ELSEVIER

Ceramics International 25 (1999) 539–543

CERAMICS INTERNATIONAL

# Preparation of alumina fibre mats by a sol–gel spinning technique

R. Venkatesh, P. K. Chakrabarty, B. Siladitya, M. Chatterjee*, D. Ganguli

*Sol–Gel Division, Central Glass and Ceramic Research Institute, Calcutta 700032, India*

Received 12 June 1997; accepted 2 September 1997

**Abstract**

High alumina fibre mats (with 2 and 4 wt% silica) having a web-like structure have been fabricated directly during synthesis by a sol–gel technique. Points of fusion in gel fibre mats helped in the formation of a web-like fibrous body having reasonable strength and very little dust formation after calcination. Incorporation of silica as an additive, extended the stability range of the metastable transition phases of alumina, thereby increasing the strength of the alumina fibres and of the mats in general. Strong and resilient fibrous preforms could be obtained by a single step sol–gel method followed by thermal treatment. 

## 1. Introduction

Pure or high alumina polycrystalline fibres find wide applications in two major areas: as reinforcement of metals or ceramics in the form of continuous fibres and as high temperature insulating materials in the form of mats, blankets, boards, etc. [1–3]. While in the former case it is generally important to obtain continuous fibres of high strength, fibres for thermal insulation can be short (staple), but woven or otherwise shaped into the forms mentioned above [3]. The staple fibres are usually post-processed to obtain the necessary forms [4]. Obviously, it is advantageous to couple the fibre preparation and shaping steps together so as to do away with or minimize any post-processing step; this necessitates contact among fibres during preparation. However, the modern techniques of fibre preparation from slurries, sols, etc. preclude the contact of the fibres before complete drying [5] so as to avoid dust formation during calcination and under service conditions.

The present work is a preliminary report describing the formation of high-alumina fibres (with 2 and 4 wt% silica) in the form of web-like structures directly during synthesis by a sol–gel technique, their conversion to reasonably dust-free mats on calcination and the properties of the fibres at different stages of calcination.

## 2. Experimental procedure

### 2.1. Fibre preparation

The alumina sols were prepared by minor modifications of the well known oxychloride route [6,7]; silica was added to the sol composition in the form of a commercial silica sol (16.5% $SiO_2$). No organic polymers or other compounds were added. The sols thus prepared were heated for several hours at 50–60°C to increase their viscosity for making fibre formation possible. The final viscosity of the sols prior to fibre formation was around 100 poise. This highly viscous sol was poured into a home-designed centrifugal spinerette with 140 holes of about 0.4 mm diameter rotating at 2000–3000 rpm. The gel fibre webs (with mat like structure) generated in situ were collected in a drum under controlled heating. The mats thus formed were dried initially at 200°C for 4 h and finally calcined at 500–1300°C at a rate of 240°C $h^{-1}$.

### 2.2. Characterization of fibres

The elemental compositions of the fibres were checked by a X-ray fluorescence (XRF) unit (Oxford; Link QX2000). Differential thermal analysis (DTA) was carried out at 25–1200°C at a rate of 4°C $h^{-1}$ on a Netzsch STA 409c equipment. The weight loss of the gel fibres between the ambient temperature and 1200°C was

* Corresponding author.

0272-8842/99/$ - see front matter 
PII: S0272-8842(97)00092-8

recorded on a Thermogravimetry (TG) unit (Shimadzu TGA 50). Microstructural features were observed under a scanning electron microscope (Cambridge S250, SEM) and an optical microscope (Prior B2000). Surface areas of the fibres were measured on a multipoint BET surface area analyzer (Quantachrome Autosorb 1). The various crystalline phases were identified from powder diffraction patterns (Philips PW 1730 X-ray unit). The fibre mats were generally calcined at 950 and 1100°C for comparison. However, phase developments were studied by calcination of the gel fibres at differerent temperatures from 500 to 1300°C. The tensile strengths of the fibres were determined by using a laboratory setup as used by Kamiya et al. [8] The measurement followed the relationship [9]

$$\text{Tensile strength} = \text{Fractional load}/\text{Fibre cross sectional area} \quad (1)$$

The gauge length of the fibres tested was 4 mm. An average of 15–20 fibres were tested for each composition.

## 3. Results and discussion

### 3.1. Formation of web-like structures in gel fibres

It has been clearly indicated in the literature [4,5] that gel or similiar fibres obtained through a wet chemical route must be carefully and immediately dried before they come in contact with one another. The logic behind this cautionary step is that wet gel fibres easily join with each other, leading to thick junctions which become centres of crack formation during subsequent calcination. Karlsson et al. [10] showed that these junctions cause formation of rigid fibre mats with poor handleability after calcination. Breakage of these mats occurs at these contact points. The present work reveals that the joining between wet fibres could be effected by the centrifugal spinning technique which forced the fibres not only to fuse and join but also to stretch into a mat or web-like structure of gel fibres, convertible to thin alumina mats on calcination. Fig. 1 shows the micrograph of one such web of alumina gel fibres where the points of fusion are easily discernible. It has further been observed that the fusion points were strong enough to resist catastrophic crack formation during calcination. Accordingly, the degree of dust formation was also tolerably small.

### 3.2. Products of drying and calcination

XRF spectra of alumina fibres indicated that the primary elements were Al and Si with trace impurities of Ca and Fe.

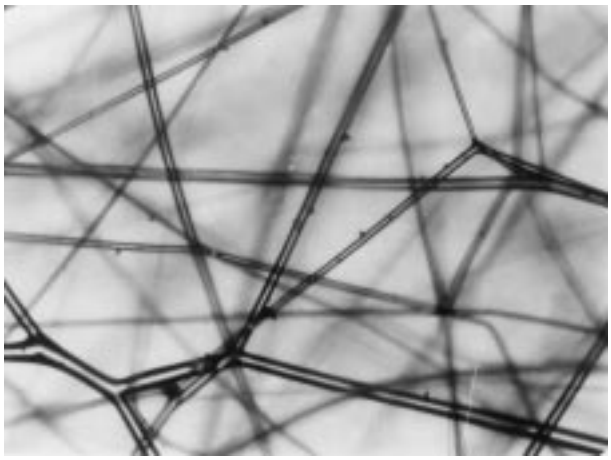

Fig. 1. Optical micrograph of alumina fibre mats showing the web-like structure (×200).

The DTA and TG curves showed similiar results for all the compositions. Endothermic peaks in the DTA curve, observed at 110, 280 and 360°C, indicated removal of bound water and most of the chlorine [11]. The corresponding TG curve showed a weight loss of about 42% up to about 360°C. The DTA curve showed an exothermic peak at 460°C attributable to the crystallization of $\gamma$-$Al_2O_3$ from amorphous Al-hydroxide [12]. The corresponding (360–460°C) weight loss was about 4%. Further weight loss (469–760°C) corresponded to the loss of hydroxyl groups and chlorine [13]. Beyond 760°C the loss was less than 1%, bringing the total to about 56%.

The fibres obtained after calcination had a smooth surface, minimum number of shots, uniform diameter and were flexible, as shown in Figs. 2(a) and (b). The diameter of the gel fibres varied between 10 and 12 μm and that of the calcined fibres between 3 and 5 μm. As mentioned earlier, the gel fibre mats showed a network of interlinked fibres forming a continuous web-like structure. These interlinked points of fusion were seen to be retained up to 1100°C in fibre mats having $SiO_2$ as a second phase additive. Thus, mats with reasonably high strength and very little dust formation were routinely obtained even by folding gel fibre webs and subsequent calcination as in Fig. 3(a)–(c). The fibres in the present study were calcined at a rate of 240°C $h^{-1}$. A slower heating schedule (60°C $h^{-1}$), however, destroyed the points of fusion and a near dusty product was obtained even in fibre mats containing 2 and 4 wt% $SiO_2$ (Fig. 4). Pure alumina fibres exhibited very brittle behaviour and a dusty product was obtained at both the heating rates.

It is now well-known [14] that for prolonged applications of alumina fibres for high temperature insulation, it is necessary to start with a transition alumina phase as the crystalline product (preferably δ-alumina) which, at service temperatures, would slowly transform to the α-phase.

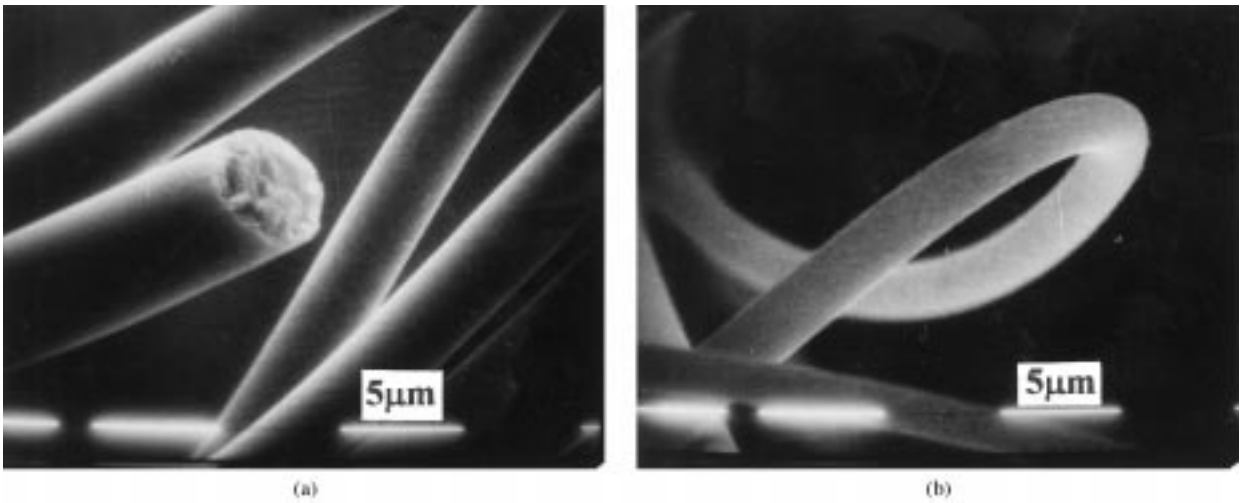


Fig. 2. (a) Scanning electron micrograph of alumina fibres calcined at 950°C showing surface smoothness and uniform fibre diameter. (b) Scanning electron micrograph of alumina fibre strand calcined at 1100°C showing good flexibility.

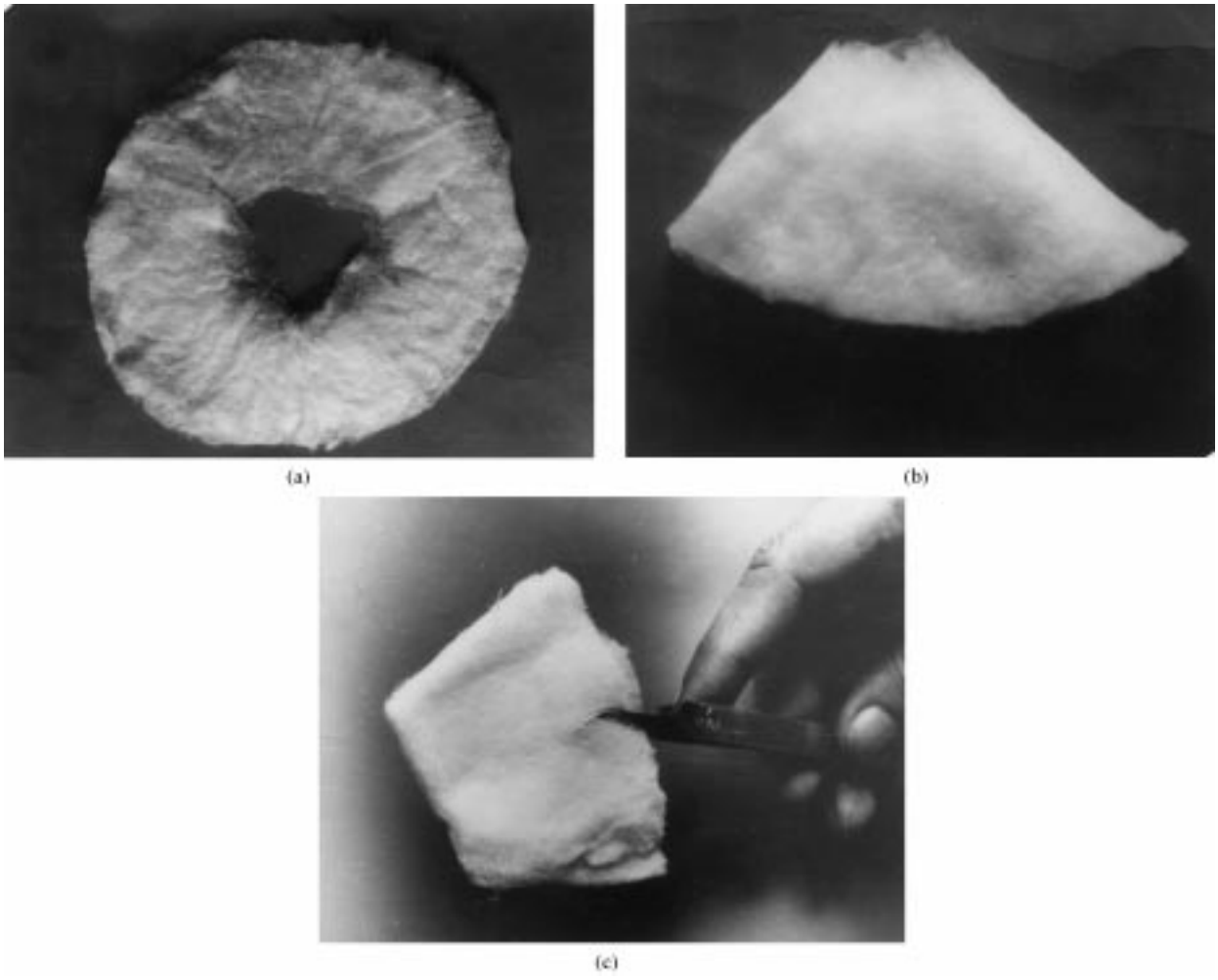


Fig. 3. (a) Alumina–4 wt% silica gel fibre mat (200 mm diameter); (b) Alumina–4 wt% silica gel fibre mat folded twice; (c) Alumina–4 wt% silica fibre mats calcined at 950°C (240°C $h^{-1}$) having reasonable strength and resilience.

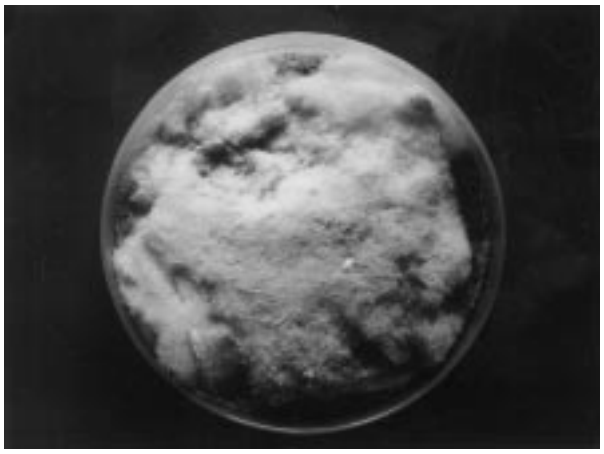

Fig. 4. Brittle alumina fibre mats obtained using a slow calcination schedule at 950°C (60°C $h^{-1}$).

Growth of the alpha phase leads to a loss of strength and a dusty fibre product.

It has been shown [5,12,15–19] that phase developments during crystallisation of amorphous alumina under thermal treatment take place through the following route

$$\text{Amorphous} \rightarrow \text{Eta}(\eta) \rightarrow \text{Gamma}(\gamma) \rightarrow \text{Delta}(\delta) \rightarrow \text{Theta}(\theta) \rightarrow \text{Alpha}(\alpha)$$

Apart from the fact that the η-phase was not detected in this work, the above route was apparently followed by the gel fibres (Table 1). However, clear differences (qualitative at this stage) in the rate of progress of crystallisation were observed with change in composition. The results of Table 1 can thus be summarized in the following way:

1. For all compositions the first transition alumina phases to be detected (500°C) were γ- and δ-alumina. The former decreased in amount and converted to the latter with increasing temperature. By 950°C the γ-phase was totally obliterated.
2. In case of pure alumina (AP), the α-phase started crystallizing below 900°C and by 1000°C became practically the only phase.
3. With 2 wt% silica (A2S), α-alumina first appeared only above 950°C and the product was phase pure at 1200°C.
4. When the silica content was increased to 4 wt% the α-phase appeared above 950°C as in (3) above, but was accompanied by the θ-phase and mullite at temperatures as high as 1300°C. This has also been observed by Stacey [20].

Table 1
Crystal phases of fibres at various calcination temperatures

| Calcination temperature (°C) | Sample designation | | |
|---|---|---|---|
| | AP | A2S | A4S |
| 500 | γ + δ(m) | γ + δ(m) | γ + δ(m) |
| 700 | δ + γ(m) | δ + γ(m) | γ + δ(m) |
| 900 | δ + θ + α(m) | δ + γ | δ + γ(m) |
| 950 | δ + θ + α(m) | δ + θ | δ + θ(m) |
| 1000 | α + θ(m) | θ + α(m) + δ(m) | δ + θ + α(m) |
| 1050 | α | θ + α(m) | θ + α + δ(m) |
| 1100 | α | α + θ(m) | θ + α |
| 1200 | α | α | θ + α |
| 1300 | — | — | θ + α + mullite |

m, minor; AP, pure (undoped) alumina; A2S, alumina with 2 wt% silica; A4S, alumina with 4 wt% silica.

The retardation of the formation of α-alumina as a consequence of the addition of silica in the compositions was evident. Addition of silica has been shown to increase the stability of γ-, δ- and θ- forms of alumina and slow down the conversion to α-alumina. Stabilisation of transition forms of alumina and retardation of the conversion to α-alumina may be effected by varying the number of point defects (cation vacancy and impurity ions) in the structure by incorporating dopant cations, e.g., $Cr^{6+}$, $B^{3+}$, $P^{5+}$, $Si^{4+}$ etc. [16–19] Silica also acts as a crystal growth inhibitor once the α-phase is formed through the formation of mullite at the grain boundaries [4,5]. Increasing addition of silica has also been observed to increase the surface area of the fibres (Table 2). This is commensurate with the earlier observation that progressive obliteration of the transition phases leads to gradual removal of porosity before transformation to alpha alumina, as also increase in the α-phase. The validity of this observation was proved by the fact that at 1100°C pure alumina fibres consisting only of the α-phase, became significantly dense (surface

Table 2
Surface areas ($m^2 g^{-1}$) of calcined fibres for selected temperatures

| Calcination temperature (°C) | Sample designation | | |
|---|---|---|---|
| | AP | A2S | A4S |
| 950 | 66 | 80 | 85 |
| 1100 | 7 | 50 | 58 |

Table 3
Tensile strength (GPa) of calcined fibres at selected temperatures

| Calcination temperature (°C) | Sample designation | | |
|---|---|---|---|
| | AP | A2S | A4S |
| 950 | 0.3–1.1(0.6) | 0.5–1.4(0.95) | 0.6–1.8(1.2) |
| 1100 | Could not be determined | 0.1–0.8(0.5) | 0.4–1(0.65) |

Figures in brackets indicate average values of tensile strength.

area $7 m^2 g^{-1}$) while those with 2 and 4 wt% $SiO_2$ still possessed a surface area of 50 and 60 $m^2 g^{-1}$ respectively.

Table 3 shows that the phase content of the calcined fibres also controlled their tensile strength at room temperature. The effect was so pronounced that after calcination at 950°C pure alumina (AP) containing minor quantities of alpha alumina along with other transition phases showed only about half the strength of A4S fibres which contained δ-alumina as the major phase. The AP fibres (containing only α-alumina) became very brittle after calcination at 1100°C, while A4S still retained some strength. The fall in strength of the A4S fibres calcined at 1100°C was again related to the development of α- and θ–phases.

## 4. Conclusions

Alumina fibres have been prepared from a sol by the spinning technique. The spun gel fibres formed web-like structures which were subsequently calcined into mats. It has been shown in the present work that for the development of relatively strong fibres it is required to extend the range of metastable existence of the transition phases γ,δ and θ to as high a temperature as possible by the addition of suitable oxide additives. Development of alpha alumina leads to a decrease in the strength of the fibres. The points of fusion in the gel fibre mats helped in the formation of a web-like fibrous body having reasonable strength and very little dust formation after calcination. The present work also demonstrates that by judiciously controlling the various processing parameters, strong and resilient fibre mats could be obtained by a single step sol-gel method followed by a thermal treatment.

## Acknowledgements

The authors are thankful to Dr C. Ganguly, Director for his kind interest in this work. They also acknowledge with thanks the assistance received from colleagues in X-Ray Laboratory, Electroceramics Division and Electro-Optic Division. Financial support provided by the National Laser Programme, CAT, Indore is also acknowledged.

## References

[1] M.H. Stacey, Developments in continuous alumina based fibres, Br. Ceram. Trans. J. 87 (1988) 168–172.
[2] O.W. Kronert, The effect of different gas atmospheres on ceramic fibre materials, Interceram 3 (1982) 223–236.
[3] J. Dinwoodie, Alumina fibre for high temperature furnace insulation, Ceram. Ind. April (1996) 58–71.
[4] W. Watt, B.V. Perov (Eds.), Strong fibres, North-Holland, New York, 1985, pp. 87–98.
[5] J.D. Birchall, The preparation and properties of polycrystalline aluminium oxide fibres, Br. Ceram. Trans. J. 82 (1983) 143–145.
[6] R. Warren (Ed.), Ceramic Matrix Composites, Chapman and Hall, New York, 1992, pp. 12–22.
[7] K.S. Mazdiyasni (Ed.), Fibre Reinforced Ceramic Composites, Noyes Publication, New York, 1990, pp. 125–133.
[8] K. Kamiya, K. Takahashi, T. Maeda, H. Nasu, T. Yoko, Sol–gel derived CaO and $CeO_2$-stabilized $ZrO_2$ fibers—conversion process of gel to oxide and tensile strength, J. Eur. Ceram. Soc. 7 (1991) 295–305.
[9] I.H. Cowdrey, R.G. Adams, Materials Testing: Theory and Practice, Wiley, New York, 1949, p. 17.
[10] D. Taylor, (Ed.), Science of Ceramics, Vol. 14, Institute of Ceramics, Shelton, Stoke-on-Trent, 1988, pp. 633–637.
[11] L.A. Dergaputskyaa, I.N. Kalinovskaya, A.N. Gaodu, Obtaining polycrystalline alumina fibres (a review), Ogneupory 1 (1983) 11–14.
[12] P.G. Lucutta, J.D. Halliday, B. Christian, Phase evolution in $Al_2O_3$ fibre prepared from an oxychloride precursor, J. Mater. Sci. 27 (1992) 6053–6061.
[13] G. De With, R.A. Terepstra, R. Metselaar (Eds.), Euro-Ceramics, Vol. 1, Elsevier Applied Science, New York, 1989, pp. 1.609–613.
[14] C. Rastetter, W.R. Symes, Alumina fibre—A polycrystalline refractory fibre for use up to 1600°C, Interceram 3 (1982) 215–220.
[15] T. Maki, T. Kokubo, S. Sakka, Formation of oxide fibers by unidirectional freezing of gel, Bull. Inst. Chem. Res., Kyoto Univ. 64 (1986) 292–305.
[16] J.L. McArdle, G.L. Messing, Transformation and microstructure control in boehmite-derived alumina by ferric oxide seeding, Adv. Ceram. Mater. 3 (1988) 387–392.
[17] G.C. Bye, G.T. Simpkin, Influence of Cr and Fe on formation of alpha $Al_2O_3$ from gamma $Al_2O_3$, J. Am. Ceram. Soc. 57 (1974) 367–371.
[18] A.M. Gavrish, E.L. Karyakina, S.V. Lysak, L.A. Dergaputskaya, I.N. Kalinovskaya, Ogneupory 6 (1988) 15–20.
[19] D. Taylor, (Ed.), Science of Ceramics, Vol. 14, Institute of Ceramics, Shelton, Stoke-on-Trent, 1988, pp. 491–495.
[20] D. Taylor (Ed.), Science of Ceramics, Vol, 14, Institute of Ceramics, Shelton, Stoke-on-Trent, 1988, pp. 291–297.