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Zirconia fibre mats prepared by a sol-gel spinning technique

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Abstract

Fine grained, polycrystalline, stabilized zirconia (with 10 wt.% Y_2O_3) fibre mats having a web-like structure were fabricated directly during synthesis by a sol-gel spinning technique using a multi-orifice spinneret. 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. Strong and resilient fibres with diameters in the range 3–10 micron were obtained by a single-step sol-gel method from spinnable acetate sols devoid of organics as the binder aid. The Y_2O_3 additive in the fibre mats helped to retain the tetragonal phase even at 1600°C by inhibiting grain growth. The health hazard involved with airborne fibres was significantly minimized in the developed zirconia mats by applying sol-gel coatings on their surfaces followed by calcination. The resulting samples exhibited reasonably coherent coatings by anchoring loose surface fibres in a network of zirconia. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sol-gel processes; Fibres; ZrO_2; Refractories

1. Introduction

Stabilized polycrystalline zirconia fibres exhibit wide applications in two major areas: as reinforcement of metals and ceramics and as high temperature insulating materials in the form of mats, boards, blankets, 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.[4] Obviously, it is advantageous to couple the fibre preparation and shaping steps together so as to eliminate or minimize any post-processing step; this necessitates contact among fibres during preparation.[5]

The calcined fibrous products sometimes become dusty in nature and cause atmospheric pollution and health hazard.[6] However, these problems are rather easily minimized by applying sol-gel coatings on the materials. After application of the coatings, handling characteristics of the coated products are known to be significantly improved.[6]

Different methods available for zirconia fibre preparation generally produce staple fibres which require post-processing steps for conversion into mats.[7–11] In-situ preparation of alumina and high-alumina fibre mats by a sol-gel spinning technique has been described in an earlier investigation.[5] Following partly the same technique, an attempt was made in the present investigation to establish a route for preparing dust-free zirconia fibre mats essentially for high temperature insulation. This route comprised the following processing steps:

i. in-situ formation of partially stabilized polycrystalline zirconia fibres (with 10 wt.% Y_2O_3) in the form of web-like structures directly during synthesis by a sol-gel spinning technique without the use of organic additives followed by their characterization;
ii. evaluation of the high temperature performance of mats obtained from the zirconia fibres; and
iii. application of zirconia sol-gel coating on the fibre surface for suppressing atmospheric pollution.

2. Experimental

2.1. Preparation of sol and fibre mats

A precipitate of hydrated zirconia was obtained by adding 1:1 vol./vol. aqueous ammonia solution (25

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wt.%, GR, E. Merck, India) to a solution of zirconium oxychloride octahydrate (ZrO_2, 36.5%; Indian Rare Earths Ltd.) in deionized water.[12] The washed (almost electrolyte free) precipitate was peptized with glacial acetic acid (99.8%, AnalaR, BDH, India) under stirring at 60–70°C. The parent sol thus obtained (1.5M equivalent ZrO_2 content) had a Zr^{4+}/OAc^- mol ratio of 0.05.

To a known volume of the parent acetate sol, a required amount of yttrium nitrate (10 wt.% equivalent Y_2O_3; Indian Rare Earths Limited, purity $> 99\%$) was mixed under stirring. The pH and viscosity of the Y-containing zirconia sol were found to be 2.52 and 2.70 mPa s, respectively. No organics were added to the sol as the spinning aid. The sol thus prepared was aged at 70–80°C for several hours to increase their viscosity for making fibre formation possible (checked by hand-drawing of the fibres). The final viscosity of the sol prior to fibre formation (spinnable viscosity) was about 20 Pa s.

The highly viscous sol was spun using a multi-orifice laboratory spinneret as described earlier.[5,12] The in-situ generated gel fibre mats in the form of web-like structures were collected in a drum under controlled heating.[5] The gel fibres were oven dried at 150°C for 1 h and finally calcined at 200, 400, 700, 1000 and 1300°C with a soaking time of 1 h at each temperature. The diameter of each of the as-produced gel fibre mats dried at 150°C/1 h was 220 mm (Fig. 1). The thickness of the gel fibre mats (and consequently the calcined fibre mats) was tailored by spinning different quantities of sols.

2.2. Determination of % linear shrinkage and % mass disintegration of the calcined fibre blocks

For measuring the % linear shrinkage and % mass disintegration, $ZrO_2 \cdot 10$ wt.% Y_2O_3 fibre mats (10 mm thick), prepared at 1300°C, were cut into several small blocks each of approximate dimensions 20 × 20 × 10 mm. Such small blocks were calcined at different temperatures in the range 1300–1600°C followed by cooling to 30°C. At each temperature the soaking time was 4 h. In each case, four small blocks of similar dimensions were used. After heat-treatment, the dimensions of each block and the weight of the fragmented materials obtained from each block were noted. From the difference in dimensions and weight (before and after calcination), the% linear shrinkage as well as% mass disintegration (wt.%) at each temperature was determined and the average value was calculated.

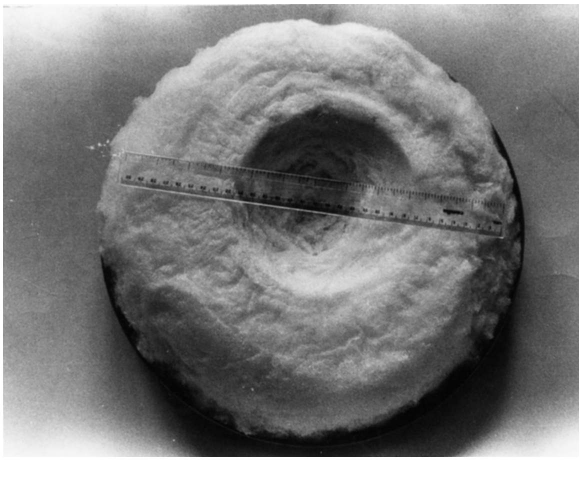


Fig. 1. Zirconia–10 wt.% yttria gel fibre mats of 220 mm diameter.

2.3. Preparation of coated $ZrO_2 \cdot 10$ wt.% Y_2O_3 fibre blocks by sol-infiltration method

For this purpose, an acetate sol of composition $ZrO_2 \cdot 10$ wt.% Y_2O_3 was prepared as described in Section 2.1. About 2 wt.% polyvinyl alcohol (PVA) was added to the sol. Two different sols of viscosities 5 ± 1 and 10 ± 1 mPa s were prepared by evaporation from the PVA-containing sols. For infiltration experiments, small fibre blocks each of dimensions 20 × 20 × 10 mm (calcined at 1300°C) were weighed and dipped into PVA-containing sols of different viscosities with varying time and kept at ambient temperature for conversion to gel coatings.[6] Finally the coated materials were calcined at 1000°C/1 h to obtain the corresponding oxide coated blocks. The wt.% gain of the coated blocks was calculated. Thin sections of dimensions 5 × 5 × 2 mm were cut from the top surface (section A) of the untreated (blank) and the oxide coated, i.e. infiltrated, blocks obtained under different treatment time for characterization. In one sample, a thin section of dimensions 5 × 5 × 2 mm was cut from the middle portion (section B) of an infiltrated block for characterization.

2.4. Characterization of the fibres

The gel and the calcined fibres were characterized by (i) differential thermal analysis (DTA; Netzsch STA 409c), (ii) thermogravimetry (TG; Shimadzu TGA 50), (iii) optical microscopy (Prior, James Swift B 3000), (iv) scanning electron microscopy (SEM; S 250 and Leo 400c), (v) X-ray diffraction (XRD; Philips PW-1730 X-ray unit) using Ni-filtered CuK_α radiation, (vi) multi-point BET surface area analysis (Quantachrome Autosorb 1), (vii) elemental analysis using X-ray fluorescence (XRF; Link QX 2000), (viii) tensile strength measurement (a laboratory made set-up) and (ix) density determination in water following Archimedes principle. The cut thin sections of dimensions 5 × 5 × 2 mm (Section 2.3) were examined under SEM and the% area unoccupied (void fractions) was determined from the photo-micro-graphs using an image analyser (Leica Q500 MC).

3. Results and discussion

3.1. Formation of gel fibre mats

It has been pointed out in the earlier investigations that gel or similar fibres generated through a wet chemical route must be carefully dried before they come in contact with one another.[5] The main reason for this is that wet gel fibres easily join with each other, causing thick junctions which become centres for crack formation during subsequent calcination. Breakage of these mats occurs at these contact points.[13] As described in the earlier work, the joining between the wet fibres of zirconia gels in this work could be effected by the centrifugal spinning technique using binder-free acetate sols, finally leading to the formation of a mat of gel fibres, transforming to zirconia mats on calcination.[5] Fig. 2 shows the optical micrograph of one such web of zirconia gel fibres where the points of fusion are easily discernible. It is believed that the contact points were strong enough to prevent catastrophic crack formation during calcination, thus causing the degree of dust formation considerably small.[5]

3.2. Thermal analyses

Thermal behaviour of the doped zirconia gel fibres was investigated by DTA/TG from 30 to 1200°C at 10°C/min. The appearance of two endothermic peaks at about 118 and 200°C in the DTA curve may be due to the removal of bound water and some organics, i.e. acetates present in the fibres.[7] The only sharp exothermic peak at 330°C indicated the decomposition of nitrates.[9] The initiation of crystallization was indicated by the broad and small exothermic peak at 405°C[6,14] which was confirmed by the XRD results described in Section 3.3.

TG of the gel fibres showed a total weight loss of about 53% up to 1200°C of which a sharp decrease in weight of 44% was noted up to 350°C. Removal of loosely bound water molecules and most of the volatiles occurred up to this temperature, thus supporting the DTA results. A further weight loss of about 9% was recorded from 350 to 1200°C; this could be due to the expulsion of residual acetates and water molecules formed through dehydroxylation of the materials along with the removal of residual carbon via oxidation.[7,14]

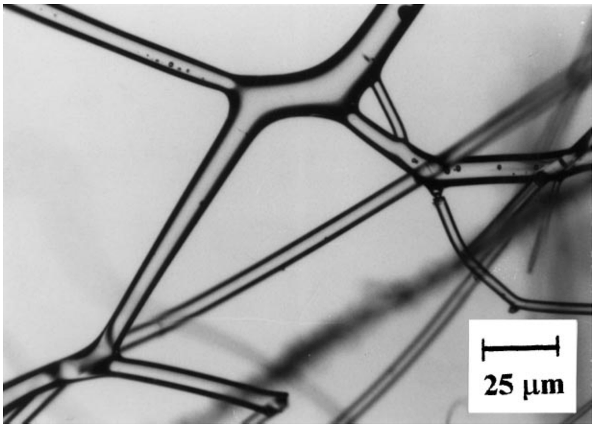


Fig. 2. Optical micrograph of zirconia–10 wt.% yttria gel fibre mats showing the web-like structure.

Thus, from the above study it is clear that the heating of the gel fibre mats, particularly up to 350°C (corresponding to a high weight loss of 44%), is very critical and to retain the points of fusion up to 1300°C or above, heat-treatment under controlled conditions is absolutely necessary.

3.3. Characteristics of the gel and calcined fibre

XRD of the gel fibre mats calcined at 400°C indicated the initiation of crystallization of cubic-/tetragonal-ZrO_2.[6,15] Further calcination at 700, 1000 and 1300°C confirmed the presence of both cubic- and tetragonal-ZrO_2 in the calcined mats, thereby indicating the stabilization of both the polymorphs even at 1300°C. Although complete removal of carbonaceous materials is known to occur at 1000°C, the fibres calcined at this temperature were considerably fragile.[7] Based on the DTA/TG results, the gel fibre mats in the present study were subjected to calcination at 1300°C and above with a two step heating schedule as follows:

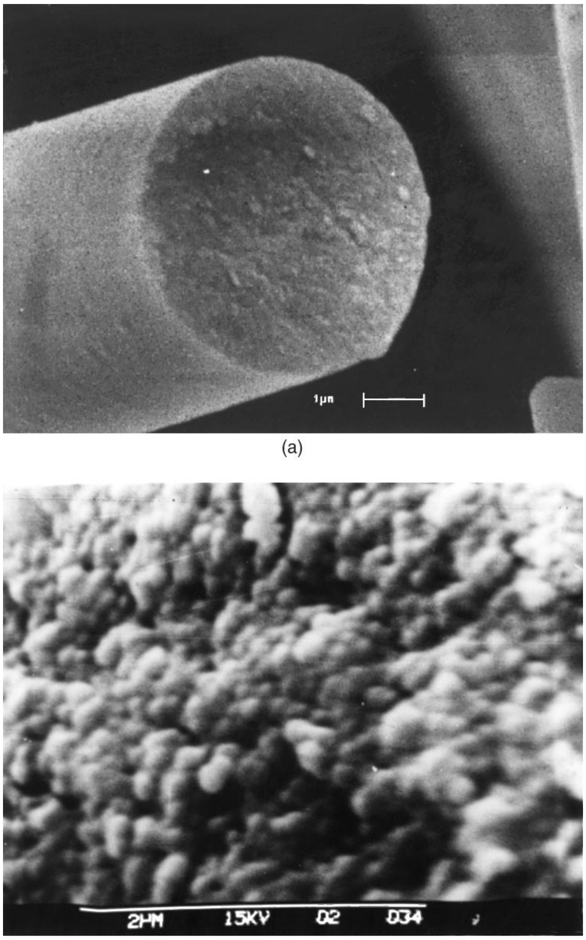
i. from 30 to 500°C at 60°C/h with 1 h soaking at 500°C and
ii. from 500 to 1300°C or above at 250°C/h with 1 h soaking at 1300°C or above.

A uniform faster heating schedule (250°C/h) from ambient temperature to 1300°C, however, caused a rapid removal of large amount of volatiles, thus destroying the points of fusion and finally generating dusty products.

The diameters of the gel fibres varied between 10 and 20 micron and that of calcined fibres between 3 and 10 micron without any sign of cracking. The calcined fibres were flexible and had smooth surfaces, minimum number of shots, uniform diameter with a circular cross-section as shown in Fig. 3(a).[5] The interlinked points of fusion were observed to be retained up to 1300°C in fibre mats. Thus, mats of reasonable strength and very little dust formation were routinely obtained even by folding gel fibre webs and subsequent calcination.[5] The microstructural feature of the calcined fibres has been presented in Fig. 3(b). The small grains (100–200 nm in size) impart a cobblestone appearance to the fibre surface as well as to the interior and exist by coalescing with each other, indicating that considerable densification occurred even at 1300°C.[11]

As discussed earlier, the fibres calcined at 1000°C were fragile. This is corroborated by the relatively high surface area of 10 m^2/g. However, after calcination at 1300°C, with gradual decrease in porosity, a sharp decrease in surface area, i.e. 1 m^2/g was noted, thus resulting in an improved strength of the fibre mats. In fact, a relatively high value of the tensile strength (determined as described in an earlier work[5]) of 1200–1600 MPa of the individual fibres calcined at 1300°C also supported such low value of the surface area, i.e. 1 m^2/g. On the other hand, the fragile character of the fibres calcined at 1000°C prevented the measurement of their tensile strength.[5,12]

The use of Y^{3+}-containing zirconium acetate sol devoid of organic binder as a precursor has already been described by Marshall et al. for the preparation of hand drawn (staple) fibres.[11] The present result is highly encouraging in the sense that instead of staple fibres, the acetate precursor could produce spun fibre mats in a single step process exhibiting reasonable strength and resilience at 1300°C and above. Moreover, the generated fibres having small diameters or cross-sectional area as well as uniform grain size [Fig. 3(b)] helped to avoid cracking during shrinkage, thus resulting in the formation of relatively high strength fibres.[11,12] The low density of calcined fibres (at 1300°C), i.e. 5.42 ± 0.01 g/cm^3 compared to that of the undoped cubic- or tetragonal-ZrO_2 could be explained to be due to the presence of low-density Y_2O_3 as well as some residual pores.[3] Presence of undesirable impurities in the calcined fibres was checked by XRF spectra which indicated the existence of ZrO_2 (+ HfO_2) and Y_2O_3 as the primary constituents, i.e. 89.55 and 9.88 wt.%, respectively, with trace impurities of TiO_2 and CaO; the rest were volatiles.



(a)

(b)

Fig. 3. (a) Scanning electron micrograph of an individual zirconia–10 wt.% yttria fibre (calcined at 1300°C) showing surface smoothness and circular cross-section; (b) scanning electron micrograph showing the micro structural feature of the zirconia–10 wt.% yttria fibres calcined at 1300°C.

3.4. High temperature performance of the calcined fibre blocks

The high temperature performance of the small fibre blocks of dimensions 20 × 20 × 10 mm were examined by determining their % linear shrinkage and % mass disintegration in the temperature range of 1300 to 1600°C and the results have been presented in Fig. 4.[16] The small increase in % linear shrinkage with the increase in calcination temperature [Fig. 4(a)] could be due to the gradual decrease in porosity of the fibres. Fig. 4(b) shows that the disintegration of the fibres was negligible (about 1.5 wt.%) even after calcination at 1600°C. Further, XRD of the fibre blocks heat-treated in the temperature range 1300–1600°C (each with 4 h soaking) showed the presence of both tetragonal- and cubic-ZrO_2 without any formation of the monoclinic polymorphs. Obviously, the Y_2O_3 additive in the fibre mats helped to retain tetragonal-ZrO_2 even at 1600°C by inhibiting grain growth.[11]

3.5. Characteristics of the sol-coated fibre blocks

As discussed in Section 3.4, the fibre blocks during heat-treatment under different time-temperature schedule

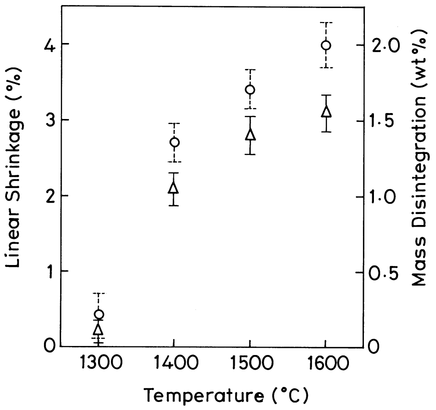


Fig. 4. Plot showing variation of (a)% linear shrinkage with calcination temperature (○) and (b) % mass disintegration with calcination temperature (△) for zirconia–10 wt.% yttria fibre blocks of dimensions 20 × 20 × 10 mm.

showed some dusty nature, although quite insignificant. The calcined fibres with diameters less than 10 micron (Fig. 5) in the untreated (blank) fibre blocks are supposed to create atmospheric pollution and become health hazardous during handling.[6] Application of sol-gel coatings on such fibre blocks helped to minimize this problem.[6,17,18] The function of PVA added to the sol was to increase the green strength of the infiltrated fibre blocks.

Of the two sols of viscosities 5 ± 1 and 10 ± 1 mPa s, the sol of higher viscosity was found to be unsuitable for infiltration experiments, forming fragmented coatings on the surface fibres only.[19] This is consistent with Darcy's law:[19–21]

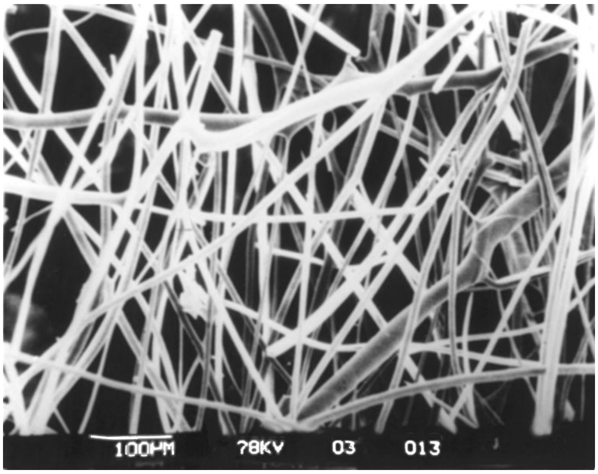


Fig. 5. Scanning electron micrograph showing diameters less than 10 micron of calcined fibres in the untreated (blank) zirconia–10 wt.% yttria fibre blocks of dimensions 20 × 20 × 10 mm.

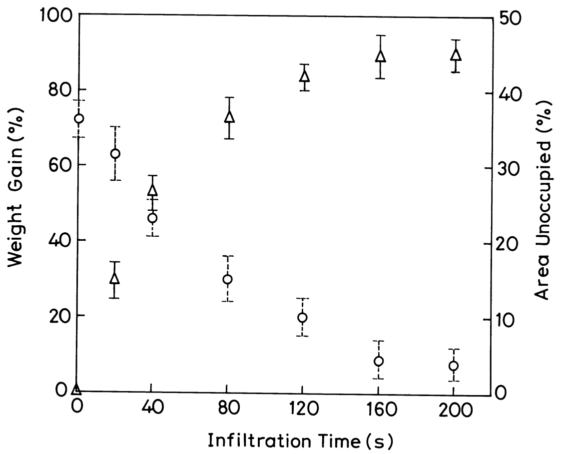


Fig. 6. Plot showing (a) weight gain characteristics as a function of infiltration time (△) and (b) progressive filling of voids (% area unoccupied) as a function of infiltration time (○) of the oxide coated zirconia–10 wt.% yttria fibre blocks of dimensions 20 × 20 × 10 mm.

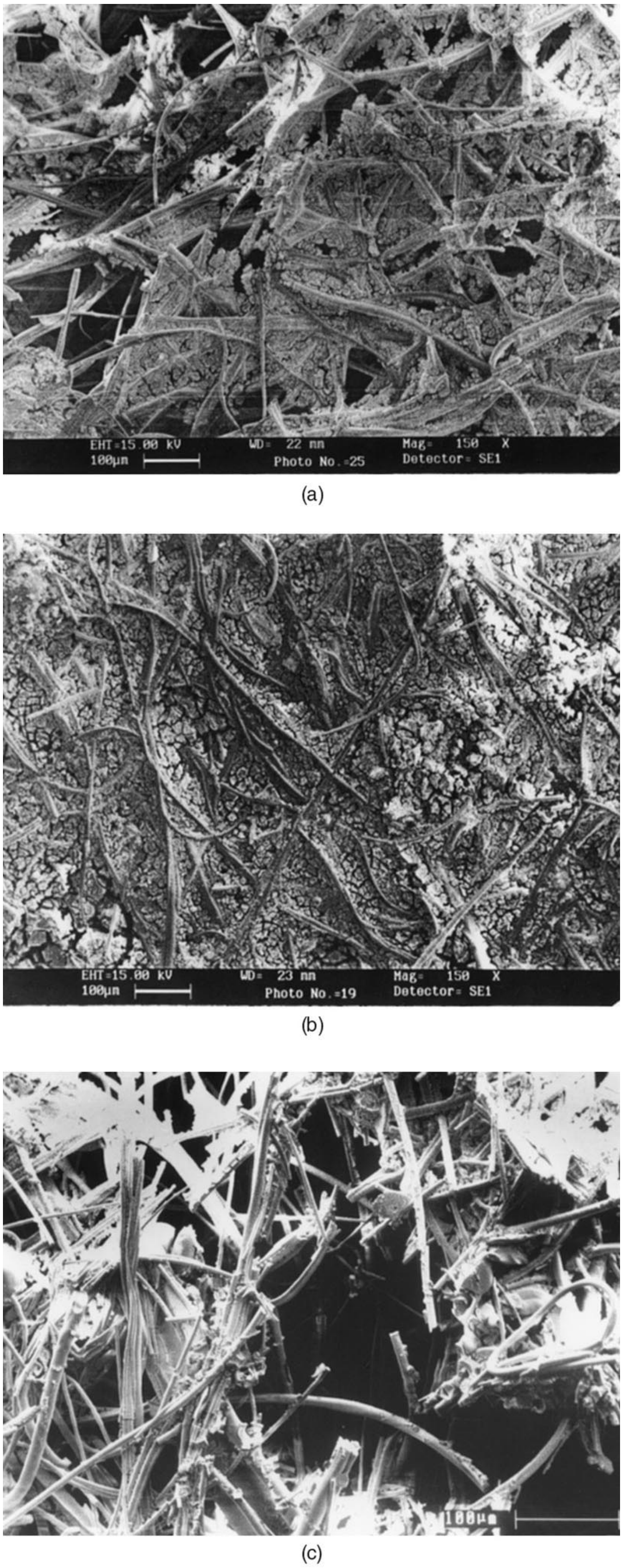


Fig. 7. Scanning electron micrographs of the oxide coated thin sections with dimensions 5 × 5 × 2 mm of zirconia–10 wt.% yttria fibre blocks showing (a) incomplete penetration of sol after 40 s of infiltration time (section A); (b) almost complete penetration of sol after 160 s of infiltration time (section A); (c) practically no penetration of sol after 160 s of infiltration time (section B).

$$J = k_x P_x / \mu\delta \quad (1)$$

(where J is the flow rate per unit area, k_x is the effective permeability of the porous medium, P_x is the pressure difference across the medium, μ is the viscosity of the fluid and δ is the thickness of the medium) which implies that other factors remaining constant, the flow of the fluid through the porous fibre blocks bears an inverse relationship with its viscosity.

The weight gain characteristics of the zirconia fibre blocks using the sol of viscosity 5 ± 1 mPa s have been presented in Fig. 6(a) which indicates that after 160 s, the % wt. gain became almost constant. The progressive filling of the voids in the surface region as a function of infiltration time is shown in Fig. 6(b). Fig. 7(a) and (b) show the SEM of the surface region (section A) of the coated blocks after 40 and 160 s, respectively. After 40 s of infiltration [Fig. 7(a)], the penetration of the sol into the interfibre pores and voids of the blocks was incomplete, while after 160 s [Fig. 7(b)] no further infiltration was observed. This is corroborated by both Fig. 6(a) and (b). Fig. 7(b) shows a situation where continuity of the pores and voids in the surface region with those in the interior was practically lost. Fig. 7(c) depicts SEM of the central region (section B) of the infiltrated fibre blocks obtained after 160 s. It is clear from Fig. 7(b) and (c) that for the same infiltrated fibre block, while infiltration in the top region (section A) reaches a saturation, the central region (section B) remains practically unoccupied with the infiltrated material.

The above figures also indicate that the surface coating of ZrO_2 formed a network after bridging loose fibres together and thus preventing their escaping tendency to the atmosphere.[6] In the infiltration process, the sol wets and encapsulates the fibres.[6,18] After calcination at 1000°C, the ZrO_2 coatings on the fibres seem to form bonds with the infiltrated part of the blocks. Crackings were caused due to the thermal expansion mismatch and interface interactions during shrinkage.[6] After application of such coatings, the dust suppression as well as the handling ease of the blocks were significantly increased.

Repeated treatment of the fibre blocks with a sol may lead to the formation of ceramic matrix composites (CMC) as the final product. As the present work aims to fabricate dust-free zirconia fibre mats suitable for high temperature insulation, repeated treatment process was avoided. Furthermore, the weight gain characteristics and the% area unoccupied (void fractions) of the infiltrated fibre blocks in Fig. 6(a) and (b), respectively, give a clear idea about the presence of different amounts of infiltrated materials in the pores and voids of the fibre blocks. Thus, by controlling the treatment time, keeping other parameters unaltered, the pore volume fraction [(Fig. 6(b)] of the fibre blocks can be easily monitored.

4. Conclusions

i. Stabilized zirconia (with 10 wt.% Y_2O_3) fibre mats have been prepared from acetate sols, without any organics as the spinning aid, by using a multi-orifice spinneret. The spun gel fibres form web-like structures through fusion in the gel stage, which are subsequently calcined into mats.
ii. The spinnable acetate sol has been found to produce strong and resilient fibres with diameters in the range 3–10 micron.
iii. The Y_2O_3 additive in the fibre mats retains the tetragonal phase even at 1600°C by inhibiting grain growth; about 4% linear shrinkage and a negligible mass disintegration (about 1.5 wt.%) are noticed at this temperature.
iv. The application of sol-gel coating on the developed fibre blocks through infiltration significantly increases dust suppression characteristics as well as their handling ease. Furthermore, the weight gain characteristics and the% area unoccupied (void fractions) of the infiltrated fibre blocks give a clear idea regarding the presence of varying amounts of infiltrated materials in the pores and voids of a fibre block which indicates that by controlling treatment time, keeping other parameters unaltered, the pore volume fraction of the fibre blocks can be easily monitored.

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