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Effect of Sinter Additives on Sol-Gel Derived Alumina Fibres

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Alumina fibre has been synthesized successfully by sol-gel technique. Boehmite sol was prepared by hydrolyzing aluminium iso-propoxide and peptizing it with nitric acid. The stable sol thus obtained was used for fibre drawing when their viscosity reached the required value as a result of progress of the hydrolyzation and polycondensation reaction. The fibres dried at 110°C for 12 hours were sintered at 1600°C for 5 hours. A reasonable sintered density with better microstructure and strength have been attained using 2 wt% of urea, magnesia and silica as sinter additives. Thermal analysis with sintering additives of 2 wt% and phase determination of the heat treated fibres using XRD and FT IR spectra confirms the phase transitions. The observation of surface and cross-section of the fibres were made using SEM. Fibres of uniform circular cross-section is obtained by fixing the shape in a setting solution.

Key words: Alumina, Sol-gel, Fibres

I. Introduction

Ceramic fibres are used as thermal insulators with low thermal mass and also as reinforcing components in ceramic matrix composites to increase the strength and fracture toughness[1]. Processing of alumina fibres have been extensively studied by many workers using methods such as unidirectional freezing of sol-gel[2,3] and sol-gel methods[4]. In the present study we report the processing of alumina fibres by sol-gel technique using aluminium iso-propoxide as the starting material as reported elsewhere[5]. It has been shown[6] that fibres can be drawn from the solutions of pertinent composition, when their viscosity reaches to spinable state as a result of progress of the hydrolyzation-polycondensation reaction. The time required for the solution to reach the drawable state is more than several days at room temperature[7] . Few hours (8 to 12) may be reasonable for the practical application which is achieved in this study, by drawing the fibres in a setting solution. The conversion of ceramic fibre is achieved by sintering the gel fibre at high temperature. The phase transition of the fibres from

$$\gamma AlOOH \rightarrow \gamma Al_2O_3 \rightarrow \delta Al_2O_3 \rightarrow \theta Al_2O_3 \rightarrow \alpha Al_2O_3$$

on heating was confirmed using XRD and FT IR studies. The effect of additives such as urea, silica and magnesia on density and microstructure has been studied.

II. Experiment

Boehmite sol was prepared by hot water hydrolysis of aluminium iso-propoxide using nitric acid as catalyst. The molar ratio of alkoxide to water and acid was maintained at 1 : 125 : 0.3. The hydrolyzation and peptization were carried out under reflux conditions with vigorous stirring for 3 hours at 80°C and then cooled to room temperature. The sol thus obtained was aged for 15 days and then concentrated by removal of water. Suitable organic binders were added to the boehmite sol in order to adjust the viscosity of the solution for drawing fibres. When the required viscosity was obtained the fibres were drawn by extrusion into a setting solution. Gel fibres drawn at room temperature can be converted to alumina fibres by sintering at 1600°C for 5 hours. Urea, silica and magnesia were used as sinter additives to obtain high density, better microstructure and strength.

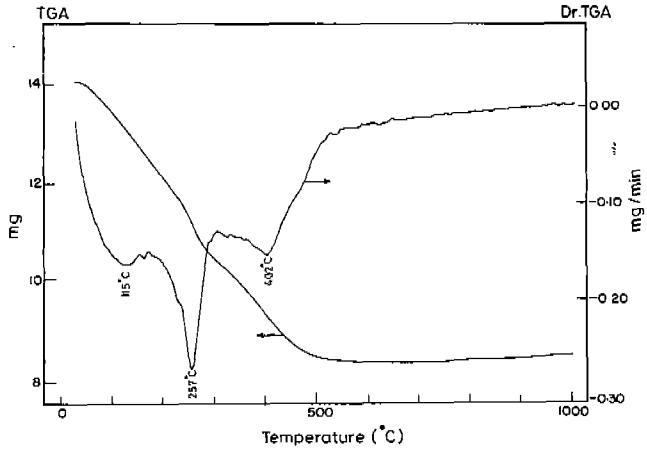

Fig. 1. TGA curve of alumina fibre from room temperature to 1000°C (heating rate=10°C/min).

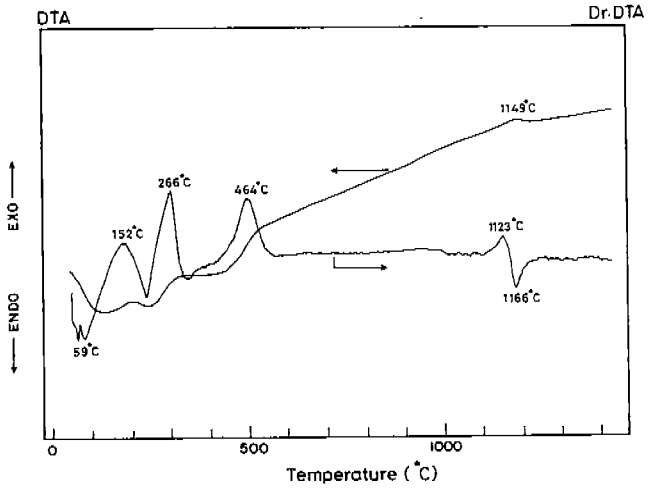

Fig. 2. DTA curve of alumina fibre from room temperature to 1300 °C (heating rate=10°C/min).

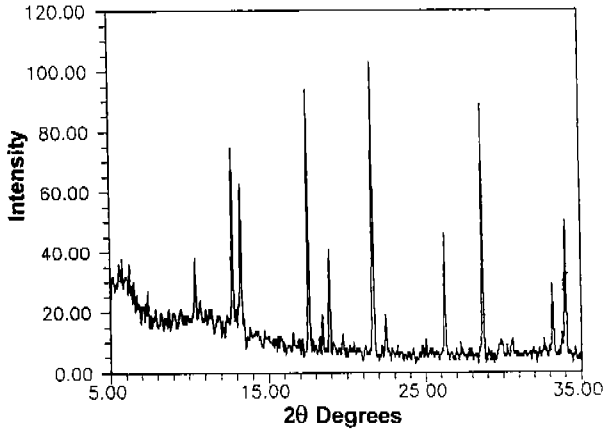

Fig. 3. XRD pattern of alumina fibre sintered at 1600°C for 5 hrs.

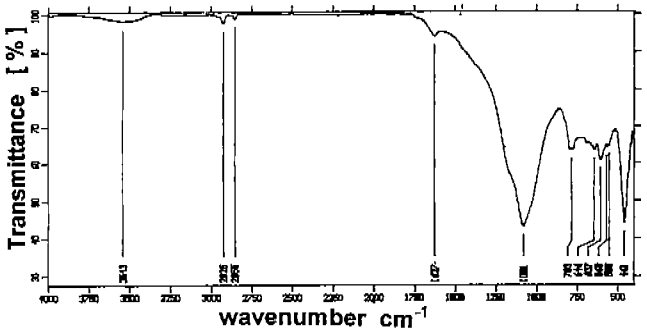

Fig. 4. FT IR spectra observed for alumina fibre sintered at 1600°C for 5 hrs.

III. Results and Discussion

3.1 Thermal analysis

Fig. 1 and Fig. 2 are the TGA and DTA curves of a alumina fibre heated at a rate of 10°C/min. The TGA curve exhibits three distinct stages of weight loss up to 464°C. The first broad endothermic peak ranges from 59-152°C with a peak at 115°C is attributed to the evaporation of water adhering to the micropore walls of the fibres. The weight loss in this range is 9.1 wt%. The second endothermic peak is observed in the range of 152-266°C and the peak is obtained at 257°C. The sample continuously losses water molecules presumable and the weight loss during this process is 12.7 wt%. The third endothermic peak observed in the range of 266-464°C corresponds to the transformation of the boehmite into γ-Al_2O_3. The peak is observed at 402°C. The weight loss during this process is 17.9 wt% which is slightly higher than the expected value of reaction.

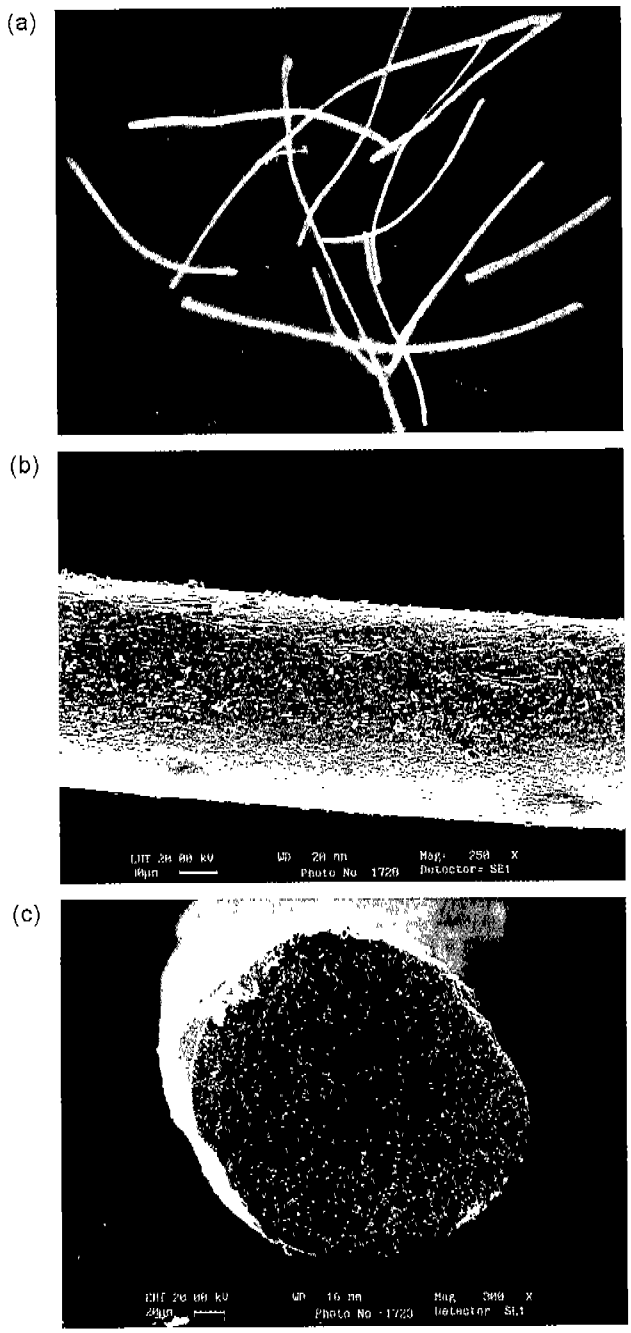

Fig. 5. Photograph of alumina fibre (a) optical (b) SEM-surface and (c) SEM-cross-section.

$$2AlOOH \rightarrow \gamma\text{-}Al_2O_3 + H_2O$$

The total weight loss observed in TGA study was about 43% of the original weight of the sample coinciding with the earlier report[8]. The α-alumina crytallisation is indicated by the exothermic peak in DTA curve at 1149°C.

3.2 XRD stuies

The XRD pattern in Fig. 3 shows that the α- phase starts at 1050° C itself and the reaction is complete at 1150°C. However, the formation temperature of α-alumina reported by Saraswathi *et al.*[9] is only around 1200°C. The formation of α-alumina at a lower temperature in the present study is due to the excess surface reactivity which is associated with the very fine γ-alumina

3.3 FT IR studies

The FT IR spectra in Fig. 4 characterized by peak at 3483 cm^{-1}, 2924 cm^{-1} and 2853 cm^{-1} shows the presence of AlO-H stretching mode. Al-OH bend mode has been observed at 1087 cm^{-1} and 1383 cm^{-1}. However a well defined peak obtained at 1631 cm^{-1} corresponds to H-O-H bend confirms the presence of free water in the sample. Poorly resolved bands in the range below 779 cm^{-1} correspond to the Al-O vibrational mode. The phase transition to α-phase is confirmed by the well defined peak obtained as expected at 412 cm^{-1}. The characteristic absorption peak at 412 cm^{-1} shows the starting of $\alpha\text{-}Al_2O_3$ in the sample. The complete conversion to $\alpha\text{-}Al_2O_3$ at 1200°C in corroboration with the XRD studies is confirmed by the analysis of the FT IR spectra

3.4. Microstructure of surface and cross section

The optical and scanning electron micrograph of the surface and that of the cross section of the fibre extruded from the boehmite gel are illustrated in Fig. 5(a) to Fig. 5(c), respectively. The surface morphology of the fibres without any additive and with 2 wt% of urea, magnesia and silica respectively are evident from the Fig. 6(a) to 6(d). The surface morphology of the pure alumina fibre exhibited uniform arrangement of the fine grain with entrapped pores. The addition of urea revealed distinct grains with homogeneous grain size. The surface morphology of the magnesia doped fibres revealed dense crystallographically distinct grains with intragrain pores. Silica doped fibre shows homogeneous platelets grains oriented with their basal plane parallel to the surface.

The impact of the additives on the microstructure of cross-section of the alumina fibres drawn without any additive and with 2 wt% of urea, magnesia and silica respectively as sinter additives was most evident from the Fig. 7(a) to 7(d). Microstructure of cross-section of the fibre with additives contrasted sharply with pure fibres as shown in the figures. When the fibres were undoped the fibres exhibited moderate densification because of the transformed alumina retained much of the uniform fine grained character. However intergrain and intragrain pores have been observed. Urea addition causes promoted densification due to more

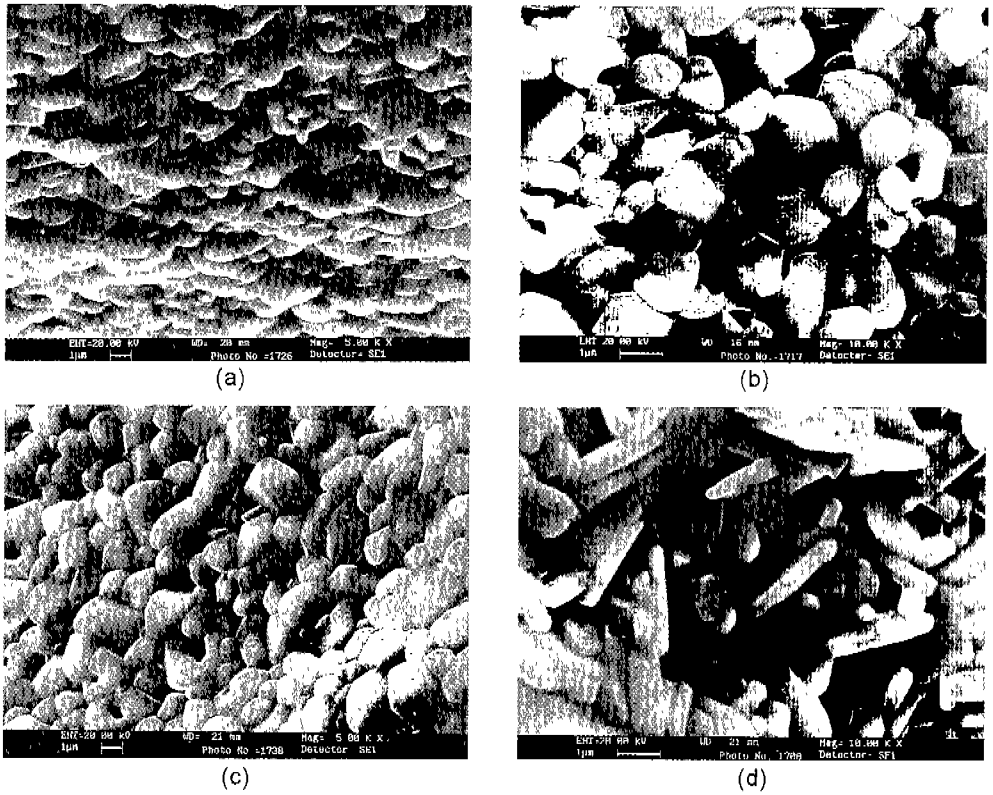

Fig. 6. Effect of additives (2.0 wt%) on microstructure of surface (a) without additive and with (b) urea (c) magnesia and (d) silica.

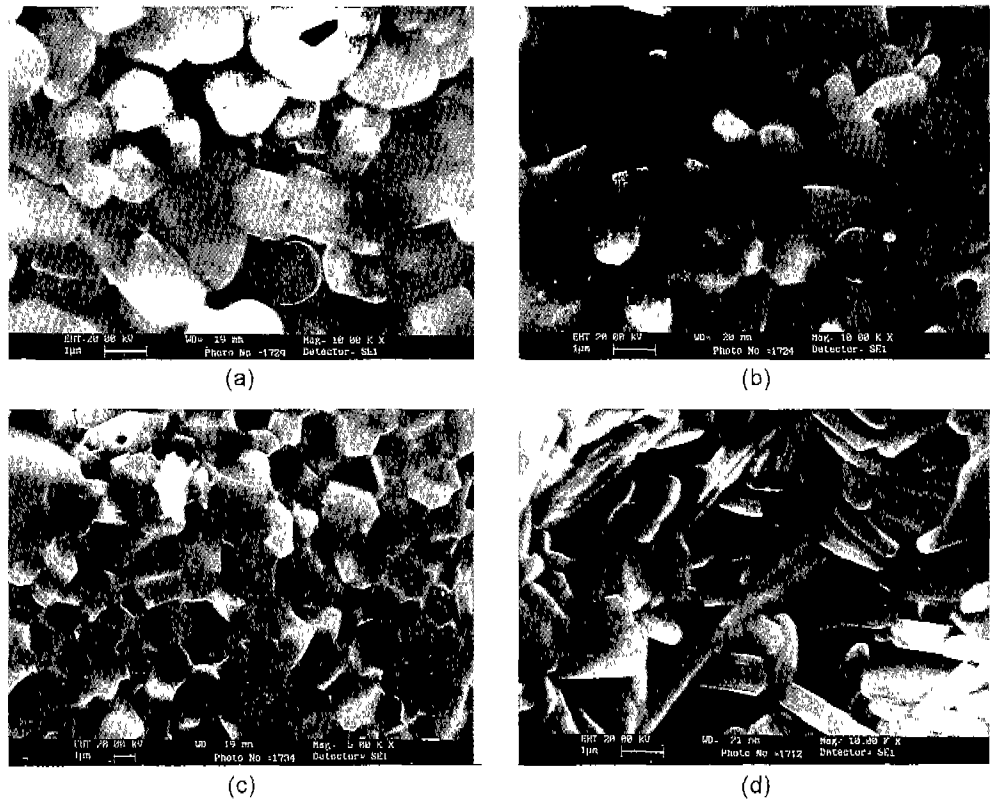

Fig. 7. Effect of additives (2.0 wt%) on microstructure of cross-section. (a) without additive and with (b) urea (c) magnesia and (d) silica.

uniform grains with very few intragrain pore. The addition of magnesia cause an increase in average grain size and grain shape with narrow distribution of small pores. However the addition of silica stimulates the formation of dense small platelets without intra /inter granular pores.

The cross-sectional shape of the sol-gel derived fibre has been reported to depend on water content of the sol and the diameter of the fibre. As reported by Sakka[7] and Muralidhran[10], increased water or decreased diameter of the fibre results more circular cross section. In the present work irrespective of the water content of the sol and the fiber diameter, fibres of uniform cross-sectional shape is obtained by fixing the shape of the fibre in the setting solution. This could be due to uniform radial shrinkage achieved during drying since the fibre shape is fixed by the setting solution.

IV. Conclusion

Alumina fibres of radii in the range 20-40 μm are formed at relatively lower temperature from boehmite sol. XRD and FT IR results confirm the transformation phenomenon from metastable orthorhombic to stable hexagonal crystalline state. The additives improve the microstructure. Urea addition causes more uniform distinct grains. The addition of magnesia improves the microstructure and eliminates the pores. Addition of silica changes the grains from equiaxial to plate like shape and more dense. Fibres of uniform circular cross-section is obtained due to uniform shrinkage during drying.

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