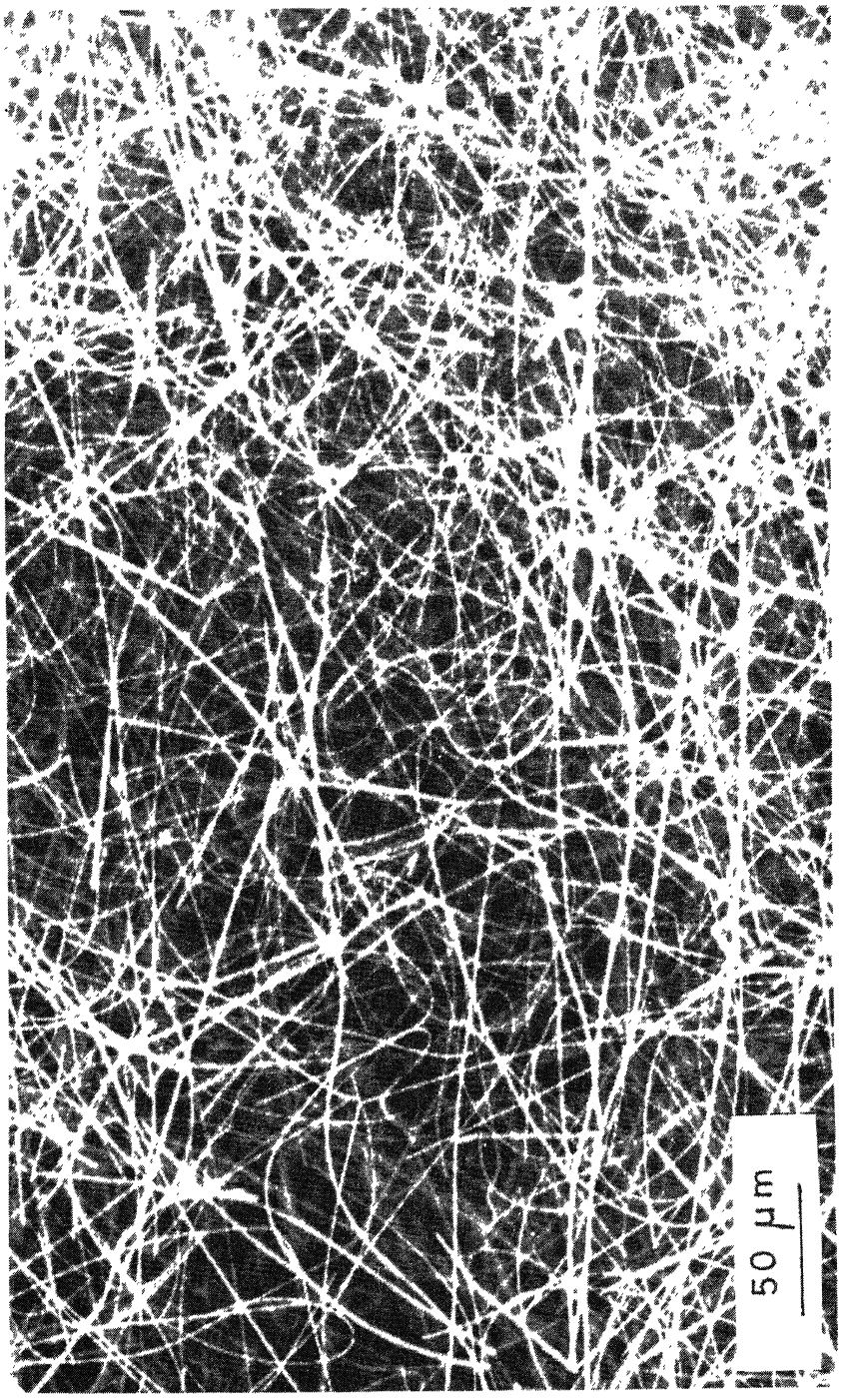

Figure 1. Scanning electron micrograph of fibres formed at the top of the carbon boat.

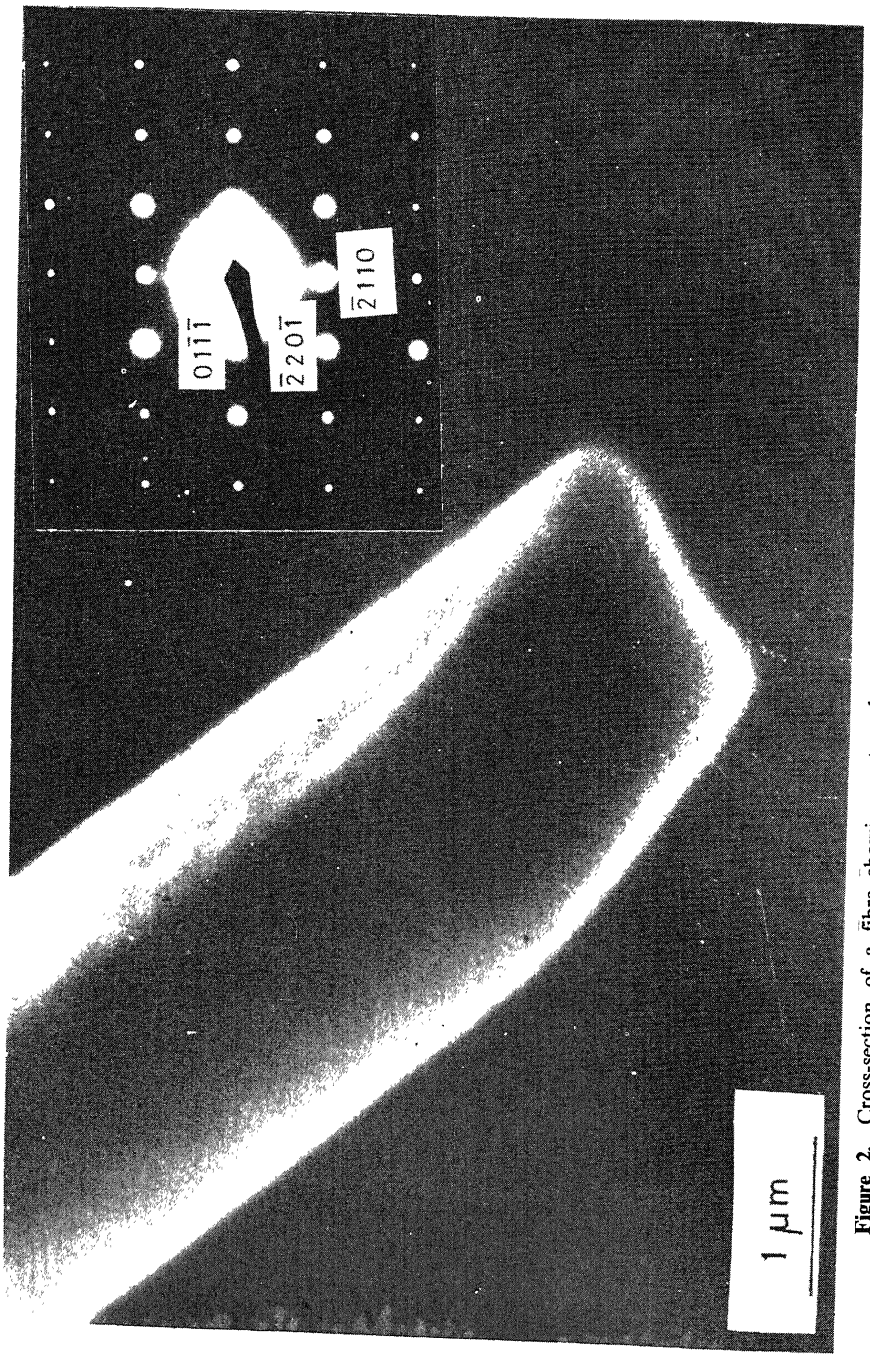

Figure 2. Cross-section of a fibre showing rectangular morphology. Inset: Electron diffraction pattern of a fibre indexed for α-Si_3N_4 structure. The zone axis is $[01\bar{1}2]$.

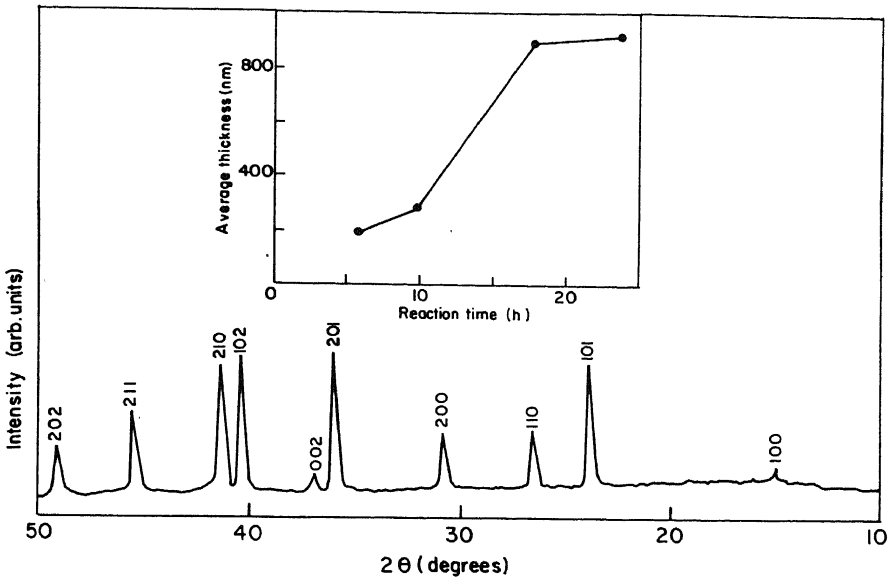

Figure 3. X-ray diffractogram of α-Si_3N_4 fibres. Inset: Variation of average fibre thickness with reaction time (thickness for an average of 50 fibres).

At this stage we also feel that α-Si_3N_4 fibres form with appropriate orientation which enhances fibre morphology of the product. Details of the kinetic study and mechanistic aspects study are communicated (Ramesh and Rao 1994) elsewhere.

Acknowledgements

Thanks are due to Prof. C N R Rao, FRS, for his kind encouragement and Prof A R Vasudeva Murthy for providing $SiO_{1.7}$ powder samples.

References

Brauer G 1963 *Handbook of preparative inorganic chemistry* (New York: Academic Press) Vol. 1, p. 458
Brewer L and Edwards R K 1954 *J. Phys. Chem.* **58** 351
Cho Y W and Charles J A 1991 *Mater. Sci. Technol.* **7** 289
Dupree R, Holland D and Williams D S 1984a *Philos. Mag.* **50** L13
Durham S J P, Shanker K and Drew R A L 1991 *J. Am. Ceram. Soc.* **74** 31
Hanna S B *et al* 1985 *Trans. J. Br. Ceram. Soc.* **84** 18
Hendry A and Jack K H 1975 *Special Ceram.* **6** 199
Mazdiyasini K S and Cooke C M 1973 *J. Am. Ceram. Soc.* **56** 628
Mizurhara M, Noguchi M, Isihara T, Satoh A, Hiramatsu K and Takita Y 1991 *J. Am. Ceram. Soc.* **74** 846
Motojima S, Ueno S, Hattori T and Iwanaga H 1989 *J. Cryst. Growth* **96** 383
Moulson A J 1979 *J. Mater. Sci.* **14** 1017
Ramesh P D and Rao K J 1994 *J. Mater. Res.* (accepted)
Siddiqi S A and Hendry A 1982 *J. Mater. Sci.* **20** 3230
Tanaka M and Kawabe T 1986 Japanese Patent 1, 324, 479
Wada N, Solin S A, Wong J and Prochazka S 1981 *J. Non-Cryst. Solids* **43** 7
Wang M J and Wada H 1990 *J. Mater. Sci.* **25** 1690
Zhang S C and Cannon W R 1984 *J. Am. Ceram. Soc.* **67** 691