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Effect of magnesium oxide on sol–gel spun alumina and alumina–zirconia fibres

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Abstract

Alumina fibres and alumina–zirconia fibres were prepared by sol–gel process. The starting materials used for the preparation of alumina and zirconia sol were aluminium-tri-isopropoxide and zirconium oxychloride respectively. Alumina sol and zirconia sol were mixed in definite proportions, so that the final composition contains 10 wt.% ZrO_2. Alumina and alumina–zirconia fibres were prepared from the alumina sol and mixed sol respectively. MgO was introduced in the fibres by adding $MgNO_3$ into the sol. Sintered alumina fibre has α-Al_2O_3 phase and alumina–zirconia fibre has α-Al_2O_3 and t-ZrO_2 phases. The phase transition to α-Al_2O_3 takes place at higher temperature in the alumina fibre with MgO, whereas the effect is less in alumina–zirconia fibre. The addition of MgO reduces the grain size and increases the tensile strength.

Keywords: Fibres; Sol–gel processes; Sintering; Al_2O_3; MgO; ZrO_2

1. Introduction

Conventionally, ceramic fibres have been prepared by drawing or blowing the high temperature melt through the orifice. This melting method requires conversion of raw materials to a homogeneous, high temperature melt, making it difficult to prepare fibres of compositions, which are high melting or immiscible in the liquid state. In the case of glassy and amorphous fibres uncontrollable crystallisation may inhibit fibre drawing from the melt.[1] The sol–gel technique[2] applied to fibre preparation is free from these difficulties. In the sol–gel technique, the sol is hydrolysed and then condensed and/or polymerised until an appropriate viscosity for spinning is achieved for the production of fibre.[3] 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 material in the form of mats, blankets, boards, etc.[4] The incorporation of alumina fibres in metal alloys and ceramics improves the mechanical properties and modifies some physical properties.[5] Alumina–zirconia fibre has been reported to improve high-temperature properties compared to alumina fibre.[6] Fibre PRD-166 was developed by Dupont and consists of a continuous polycrystalline filament containing about 80% alumina, 20% zirconia and small quantities of yttria. It has excellent mechanical and physical properties with good retention of these properties after exposure to high temperature, which make the fibre, a potential candidate for high temperature application in composites with metal or ceramic matrices.[6–8] The fine dispersion of tetragonal zirconia has been reported to contribute to the higher strength of alumina–zirconia fibre.[9,10] It has been long recognised that very small amounts of MgO additions can lead to densification of alumina to theoretical level.[11] In this paper, the effect of magnesium oxide on sol–gel spun alumina and alumina–zirconia fibres is reported.

2. Experimental procedures

Alumina sol was prepared according to the procedure described by Yoldas.[12] Aluminium-tri-isopropoxide (CDH,

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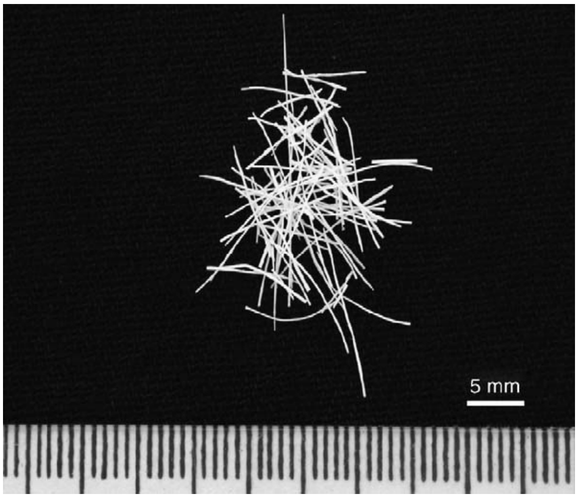

Fig. 1. Photograph of sintered Al_2O_3–1 wt.% MgO.

New Delhi) was dissolved in distilled water in a molar concentration of 1 M refluxed at 80 °C for 3 h in the presence of acid catalyst (0.07 mol nitric acid) and then cooled. Zirconium oxychloride (Otto Kemi, Mumbai) was dissolved in distilled water taken in a beaker to a molar concentration of 1 M. Oxalic acid was taken in another beaker and dissolved in distilled water to a molar concentration of 1 M. Both the solutions were mixed and stirred continuously until the solution becomes transparent. To prepare Al_2O_3–10 wt.% ZrO_2, required amount of alumina and zirconia sols were mixed. $MgNO_3$ was added to the sol such that the final composition contains 1 and 2 wt.% MgO. Hydroxy ethyl cellulose (HEC) was added as binder to the sol to impart green strength and plasticity. The sol was then concentrated by the removal of water to achieve required solid loading. When the sol was appropriate for forming fibres, it was taken in a 10-ml syringe and then fibres were drawn in a rectangular glass tray containing ammonia solution. The gelled fibres were separated from the ammonia solution and then dried at room tempera-

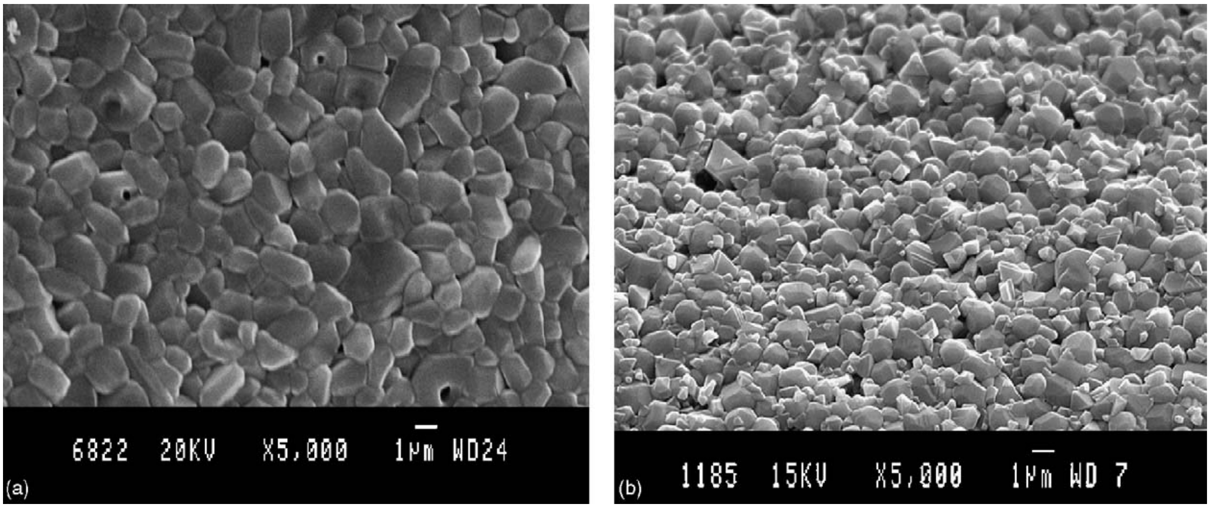

Fig. 2. Microstructure of alumina fibre: (a) without MgO and (b) 2 wt.% MgO.

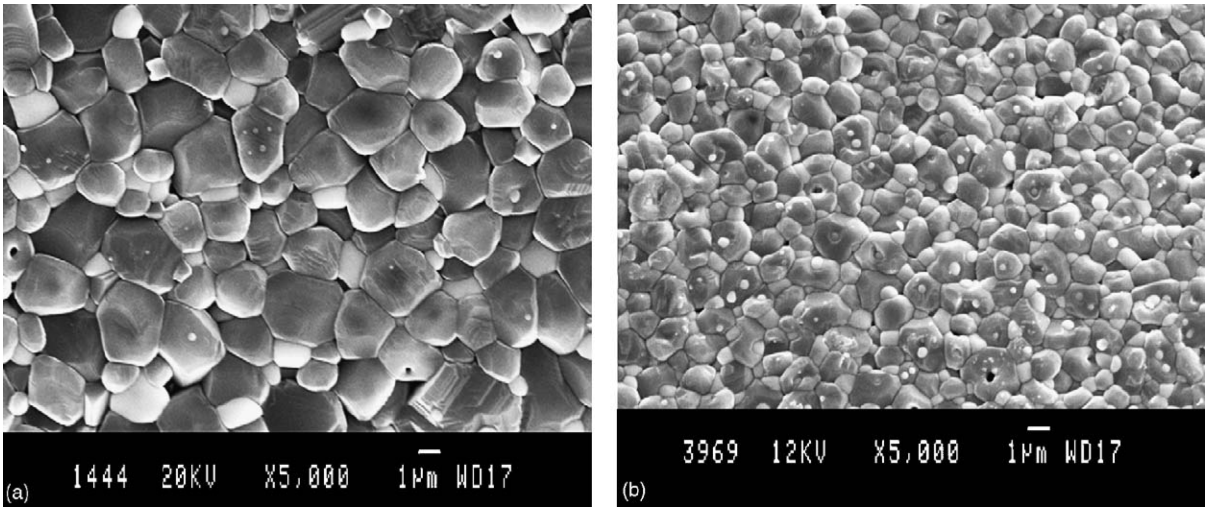

Fig. 3. Microstructure of alumina–zirconia fibre: (a) without MgO and (b) 2 wt.% MgO.

ture. The dried fibres were then sintered at 1600 °C for 2 h at a heating rate of 5 °C/min.

The fibres were characterised using X-ray powder diffractometer with Cu Kα radiation (SHIMADZU, XD-DI), Thermal analyser (NETZSH, STA409PC), Fourier transform infrared spectrometer by the KBr method (PERKIN ELMER, RXI) and Scanning electron microscope (JEOL, JSM-840A). Tensile strength of the sintered fibres was determined by Universal testing machine (INSTRON 4301). Fibre was mounted with adhesive on chart paper tabs for aligning and gripping. A 5 mm gauge length and a crosshead speed of 0.5 mm/min was used in all these tests. The fracture load was converted to tensile strength by measuring the cross-sectional area of the fibre with an optical microscope. Ten samples were tested for each set and the average values are reported.

3. Results and discussions

A typical photograph of sintered alumina fibres is shown in Fig. 1. The diameter of the sintered fibre varies from 115

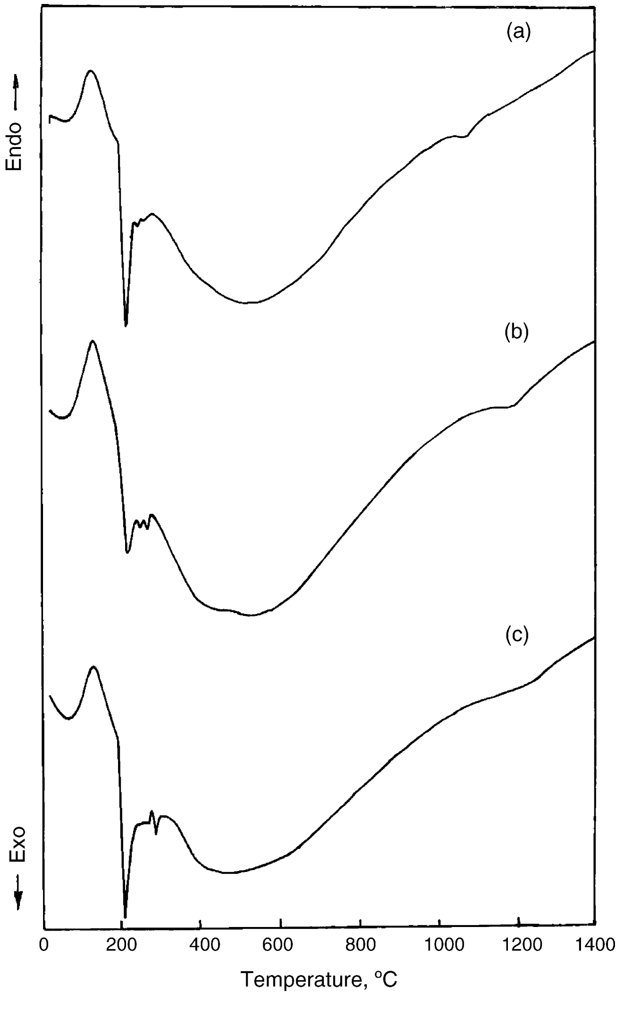

Fig. 4. Differential thermal analysis of dried alumina fibre: (a) without MgO; (b) 1 wt.% MgO and (c) 2 wt.% MgO.

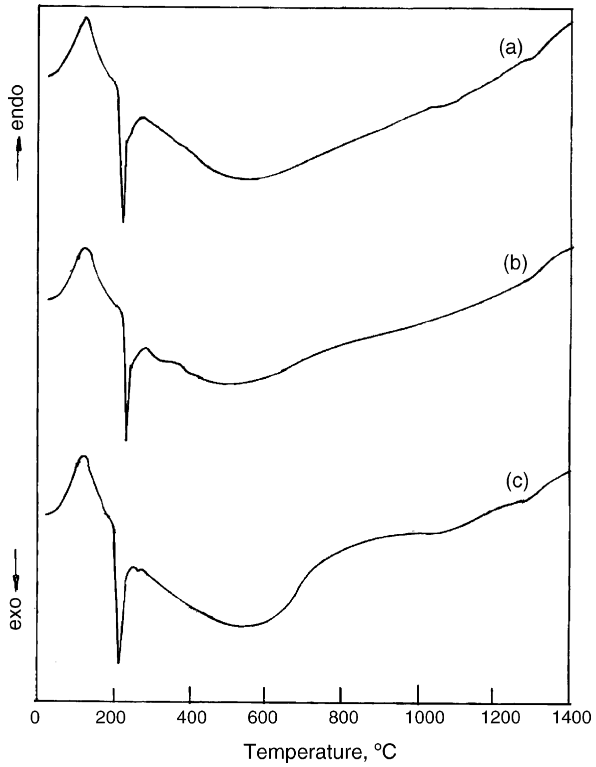

Fig. 5. Differential thermal analysis of dried alumina–zirconia fibre: (a) without MgO; (b) 1 wt.% MgO and (c) 2 wt.% MgO.

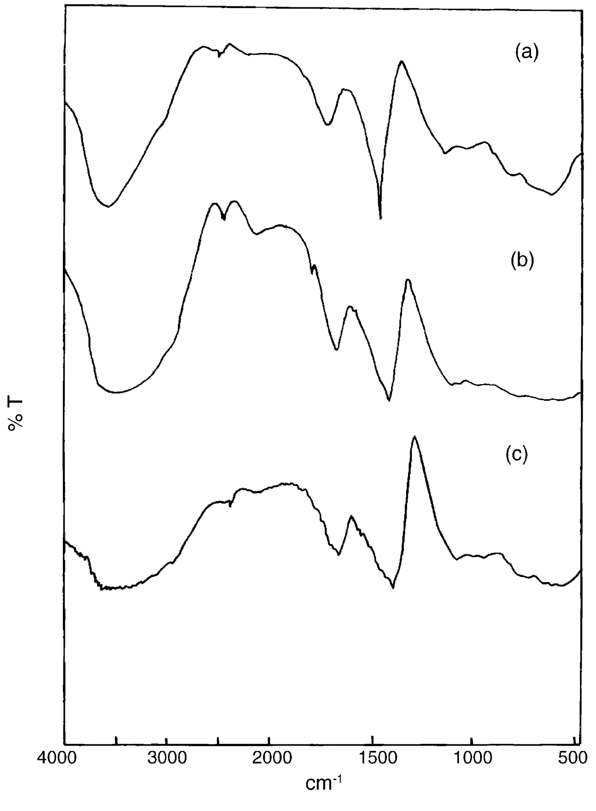

Fig. 6. FTIR analysis of dried alumina fibre: (a) without MgO; (b) 1 wt.% MgO and (c) 2 wt.% MgO.

to 200 μm. Figs. 2 and 3 show the microstructure of alumina and alumina–zirconia fibres. As the MgO content increases to 2 wt.% the grain size decreases. The grain size of alumina fibre without MgO varies from 1 to 4 μm, whereas it varies from 1 to 2.7 μm with 2 wt.% MgO. For alumina–zirconia fibre without MgO, the grain size varies from 1 to 4 μm, whereas the grain size varies from 1 to 3 μm as the MgO content increases to 2 wt.%. One theory states that grain growth is inhibited by the reduction of grain boundary mobility upon forming a solid solution, i.e., by the mechanism of solid drag.[13] One of the hypotheses is based on the assumption that grain boundary movement in alumina occurs by the addition and subtraction of atoms to and from kinks in steps on adjoining grains. It is suggested that Mg^{2+} ion can poison these kinks in steps on attachment or detachment and thus reduce grain boundary mobility.[14] Experimental evidence suggests that the role of MgO can be attributed mainly to its ability to lower the grain boundary mobility.[15]

Differential thermal analysis of alumina fibre and alumina–zirconia fibre containing 0, 1 and 2 wt.% MgO was performed at 10 °C/min. and is shown in Figs. 4 and 5. The curve has an endothermic peak at ~125 °C corresponds to the loss of adsorbed water. The exothermic peak at ~215 °C corresponds to decomposition of organic binder. The small exothermic peak around 1100 °C in alumina fibre without MgO corresponds to crystallisation of α-Al_2O_3. In the presence of MgO, the α-Al_2O_3 phase crystallisation temperature was at ~1250 °C. The increase in transition temperature is due to increase in resistance to phase transformation with decreasing grain size.[16] The small exothermic peak around ~1290 °C in alumina–zirconia fibre without MgO corresponds to crystallisation of α-Al_2O_3. The hydroxides of aluminium and its derivatives are dehydrated to transitional aluminas with change in pore structure to accommodate densification.[17,18] The formation of α-alumina from transitional aluminas involves the rearrangement of the oxygen lattice from a more or less distorted cubic array to a hexagonal close packed structure. After this transformation, the cations occupy the octahedral sites and there is an increasing ordering of the cation vacancies. As α-Al_2O_3 forms by nucleation and growth process, spherical colonies of α-Al_2O_3 nucleate in a porous matrix of transitional aluminas and then grow. Higher amount of zirconia can be dissolved in transitional aluminas than in α-Al_2O_3 because of the cubical spinel structure with a considerable number of defects and disorder.[17] During the transformation to α-Al_2O_3, the zirconium ions come out of the cubic lattice sites and enter the interstitial and vacant sites causing expansion of the lattice along the *a*-axis. The zirco-

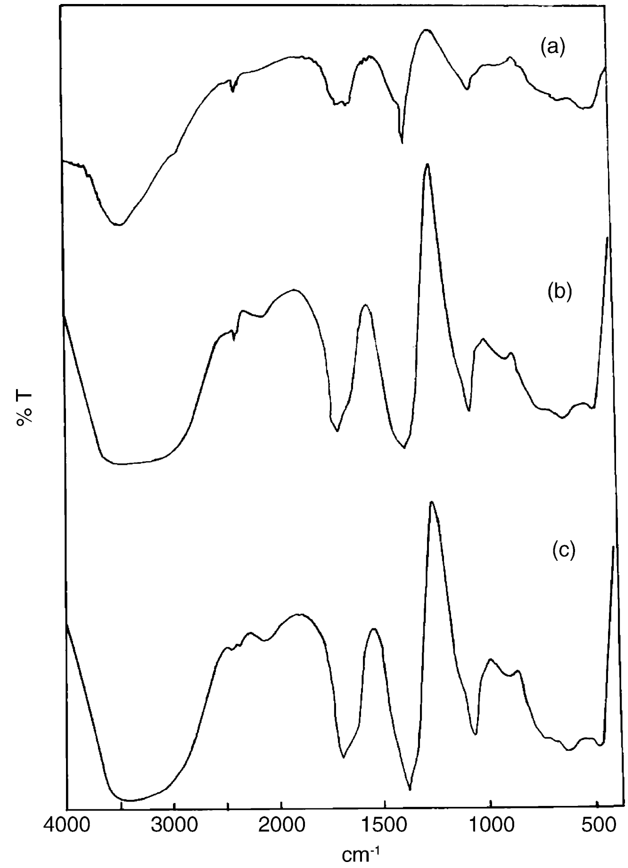

Fig. 7. FTIR analysis of dried alumina–zirconia fibre: (a) without MgO; (b) 1 wt.% MgO and (c) 2 wt.% MgO.

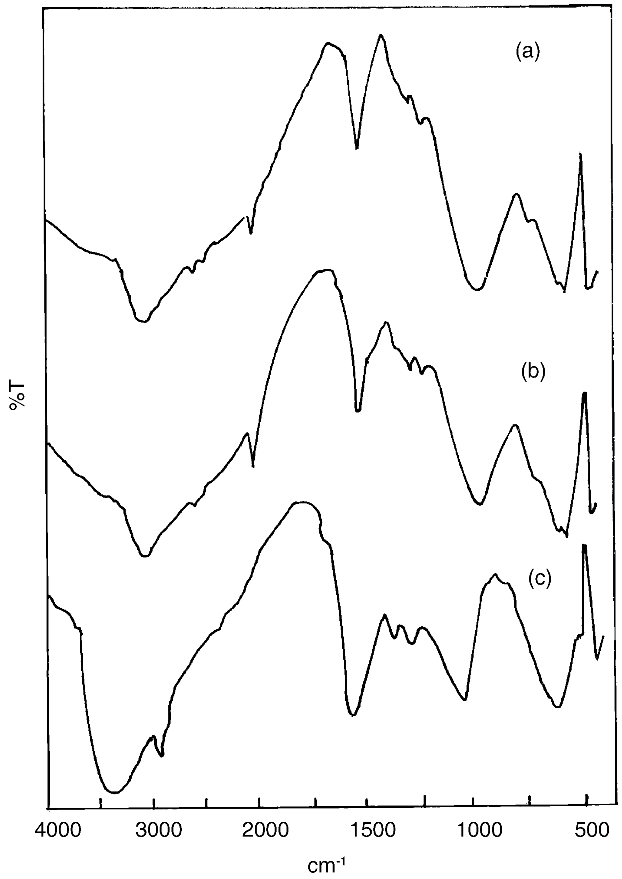

Fig. 8. FTIR analysis of sintered alumina fibre: (a) without MgO; (b) 1 wt.% MgO and (c) 2 wt.% MgO.

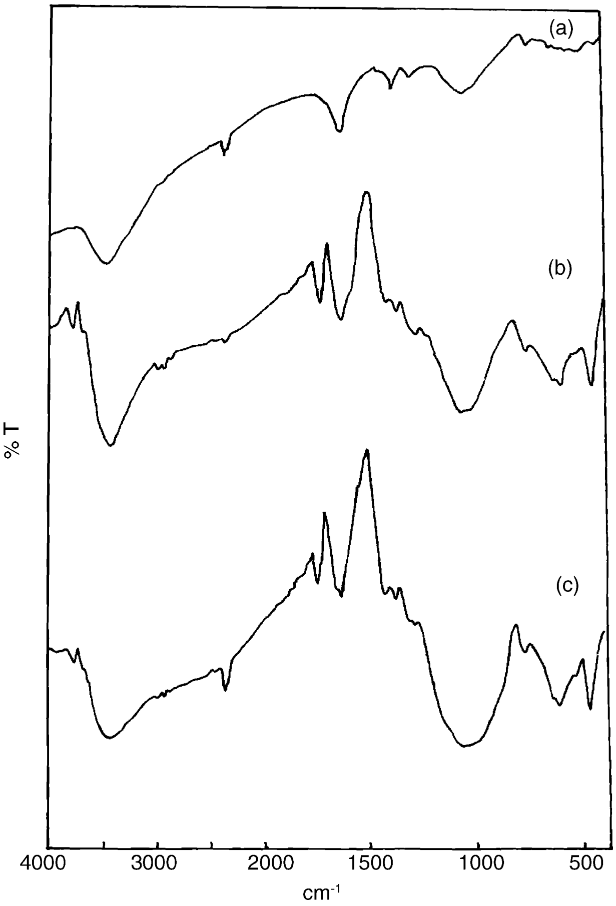

Fig. 9. FTIR analysis of sintered alumina–zirconia fibre: (a) without MgO; (b) 1 wt.% MgO and (c) 2 wt.% MgO.

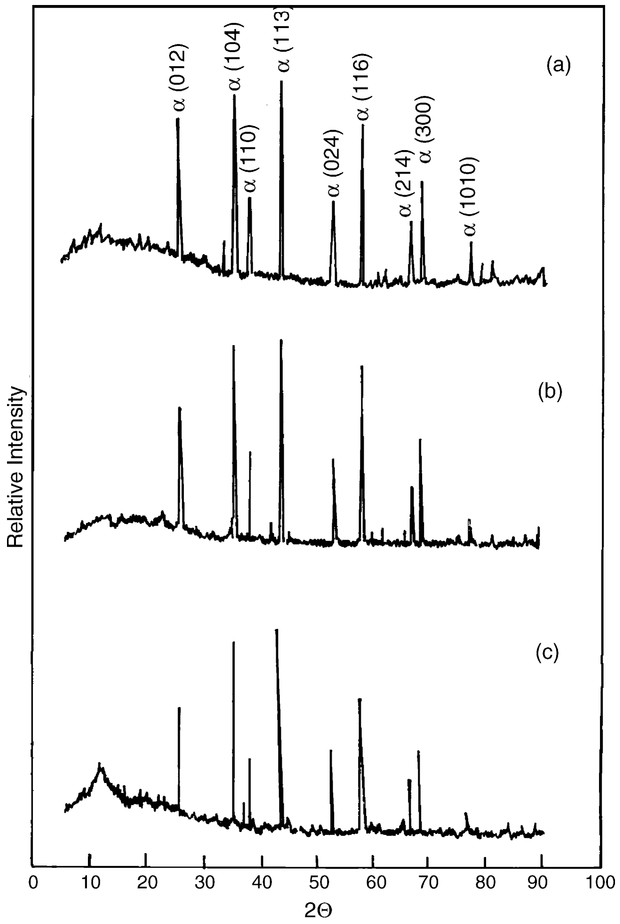

Fig. 10. X-ray diffraction analysis of sintered alumina fibre: (a) without MgO; (b) 1 wt.% MgO and (c) 2 wt.% MgO.

nium ions probably exert a dragging force on the diffusion of aluminium ions. Because of these reasons, the transformation to α-Al_2O_3 occurs at higher temperature in the presence of zirconia.[19] As the MgO content increases to 2 wt.% the transformation temperature increases to 1302 °C. The combined effect of MgO and ZrO_2 is responsible for the increase in transformation temperature. The effect of MgO is less in alumina–zirconia fibre when compared to alumina fibre due to the dissolution of MgO in zirconia.

FTIR analysis was performed for both the gel and oxide fibres in the wavenumber region of 4000–400 cm^{-1}. The spectra of dried and sintered alumina and alumina–zirconia fibre is shown in Figs. 6–9.The absorption recorded at about 3450 cm^{-1} is due to the presence of adhesive water.[20] This is also present in the fibres sintered at 1600 °C for 2 h. This may be due to the absorption of moisture during testing. The broad band at 2060 cm^{-1} indicates the presence of hydrogen bonded OH.[21] This is absent in sintered fibre. The absorption at 1650 cm^{-1} is due to O–H bending mode confirming the presence of adhesive water.[20] The bands observed at 1380 cm^{-1} and 1070 cm^{-1} correspond to Al–OH bending mode.[22] The broad band in the region 540 cm^{-1} corresponds to Al–O vibration mode.[23] In addition to that, a band is observed at 610 cm^{-1} corresponds to AlO_6 vibration.[22] A well-defined absorption at 460 cm^{-1} corresponds to Al–O vibration of α-Al_2O_3.[22] In addition to the bands observed for alumina fibre Zr–O stretching vibration bands are observed in alumina–zirconia fibre at 480 cm^{-1} in dried fibre[24] and at 550 cm^{-1} in sintered fibre.[24]

Figs. 10 and 11 show the X-ray diffraction patterns of sintered alumina and alumina–zirconia fibres containing 0, 1 and 2 wt.% MgO. The phase present in alumina fibre is α-Al_2O_3. The phases present in the sintered alumina–zirconia fibre without MgO are α-Al_2O_3, t-ZrO_2 and m-ZrO_2. Only α-Al_2O_3 and t-ZrO_2 phases are present when MgO is added. Thus, MgO acts as a stabilising agent of t-ZrO_2.

The tensile strength values of alumina and alumina–zirconia fibres are given in Tables 1 and 2.

Table 1
Tensile strength values of alumina fibres

Sample	Tensile strength (MPa)
Al_2O_3	128 ± 10
Al_2O_3–1 wt.% MgO	162 ± 10
Al_2O_3–2 wt.% MgO	183 ± 10

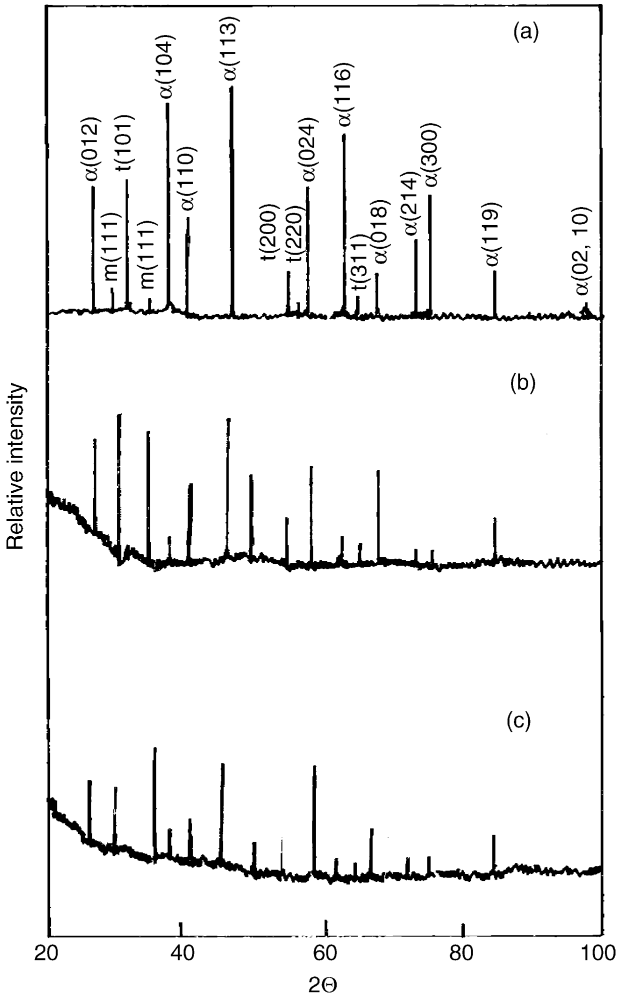

Fig. 11. X-ray diffraction analysis of sintered alumina–zirconia fibre: (a) without MgO (b) 1 wt.% MgO and (c) 2 wt.% MgO.

Table 2
Tensile strength values of alumina–zirconia fibres

Sample	Tensile strength (MPa)
Al_2O_3–10 ZrO_2	846 ± 100
Al_2O_3–10 ZrO_2–1 wt.% MgO	901 ± 40
Al_2O_3–10 ZrO_2–2 wt.% MgO	1057 ± 60

The tensile strength of alumina fibre and alumina–zirconia fibre was found to increase with increasing MgO. This is due to the decrease in grain size in the presence of MgO, as is evident from the microstructural analysis.

4. Conclusion

Alumina and alumina–zirconia fibres were prepared by sol–gel process. The phase present in alumina fibre is α-Al_2O_3 and α-Al_2O_3 and t-ZrO_2 phases are present in alumina–zirconia fibre. The retention of t-ZrO_2 is possible with the addition of MgO in alumina–zirconia fibre. The tensile strength of fibres was found to increase with MgO addition.

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