Single crystal β-Si_3N_4 fibers obtained by the Self-Propagating High Temperature Synthesis method

M. A. Rodríguez, N. S. Makhonin, J. A. Escriña, I. P. Borovinskaya,
S.H.S. España, Paracuellos del Jarama, Sta. Barbara,Madrid

M. I. Osendi, M. F. Barba, J.E. Iglesias* and J. S. Moya.
Instituto de Cerámica y Vidrio, C.S.I.C. Arganda del Rey,Madrid
*Instituto de Ciencia de Materiales, C.S.I.C,Madrid

Resumen. En el presente trabajo se reporta la obtención de fibras monocristalinas de β-Si_3N_4 de varios mm de longitud mediante la técnica de síntesis autopropagada de alta temperatura (SHS). Las fibras obtenidas muestran una dirección preferencial de crecimiento, tienen elevada pureza y son estables a alta temperatura. Se discute brevemente el posible mecanismo de crecimiento de estas fibras.

Abstract. The synthesis of monocrystallines β-Si_3N_4 fibers by the SHS method is described. Fibers obtained by this route show high purity, are stable at high temperature and grow along a preferential crystallographic axis. The grow mechanism for this fibers is not a VLS and the possible grow mechanism is discussed.

1. INTRODUCTION

The development of high strength ceramic fibers stable at high temperature is a basic requirement for the progress of metal matrix composites (MMC) and ceramic matrix composites (CMC) [1, 2].

SiC whiskers have been the most studied and employed for the fabrication of composites in the last decade [3]. Nevertheless Si_3N_4 fibers show outstanding properties such as its tensile strength (30-50 GPa), the highest reported to date [4].

Nowadays, crystalline Si_3N_4 fibers are synthesised by three basic methods:(i) nitruration of silicon powders by a nitriding gas [5], usually N_2/H_2 mixtures or ammonia; (ii) catalyzed reaction between silicon hydrides and ammonia [4,6] and (iii) carbothermal reduction of SiO_2 by the same gases [7, 8]. Mixtures of SiO_2 + Si have been also used as reacting powders [9].

The temperatures at which these fibers are grown by the mentioned methods vary between 1300°C and the melting point of Si (1412°C). In these conditions the α-Si_3N_4 is the stable phase, and hence this crystalline form has been the one developed. The morphology and properties of the fibers/whiskers obtained by these methods depend on (a) the substrate employed to grow the fibers [7] and (b) the type of catalyst or nucleating agents that favour the whisker growth [4, 8].Very often metallic impurities, specially Fe, are used to harvest the whiskers which originate fiber growth by the so called VLS method [2, 9]. In this case a droplet is often observed microscopically at the tip of the fibers, in which the impurities (mainly Fe) concentrate [4, 6, 9].

In the present investigation, the obtention of high purity single crystalline β-Si_3N_4 fibers by Self-Propagating High Temperature Synthesis (SHS) method [10] is described.

2. SYNTHESIS OF THE FIBERS

The synthesis was performed in a pressurised water cooled cylindrical stainless steel reactor vessel 1 m in length and 30 l capacity. A homogeneous mixture of silicon powder (>99.6 wt% purity, Al<0.1 wt%, Fe<0.05 wt%) of 6 mm average particle size, a small amount (1-3 wt%) of ammonium fluoride NH_4F (99.99 wt% purity) and 5 wt% β- Si_3N_4 powder with » 4 mm particle size was placed lengthwise in the reactor and it was subsequently pumped with N_2 (99.95% purity) up to a pressure of 100 atm. The ignition was initiated by a tungsten electrical resistance producing a reaction wave with temperature above 1600°C at its front. The temperature was monitored by a battery of W-Re thermocouples located along the reaction mixture. The reaction was completed after 30 minutes, and the reactor was then cooled in about 20 minutes.

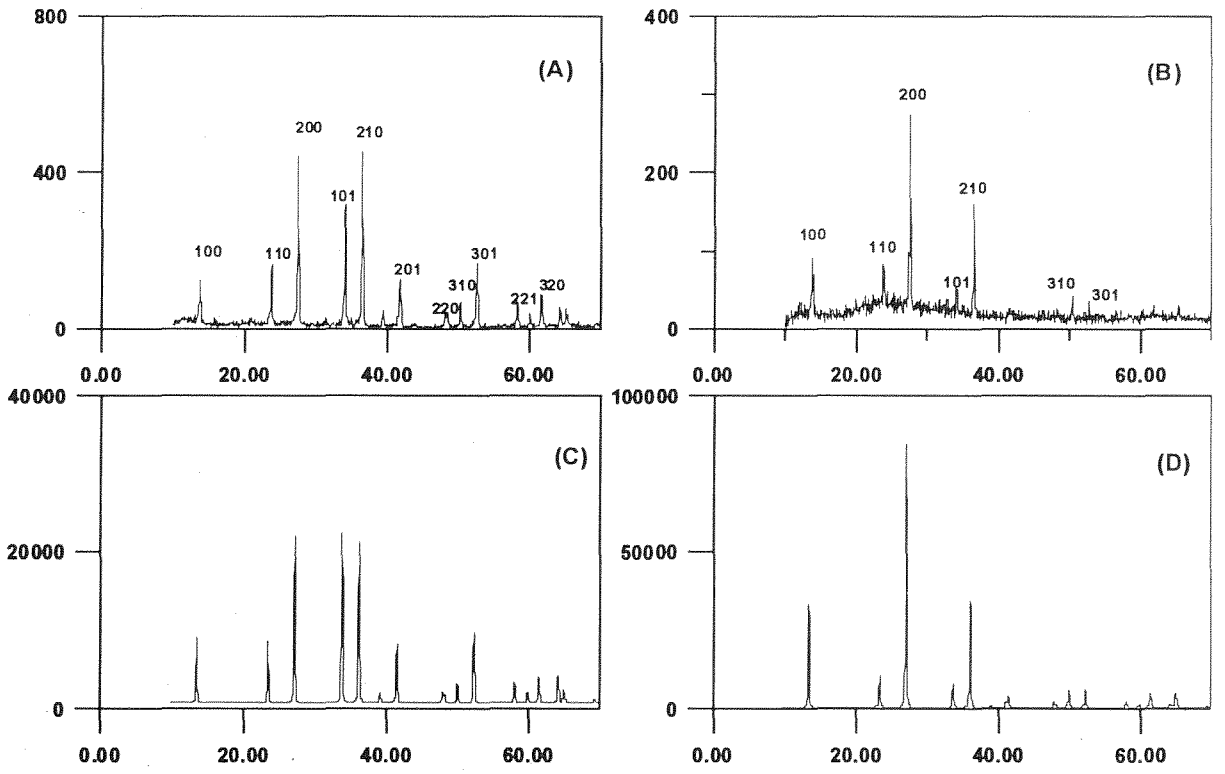

Fig. 1 XRD patterns corresponding to (a) random powder obtained from fibers; (b) oriented fibers (c) calculated β- Si_3N_4 pattern according to structural data reported by Grün [11]; and (d) calculated powder with a preferrential orientation after March's method [12].

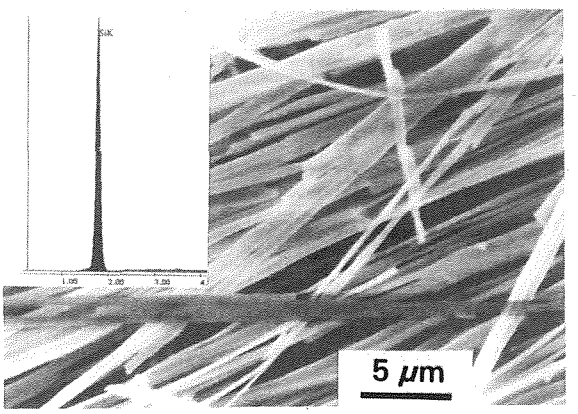

Fig. 2 .-SEM micrograph and corresponding EDS the spectrum of the β- Si_3N_4 fibers.

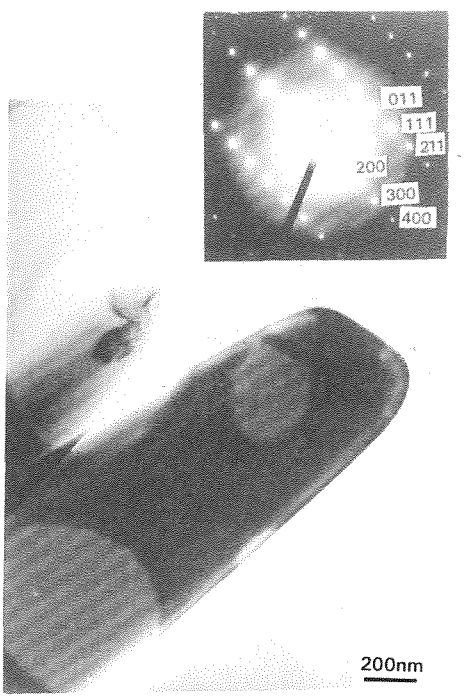

Fig. 3 TEM micrograph of a β- Si_3N_4 fiber and corresponding SAD pattern.

3. RESULTS AND DISCUSSION

The reaction product was a mixture of fibers (60 wt%) and powder of β-Si_3N_4. The fibers were white and had a wool-like appearance. These were analysed by ICP-AES, oxygen detector (LECO), X-ray diffraction, SEM-EDS, and TEM. The main impurities detected were the following (in wt%): O_2, 0.8; Fe, 0.01; Ti, 0.001; Mg, 0.002; Ca, 0.003.

In figure 1 the x-ray diffraction patterns corresponding to a random powder obtained after grinding the fibers down to 10 mm and that corresponding to oriented fibers are shown. The latter one was obtained by dispersion of the wool-like fibers in isopropanol with an ultrasonic device and subsequently drying a few drops of the suspension in a glass sample holder. After this, the fibers were observed by optical microscopy to confirm that most of them were lying on the plane of the sample holder.

The β- Si_3N_4 calculated patterns of figure 1 are based on space group $P6_3$,

a = 0.7595 nm, c = 0.2902 nm, Z = 2, and the structural data reported by Grün [11]. It can be seen that the pattern of the random powder is adequately matched by calculation. For the oriented sample, a powder pattern calculation with prefered orientation was carried out after the method of March, as reported by Dollase [12]; in this method the density of poles of reflection *hkl* at the scattering vector is given by $(r^2\cos^2 a + r^{-1}\sin^2 a)^{-3/2}$, where r is a measure of the degree of preferred orientation, and a the angle between both directions. A good agreement with the observed data is found if a platy habit is assumed for the crystallites, with **a*** parallel to the diffraction vector, and $r = 0.45$. This result implies that the fiber axis of elongation is normal to **a***.

Figure 2 shows the SEM micrograph and EDS spectrum of the fibers. As can be observed these have a ribbon-like shape. The thickness ranges from 0.5 to 1 mm and lengths ranging between 0.1 and 10 mm.

According to the EDS spectrum only Si was detected. After careful analysis of different fiber samples by SEM it can be stated that no droplets exist at the tip of the SHS fibres, as in those obtained by the VLS method [2, 4, 6, 9].

Figure 3 shows the TEM micrograph of the fibers as well as the corresponding selected area electron diffraction pattern. This pattern clearly shows the single crystalline nature of the SHS β-Si_3N_4 fibers, and that the fiber axis is close to the [001] direction. From this and the XRD data (Fig. 1) it can be concluded that the fiber axis is indeed [001].

Although the actual growth mechanism is not completely understood yet, the absence of droplets at the tip of the fibers suggest that once a nucleus of *b*-Si_3N_4 is formed in the molten silicon the fibers probably grow through a vapour-solid mechanism in which the additive NH_4F plays an important role, according to the following reaction sequence:

$$NH_4F \Rightarrow FH + NH_3 \quad (1)$$

$$3Si_g + 2N_2 \xrightarrow{NH_3} Si_3N_4 \quad (2)$$

The low metallic content of the SHS fibers make them particularly attractive to produce CMC and MMC. Metallic impurities are detrimental for high temperature applications because of the formation of low melting point phases and/or decompositon of the matrix [13].

4. CONCLUSIONS

In summary the data reported in the present investigation show that growth of single crystal *b*-Si_3N_4 fibers [001] elongated, several milimeters long, is feasible by the SHS method. The main advantages of this process are: (i) high purity of the fibers that do not show concentration of metallic impurities; (ii) the crystalline phase β-Si_3N_4 is stable at temperatures above 1400°C [14], in fact, this fiber can be used in conditions up to 2000°C without any crystallographic transformation taking place; (iii) the SHS method is economically appealing due to its low cost.

Acknowledgements

The authors thank A. P. Tomsia, J. Bermudo and F. Güitián for experimental assistance.
This work has been supported with Spanish public funds trough MINER (project n.1223/94) and CDT I and by the following corporations: TGI, United Technologies, ENSB and ISMAN.

5. REFERENCES

[1] T. M. Clyne, M. G. Bader, G. R. Caplleman, P. A. Hubert, J. Mat. Sci. **1985**, 20, 85.

[2] T. F. Cooke, J. Amer. Ceram. Soc. **1991**, 74, 2959.

[3] K. Okamura, M. Sato, T. Matsuzawa, T. Seguchi, S. Kawanishi, Ceram. Eng. Sci. Proc. **1988**, 9, 909.

[4] K. Hüttinger, P. Pieschnick, Adv. Mater. **1994**, 6, 62.

[5] P. S. Gopalakrishnan, P. S. Laksminarasimham, J. Mater. Sci. Lett. **1993**, 12, 1422.

[6] P. F. Becher, G.C. Wei, J. Amer. Ceram. Soc. **1984, 67, C-267.**

[7] D. Gray, A. Hendry, J. Eur. Ceram. Soc. **1992**, 10, 75.

[8] U. Vogt, H. Hofmann, V. Krämer, Key Eng. Mat. **1994**, 89-91, 29.

[9] M. Wang, H. Wada, J. Mater. Sci. **1990**, 25, 1690.

[10] A. G. Merzhanov, I. P. Borovinskaya, Doklo. Akad. Nauk. SSSR (Chem) **1972**, 204, 429.

[11] R. Grün, Acta Cryst. **1979**, B35, 800.

[12] W.A. Dollase, J. Appl. Cryst. **1986**, 19, 267.

[13] M. I. Osendi, J. S. Moya, Ceram. Eng. Sci. Proc. **1987**, 7-8, 693.

[14] D. P. Thompson, Materials Science Forum **1989**, 47, 21