

Effect of organic additives on the properties of sol-gel spun alumina fibres

Ramanan Venkatesh*, Sutapa Roy Ramanan

School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (KCP), 31750 Tronoh, Perak, Malaysia

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Abstract

High alumina fibre mats (Al_2O_3 –4 wt.% SiO_2) were prepared with and without organic additives (lactic acid and PVA) using a sol-gel spinning technique. As the organic content increased, surface roughness after calcination increased, phase transition was retarded and the strength of the fibres decreased. The effect of lactic acid was more pronounced than PVA probably because of the formation of aluminium lactate resulting in an increase in its decomposition temperature as compared to PVA. Variations in heating schedules used in the calcination of alumina fibre had a significant effect on phase transition and properties of alumina fibres. It was found that at very low (60°C/h) and very high (400 and 600°C/h) heating rates the strength and handleability of the fibres decreased. Fibres having good strength (1.2 GPa) and handleability were obtained using a heating rate of 240°C/h. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3 -fibres; Mechanical properties; Sol-gel process; Spinning

1. Introduction

Alumina fibre is an important engineering material because of its high strength and modulus, resistance to attack by molten metals and non-oxide materials, chemical inertness in both oxidizing and reducing atmospheres up to 1000°C, low thermal conductivity and good electrical insulation.^{1–4} Typical applications of alumina fibre include thermal insulation, fire protection, catalysis and as reinforcement for composites.⁵ For thermal insulation alumina fibres have important advantages over the conventional aluminosilicate fibres. They can be used to much higher temperatures, i.e. 1700°C for a longer period of time with a 20% greater energy savings as compared to aluminosilicate fibres. However, one of the major disadvantages of alumina fibre is its high cost of production and the deterioration in strength at temperatures greater than 1000°C in corrosive atmospheres.^{6,7} One of the most versatile methods of producing ceramic fibres is the sol-gel technique.^{8–16} The primary advantages of sol-gel processing over other conventional melt routes are low

temperature processing, homogeneity of the products, uniform diameter of the fibres, fine grain size and good control over final properties of the fibres. Ceramic fibres have been formed through sol-gel processing either using alkoxides or inorganic sol precursors. The inorganic route is favored for producing alumina fibres at lower cost. The precursors for the sol-gel processing of alumina fibres include, aluminium oxychloride, basic aluminium chloride, aluminium formoacetate, aluminium monoacetate, etc.^{17–31} Essentially sol-gel processing of alumina fibres involves the following steps:

1. Preparation of sol with suitable additives and achieving the right rheology for spinning.
2. Spinning of the solution to obtain gel fibres.
3. Calcination of the gel fibres to obtain final oxide fibres.

It is important, however, to control all of the above three stages in order to obtain high quality fibres with the desired final properties. In the case of alumina fibres used for thermal insulation, fibres having a strength of about 1 GPa and δ -alumina phase are desired whereas for composite applications fibres having strengths of about 2 GPa are required with the resulting phase of

* Corresponding author.

E-mail address: ram5nam@tm.net.my (R. Venkatesh).

α -alumina.^{32,33} In fibres used for thermal insulation, they are normally calcined at 900°C to retain the δ -phase.³⁴

In the sol-gel spinning process, organics e.g. PVA, PEG, lactic acid, acetic acid etc. are added as spinning aids. In the present work, the effects of organics and heating schedules on the properties of the high alumina fibre mats prepared by sol-gel spinning technique have been studied.

2. Materials and experimental procedure

2.1. Preparation of alumina fibres

The alumina sols were prepared by minor modifications of the well known oxychloride route.^{32,33} The processing steps are shown in Fig. 1. Sols of aluminium oxychloride with an alumina content of 30.5 wt.% were prepared. The as-prepared sols had a viscosity of 5 P. These sols were then mixed with SiO₂ sol and lactic acid or PVA in stoichiometric proportions. The sols were then heated at 70°C to a viscosity of about 100 P and then spun using an in-house fabricated spinnerette having 120 holes of 0.4 mm diameter and rotating at a speed of 2000 rpm. The spun gel fibres were collected in a mat form in a drum heated at 60°C to prevent the sticking of fibres. The dried gel fibres were then calcined using various heating schedules at 500, 950 and 1200°C. Sols of five different compositions designated as A4S (Al₂O₃–4 wt.% SiO₂), A4S4L (Al₂O₃–4 wt.% SiO₂–4 wt.% lactic acid), A4S8L (Al₂O₃–4 wt.% SiO₂–8 wt.% lactic acid),

A4S4P (Al₂O₃–4 wt.% SiO₂–4 wt.% PVA) and A4S8P (Al₂O₃–4 wt.% SiO₂–8 wt.% PVA) were prepared.

2.2. Characterisation of fibres

Fourier transform infrared spectrometer was used to identify the species present in the gel and calcined fibres (Nicolet 5pc). Differential thermal analysis (DTA) was carried out from 25 to 1200°C at a rate of 4°C/min on a Shimadzu analyzer. The weight loss of the gel fibres in air between the ambient temperature and 1200°C were recorded on a thermogravimetric (TG) unit (Shimadzu TG 560). Microstructural features were observed under scanning electron microscope (Cambridge S250) and optical microscope (Zeiss). Surface area of the fibres were measured on a multipoint BET surface analyzer (Quantachrome Autosorb 1c) by first degassing under vacuum at about 200°C for 6–8 h. Surface area, pore volume and pore diameter were then measured using nitrogen absorption–desorption technique. Rheological properties of as-prepared and spinning sols were measured using a Haake VT550 viscometer. For as-prepared sols a cup and cone set-up was used whereas for high viscosity spinning sols, a cone and plate arrangement was used. Tensile strength of the fibres was measured using a modified set-up of Kamiya et al.³⁵ About 20 fibres were tested at a gage length of 4 mm for each composition and the average strength of the fibres were evaluated using the relationship,

Tensile strength = fractional load/fibre cross-sectional area.

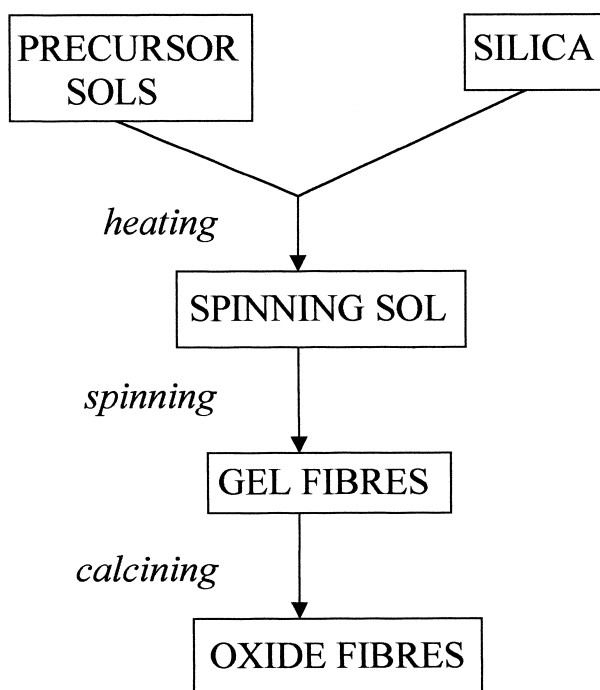


Fig. 1. Steps involved in the processing of alumina fibres.

3. Results and discussion

Rheological behavior of as-prepared and spinning sols (Fig. 2), showed Newtonian behavior which is known to be a prerequisite for fibre spinning sols.^{36,37}

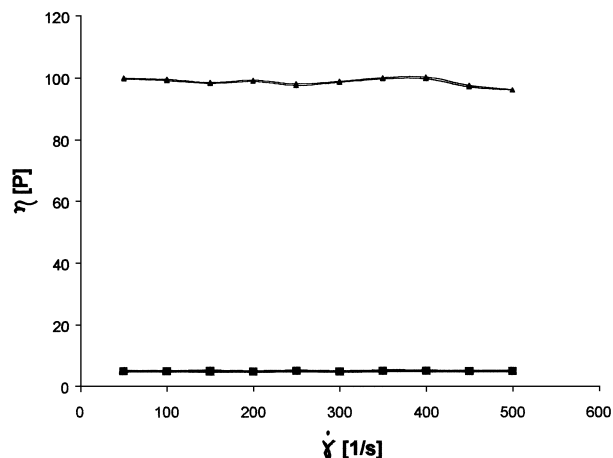


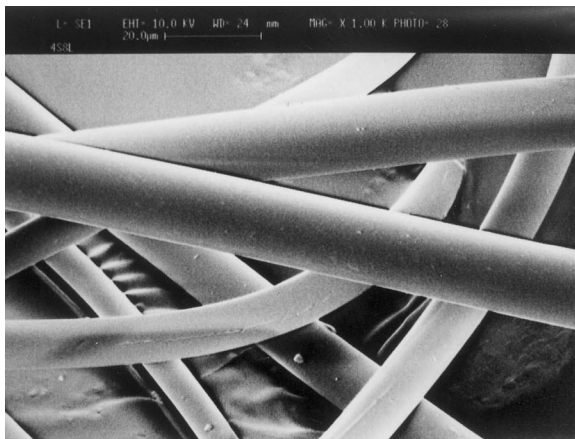
Fig. 2. Rheological properties of as-prepared and spinning sols.

The average diameter of the spun gel fibres was about 12 μm whereas that of the calcined fibre was about 6 μm . The fibres of A4S were quite smooth and flexible even after calcination at 1200°C (Fig. 3a and b). Fibres containing organics had an increased amount of surface roughness after calcination (Fig. 4a and b). Defects that can occur during fibre processing include shots, sticking of fibres, non-uniform fibre diameters, porous fibres and cone and sheath structures. Some of the defects observed in the present study are shown in Fig. 5. Fig. 5a–c shows the presence of shots, fibre fusion and porous fibres. A liquid jet unstable with respect to surface tension breaks up due to axisymmetrical surface pressure. The breakup of the jet occurs by the growth of Raleigh waves or periodic variations of increased amplitude in the jet diameter resulting in separate droplets or shots (Fig. 5a).³⁸ Improper spinning viscosity (fibre shrinkage) or drying of the gel fibres cause fibres to stick (Fig. 5b). Defects that occur during calcination are porosity and cone and sheath structures (Fig. 5c). The fibres are also found to be curved because of the centrifugal force employed during spinning. The curvature was maintained

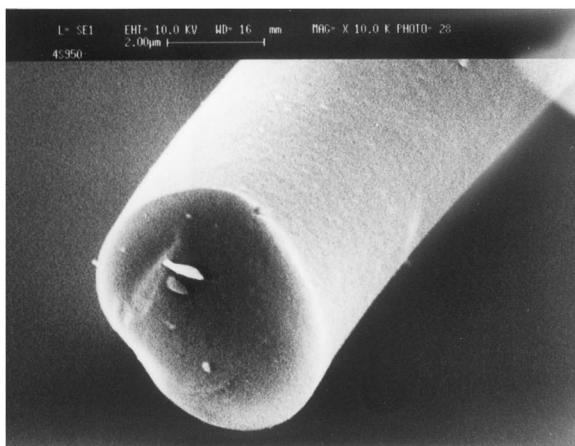
even after calcination at 1200°C (Fig. 6). The volume and diameter shrinkage after calcination increased with organic content of the gel fibres (Table 1). The highest diameter shrinkage of 67% was noted for fibres spun with 8 wt.% lactic acid. TG analysis showed maximum and minimum shrinkage of 62 and 54% for A4S8L and A4S fibres respectively (Table 1). The maximum shrinkage of about 50% occurred in all the fibres below 400°C.

The FTIR results can be divided into four regions, the details are provided in Table 2.

(i) In the region between 3000 and 4000 cm^{-1} , the peak recorded at about 3443 cm^{-1} in the gel fibres was due to the presence of molecular water.³⁹ This peak was absent in the fibres calcined at 950 and 1200°C. (ii) In the region 2 between 2000 and 3000 cm^{-1} , a broad peak noted at 2542 cm^{-1} was due to OH in Al-lactate.⁴⁰ The peaks observed at 2536 and 2343 cm^{-1} were due to Cl^- . These peaks were also present in the fibres calcined at 950°C though their intensities were considerably reduced. This was also indicated by the yellow colour of the fibres. It has been shown that minor amounts of Cl^- are present in the fibres up to a calcination temperature

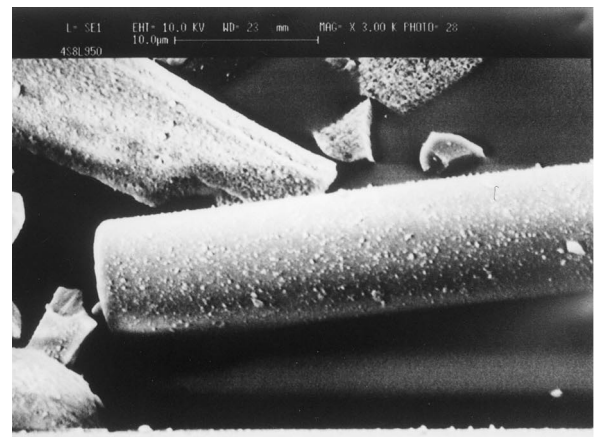


(a)



(b)

Fig. 3. (a) and (b) Smooth and flexible fibres after calcination at 1200°C.

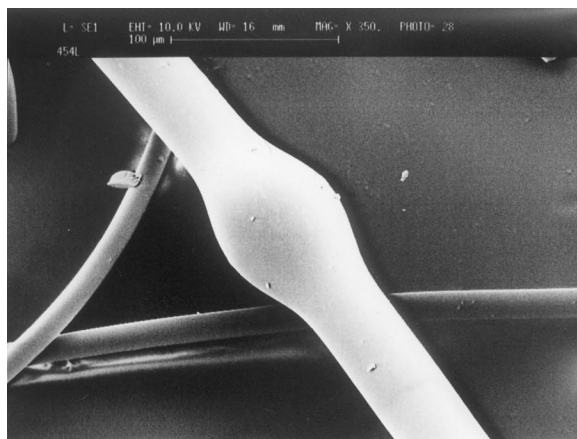


(a)

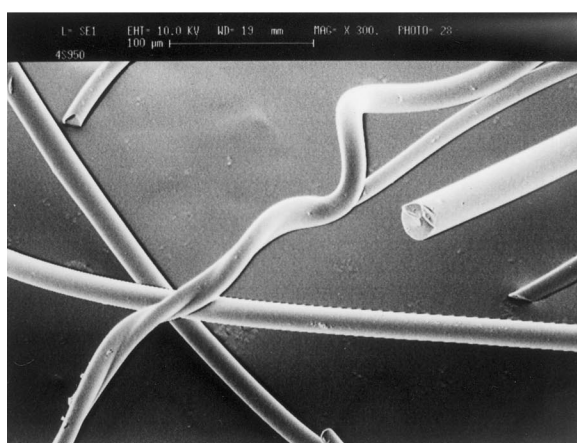


(b)

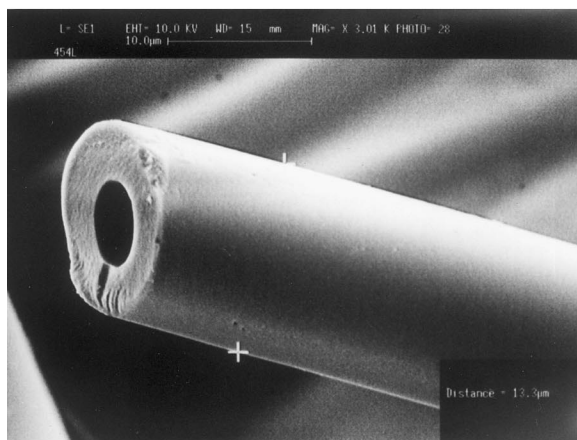
Fig. 4. (a) and (b) Fibres containing 8 wt.% lactic acid showing increased amount of surface roughness.



(a)



(b)



(c)

Fig. 5. Fibre defects originating during processing: (a) shots; (b) fibre fusion; (c) porous fibres.

of 1100°C.³⁹ The Cl⁻ peak was absent in the fibres calcined at 1200°C. (iii) In the region between 1000 and 2000 cm⁻¹ the peak recorded at about 1638 cm⁻¹ in the gel fibre is due to molecular water. The peaks observed between 1547 and 1443 cm⁻¹ in fibres containing organic additives could be due to the presence of carbon

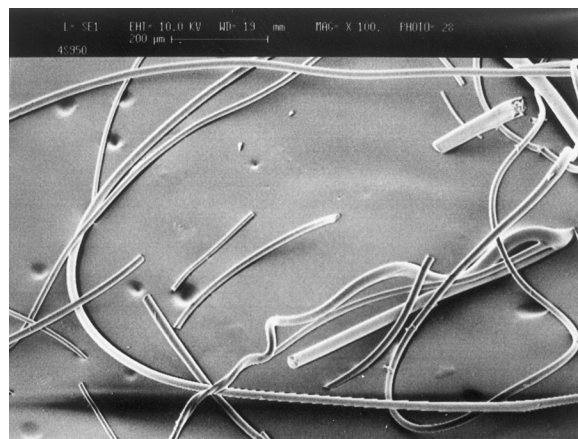


Fig. 6. Alumina fibres calcined at 1200°C showing good flexibility.

as C–O, C–C and CH₃ deformation.⁴⁰ The peak at about 1088 cm⁻¹ is due to Al–OH stretching.³⁹ Both these peaks were missing in the calcined fibres. (iv) In the region between 1000 and 400 cm⁻¹ most of the peaks recorded were due to bonds involving Al. The peak at 976 cm⁻¹ was due to Al–OH deformation.³⁹ This peak was absent in the calcined fibres. Peaks at 780 and 590 cm⁻¹ noticed in the gel fibres were due to either Al–O stretching or valence vibration in AlO₄ tetrahedra and vibration of AlO₆, respectively.³⁹ In the calcined fibres both the peaks broadened and their intensities increased. The peak broadening could be due to the high degree of disorder in the structure. In summary, the IR data indicated that as the fibres were calcined, the water, carbon and Cl⁻ are removed, Al–OH bonding was lowered whereas the formation of Al–O bond increased. Cl⁻ was present in fibres calcined up to 1100°C.

The XRD results (Table 1) show that with increase in organic content a retardation in the phase transformation of alumina was noted. In a previous work³¹ it was shown that addition of SiO₂ to alumina fibres produced without organics had a pronounced effect in retarding its phase transformation to α-Al₂O₃. α-Al₂O₃ was formed at 1200°C in fibres containing 4 wt.% SiO₂ as compared to 900°C in pure alumina fibres.³¹ In this work it was observed that the presence of organics enhanced this effect. The effect of lactic acid was more than PVA. In fibres containing lactic acid, at 1200°C, presence of δ-Al₂O₃ was noted along with θ-Al₂O₃ as compared to only θ-Al₂O₃ in fibres containing PVA. This could possibly be due to the formation of Al-lactate as indicated by FTIR (Table 2). The decomposition temperature of aluminium lactate is about 350°C⁴⁰ as compared to PVA which decomposes at 200°C.⁴¹ The DTA measurements showed endothermic peaks at 110, 280 and 360°C associated with removal of bound water and most of the chlorine.³¹ It did not show the presence of Al-lactate probably because of over-

lapping of lactate decomposition with evolution of bound water and chlorine in the fibre. Phase transformation and densification of fibres proceed after the evolution of the bound water and organics. An increase in decomposition temperature of Al-lactate as compared to PVA could retard the phase transformation of the fibres containing lactic acid.

The surface area, pore volume and pore diameter data for A4S, A4S8L and A4S8P fibres calcined at 950 and 1200°C is shown in Table 3. Pore volume, pore diameter and surface area decreased with increase in calcination temperatures for all the compositions. The minimum

average pore size and pore volume was noted for the fibres without organics and the maximum values were recorded for fibres with 8 wt.% lactic acid. This indicates the slower densification of fibres containing lactic acid during calcination as compared to fibres containing PVA. It was also found that as the organic content increased, the fibres after calcination became more brittle (Fig. 7a and b) due to increased evolution of fugitive materials during calcination. Average tensile strength of the fibres with and without organics is shown in Table 4. Maximum strength of 1.2 GPa was recorded for A4S fibres calcined at 950°C. The fibres

Table 1
Effect of organics on the phase transformation, weight loss and diameter shrinkage of alumina–4 wt.% SiO₂ fibres

Sample no.	XRD phases			Total wt. loss % at 1200°C	Total diameter shrinkage % at 1200°C
	500°C	950°C	1200°C		
A4S	$\gamma + \delta$	$\delta + \theta$ (m)	$\theta + \alpha$	54	50.7
A4S4L	A ^a	$\delta + \gamma$ (m)	$\theta + \delta$ (m) ^b	58	57
A4S8L	A	$\delta + \gamma$	$\theta + \delta$ (m)	62	67
A4S4P	A	$\delta + \gamma$	$\theta + \delta$ (m)	56	54
A4S8P	A	$\delta + \gamma$	$\theta + \delta$ (m)	59	63

^a A, amorphous.

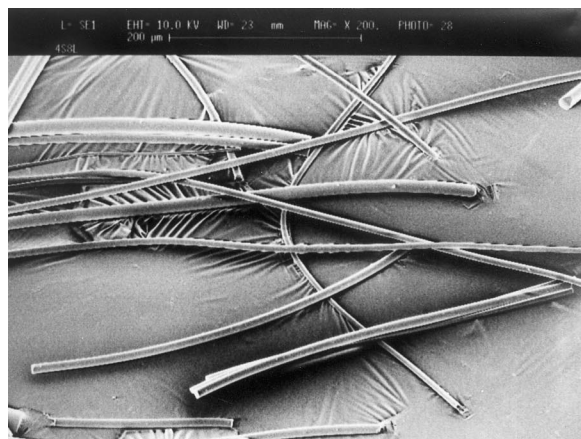
^b (m), minor phase.

Table 2
FTIR of gel and calcined alumina fibres

Wavenumber cm ⁻¹	Gel fibre	Calcined fibre		Comments
		950°C	1200°C	
3443	Major	–	–	Molecular water
2452	Minor	–	–	OH in Al-lactate
2356	Major	Minor	–	Chlorine
2343	Major	Minor	–	Chlorine
1633.9	Major	–	–	Molecular water
1443, 1478	Minor	–	–	C–C, C–O,
1486, 1547				CH ₃
1089.92	Major	–	–	Al–OH vibration
974.18	Major	–	–	Al–OH deformation
779.34	Minor	Major	Major	Al–O stretching AlO ₄ vibration
590	Minor	Major	Major	Al–O stretching AlO ₆ vibration

Table 3
The effect of organics on the surface area, pore volume and pore diameter of Al₂O₃–4 wt.% SiO₂ fibres

Sample no.	Surface area (m ² /g)		Pore volume (cc/g)		Pore diameter (nm)	
	950°C	1200°C	950°C	1200°C	950°C	1200°C
A4S	58	12	1.34	0.28	18	7.4
A4S4L	70.2	15	–	–	–	–
A4S8L	78	20	2.42	2.03	63	35.8
A4S4P	60.3	13	–	–	–	–
A4S8P	69	17	2.42	1.7	28.6	14



(a)



(b)

Fig. 7. Fibres containing organics showing increased brittleness: (a) no organics; (b) A4S8L fibre.

with PVA were very brittle. This could possibly be due to the fact that these fibres had lower average pore diameter than that containing lactic acid thereby resulting in increased capillary pressure during volatile evolution⁴² which causes the fibre to become brittle.

The various heat treatment schedules and the phases obtained for A4S fibres are shown in Table 5. It was observed that as the heating rate increased the phase transition became faster. Generally in sol-gel processing due to the high shrinkage, heating rate has to be slow in order to prevent cracking. In an earlier work³¹ it was noted that as the calcination schedule increased from 60 to 240°C/h the strength and handleability of the fibres increased. At lower heating rates (60°C/h) the fibres were exposed to higher temperatures for longer times. This exposure for fine diameter alumina fibres caused accelerated phase transformation and grain growth resulting in decreased strength. Rapid heating of the fibres (400 to 600°C/h) to high temperatures enhanced thermal shock because of high volume shrinkage and resulted in a dusty product.³¹

Table 4
Strength of the prepared alumina fibres

Sample	Strength (GPa)	
	950°C	1200°C
A4S	1.2	0.6
A4S4L	0.95	0.54
A4S8L	0.78	0.46
A4S4P	c.n.d ^a	c.n.d
A4S8P	c.n.d	c.n.d

^a c.n.d, could not determine.

Table 5
Crystal phases formed in alumina fibres calcined at various heating schedules

Temperature (°C)	Heating rate (°C/h)	Soaking time (h)	Phase
950	60	1	$\theta + \alpha$
1100	60	1	α
950	240	1	$\delta + \theta$ (m) ^a
1200	240	1	$\theta + \alpha$
950	400	1	$\theta + \alpha$
1200	400	1	α
950	600	1	$\theta + \alpha$
1100	600	1	α
25–500	60	1	$\theta + \delta$ (m)
500–950	240	1	$\theta + \delta$ (m)
25–500	120	1	$\theta + \delta$ (m)
500–950	240	1	$\theta + \delta$ (m)

^a (m), minor phase.

4. Conclusion

Fibres with uniform diameter and good strength and handleability can be formed using sol-gel spinning technique. As the organic content increased, the surface roughness of the fibres increased and the strength of the fibre decreased. The effect of lactic acid was more than PVA probably because of the formation of Al-lactate. Calcination schedules also had important effects on the phase transformation and properties of the alumina fibres. At very slow (60°C/h) and very high (400–600°C/h) heating rates the fibres became very brittle and a dusty product was obtained. Fibres having good strength and handleability were obtained using an intermediate heating rate of 240°C/h for 1 h. Controlling the amount of organics and its decomposition temperature and also calcination schedule can be used to generate fibres having optimum strength and handleability.

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