

# The preparation of alumina fibre by sol–gel processing

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Attempts have been made to prepare alumina fibre from the colloidal sol and polymerized alkoxides. The aluminium chloride or aluminium nitrate systems were found to be potential methods for producing continuous alumina fibre: the aluminium nitrate system had a better sintering behaviour than the aluminium chloride system. The aluminium isopropoxide system, however, was unsuitable for preparing alumina fibre but was suitable for the preparation of monoliths, membranes, powders, and multicomponent ceramics. The thermal changes of these precursors were studied by transmission electron microscopy, Fourier-transform infrared spectroscopy and X-ray diffraction. The results demonstrated the different routes of phase transformation as the temperature increases. The aluminium chloride system exhibits two routes for phase transformation: (a) boehmite  $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\text{-Al}_2\text{O}_3$ , and (b) gibbsite  $\rightarrow \chi \rightarrow \kappa \rightarrow \alpha\text{-Al}_2\text{O}_3$ .

## 1. Introduction

Special environments, such as aerospace, automotive, and chemical industries require materials possessing excellent mechanical strength and heat resistance (1). For example, automotive industries select fibre-reinforced ceramic-matrix composites as viable candidates for rocket engines.

Attempts have been made to use alumina fibre as a reinforcement for composite materials, because it is cheaper than other oxide fibres and is known to be stable in an oxidative atmosphere. Owing to the high melting temperature of alumina, it can still retain its excellent mechanical strength [2, 3] even at higher temperatures in comparison with carbon fibre or metal fibres. In aluminium and magnesium metal matrix composites especially, the stiffness and fatigue properties of alumina fibre are equal to those of a steel component of twice the weight [4].

The preparation of alumina fibres by spinning melt is very difficult, due to the exceedingly high melting temperature and the low viscosity of the melt. Therefore, an alternative process, the sol–gel method, has been adopted, in which the solution is hydrolysed and then condensed and/or polymerized until an appropriate viscosity for spinning is achieved for the production of alumina fibre [5–8]. Some advantages of the sol–gel method over the conventional melting method are better homogeneity, purity, lower sintering temperature, and special item control [9].

Depending on the starting materials, such as aluminium salts, and alkoxides, the sol–gel processing can be categorized to colloidal gel and polymerized gel [10]. In the present work, alumina fibre was synthesized by the two methods to compare the properties of these preparations. To establish a learning

curve for the present process was a significant aim of this research, which could be potentially applied to other continuous and multicomponent fibres.

## 2. Experimental procedure

### 2.1. Colloidal sol processing

Alumina fibres formed by the sol–gel method are similar to those previously reported [5, 11]. The processing flow diagram for alumina fibre is shown in Fig. 1. Aluminium chloride ( $\text{AlCl}_3$ ), aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), aluminium metal pellets, and deionized water were the starting materials for the colloidal sol method. The processing difference between the aluminium chloride and aluminium nitrate systems was solely that the aluminium metal pellets of the aluminium nitrate system had been treated to dissolve easily in aluminium nitrate solution.

### 2.2. Polymerized alkoxides processing

Fig. 2 summarizes the flow chart of the polymerized alkoxides process. Aluminium isopropoxide ( $\text{Al}(\text{OC}_3\text{H}_7)_3$ ), isopropyl alcohol ( $\text{C}_3\text{H}_7\text{OH}$ ), and deionized water were the starting materials for the polymerized alkoxides method.

### 2.3. Characterization and analysis

The structure of post-refluxing solutions was studied by infrared transmission spectroscopy. TEM was used to determine the structure of the aerogel. The weight loss and phase transformation of dried precursors was determined by thermogravimetric analysis/differential thermal analysis (TGA/DTA) and X-ray

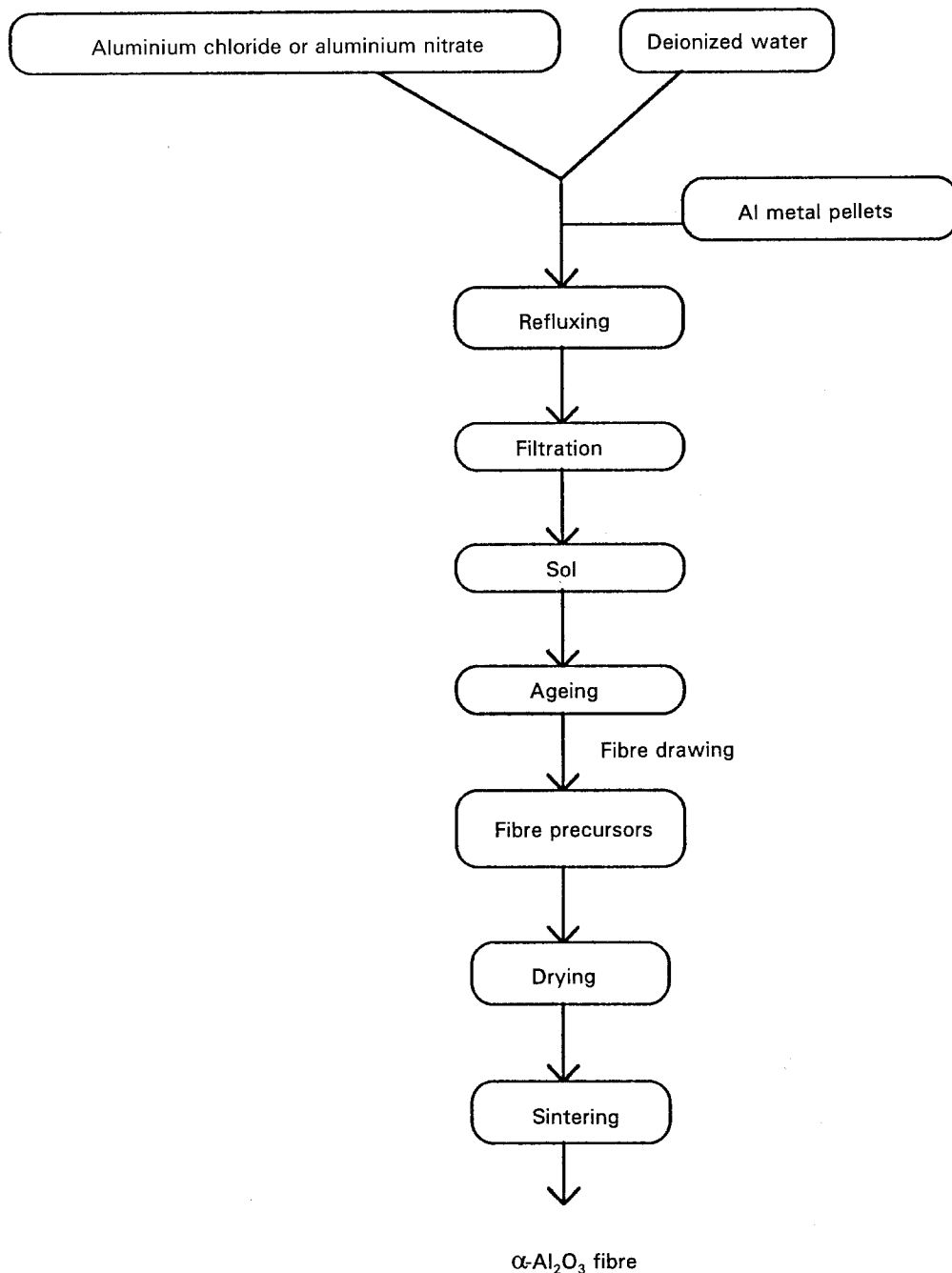


Figure 1 Colloidal processing flow diagram for the preparation of alumina fibre.

diffraction (XRD). Fibre morphologies were also characterized by scanning transmission electron microscopy (SEM).

### 3. Results and discussion

#### 3.1. Characterization of sol-gel conversion

##### 3.1.1. Colloidal sol for the aluminium chloride system

Tables I and II show the characterization of sols prepared by heating a suspension of 1 mol  $\text{AlCl}_3$  in 22.2 mol  $\text{H}_2\text{O}$  at about 80–85 °C and 100–110 °C in reflux for 1–3 h. The characteristics of sol-gel conversion change with the dissolved content of aluminium pellets and various ageing conditions. Four interesting results were observed and are summarized in Tables I and II.

1. The more aluminium dissolved, the more opaque and the more viscous the initial state of the post-refluxing solution became.

2. The spinnability of the solution was determined by the dissolved content of aluminium pellets. Sample 4 of Table II shows that a solution will not become spinnable when the  $\text{H}_2\text{O}/\text{Al}^{3+}$  molar ratio (initial  $\text{H}_2\text{O}$  mole/ $\text{Al}^{3+}$  mole in solution) is more than 11.3.

3. In addition to the dissolving rate of the aluminium pellets, refluxing at 80–85 °C was not apparently different from refluxing at 100–110 °C.

4. Comparing Samples 1–3 of Table I with the Samples 1–3 of Table II, reveals that the gelation time is not only dependent on the dissolved content of aluminium pellets but also strongly on the ageing conditions and additives. The more aluminium that is

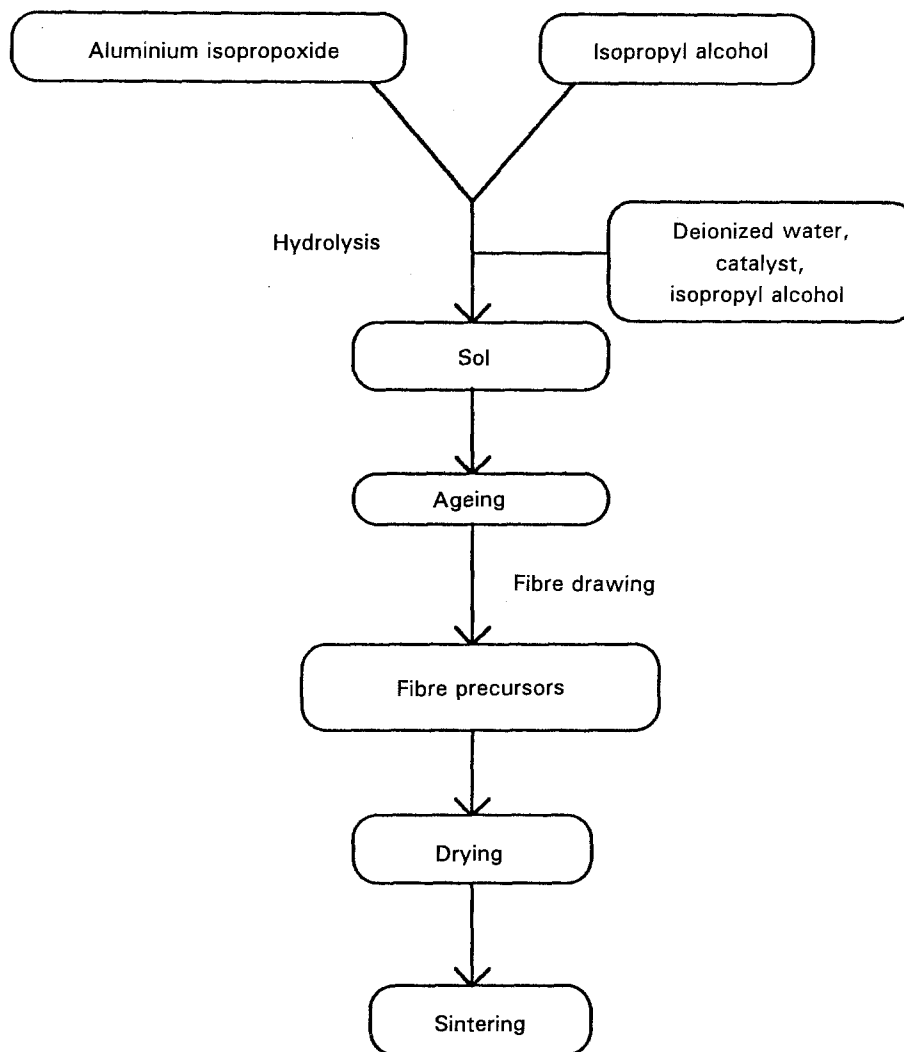


Figure 2 Polymerized alkoxide processing flow diagram for the preparation of alumina fibres.

dissolved, the shorter the gelation time becomes. Higher temperatures of ageing conditions will accelerate the gelation, but acetic acid will delay the gelation time sufficiently to spin fibres.

**3.1.1.1. Influence of various acid additives.** The influence of the different acids on the hydrolysis and gelation of the aluminium chloride system was investigated for application to the future synthesis of a multicomponent fibre. Except for acetic acid added after refluxing, both boric acid and silicic acid are added to the solution during refluxing. Table III and Fig. 3 show the effect of different acids on the aluminium chloride system at room temperature and 60 °C.

(a) Effect of boric acid. Comparing Sample 9 of Table III with Sample 11 of Table III, the initial state of the sol implies that boric acid will improve the viscosity of the sol and the solution will become opaque, but observing gelation time of Samples 2, 9 and 11, it is seen that the boric acid delays the gelation time for the solution above 3000 P (1 cP = 10<sup>-3</sup> N s m<sup>-2</sup>).

Sample 11 of Table III indicates that the solution should contain less than 5.54% boric acid with respect to the Al<sup>3+</sup> molar ratio, otherwise its gelation time will be too short to spin fibres.

(b) Effect of silicic acid. Comparing Sample 4 of Table III with Sample 5 of Table III shows that silicic acid, unlike boric acid, will obstruct the increasing viscosity during the whole gelling process.

(c) Effect of acetic acid. According to Fig. 3, acetic acid, like silicic acid, also delays the gelation time. For example, the viscosity of Sample 3 of Table III will decrease when the acetic acid was added and the solution was heated after refluxing. The viscosity will be reduced to 15.2 P from 19.5 P after heating at 60 °C for 1 h. Both acetic acid and the heat energy can break down the molecules' linkage in the solution. To respin the overaged gel, whose viscosity is unsuitable for spinning fibres, acetic acid is added to the solution which is subsequently heated.

The solution transforms into a yellow opaque sol from the original clear sol when acetic acid is added.

### 3.1.2. Colloidal sol for the aluminium nitrate system

Table IV shows the characterization of sols synthesized by heating the suspension of 1 mol Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 10 mol H<sub>2</sub>O at 100–110 °C in reflux. Two interesting results are indicated in Table IV.

TABLE I Apparent properties of sol-gel conversion from the aluminium chloride system after refluxing at 80–85 °C for 2 h

Sample	H <sub>2</sub> O(mol) <sup>a</sup>	Al(mol) <sup>a</sup>	Acetic acid (mol) <sup>a</sup>	Initial state of sol <sup>b</sup>	Ageing conditions	Spinnability	Gelation time (h)	Appearance of gel
1	22.2	1.28	–	Silver-grey clear sol	RT	Yes	531	Translucent
2	22.2	1.28	–	Silver-grey clear sol	75 °C(1 h)	Yes	48(RT)	Translucent
3	22.2	1.28	0.04	Silver-grey clear sol	75 °C(1 h)	Yes	> 72(RT)	Translucent
4	22.2	0.573	–	Clear sol	RT	No	> 720(RT)	–
5	22.2	0.573	–	Clear sol	80 °C	No	4.5	Yellow, transparent
6	22.2	0.573	0.07	Clear sol	80 °C	No	10	Yellow, transparent

<sup>a</sup> Mol ratio to AlCl<sub>3</sub>.

<sup>b</sup> After reflux at 80–85 °C for 2 h.

TABLE II Apparent properties of sol-gel conversion from the aluminium chloride system after refluxing at 100–110 °C for 1–3 h

Sample	H <sub>2</sub> O(mol) <sup>a</sup>	Al(mol) <sup>a</sup>	Acetic acid (mol) <sup>a</sup>	Initial state of sol <sup>b</sup>	Ageing conditions	Spinnability	Gelation time (h)	Appearance of gel
1	22.2	1.195	–	Silver-grey clear sol	RT	Yes	574	Transparent
2	22.2	1.195	–	Silver-grey clear sol	75 °C, 45 min	Yes	60(RT)	Translucent
3	22.2	1.39	–	Silver-grey clear sol	RT	Yes	520	Translucent
4	22.2	0.955	–	Clear sol	80 °C, 12 h	No	–	Yellow transparent
5	22.2	0.814	0.3	Clear sol	80 °C, 6 h	No	–	Yellow transparent
6	22.2	1.8	–	Silver-grey opaque (19.5 P)	RT	Yes	457	Translucent
7	22.2	1.8	–	Silver-grey opaque (19.5 P)	60 °C, 3.66 h	Yes	44(RT)	Opaque
8	22.2	1.21	–	Silver-grey clear sol (< 1.2 P)	60 °C, 5.91 h	Yes	90(RT)	Opaque

<sup>a</sup> Mol ratio to AlCl<sub>3</sub>.

<sup>b</sup> After reflux at 100–110 °C for 1–3 h.

1. The solution becomes spinnable when the H<sub>2</sub>O/Al<sup>3+</sup> molar ratio (initial H<sub>2</sub>O mole/Al<sup>3+</sup> mole in solution) is less than 6.62, but unspinnable when it is more than 9.12.

2. Comparing Samples 2 and 4 implies that the viscosity of the solution will dramatically increase when ethyl silicate (TEOS) is added to the solution by mixing alcohol and deionized water.

Two differences are apparent on comparing the aluminium chloride system with the aluminium nitrate system.

1. The aluminium nitrate system has a lower critical value of spinnability of H<sub>2</sub>O/Al<sup>3+</sup> molar ratio than the aluminium chloride system. Thus the aluminium nitrate system requires more aluminium to be dissolved in the solution than does the aluminium chloride system to enable fibres to be spun.

2. Fig. 4 shows that the aluminium nitrate system has a rather smooth viscosity – ageing time curve until the viscosity of solution reaches ~ 20 P. The gelation process of the aluminium nitrate system is faster than that of the aluminium chloride system when the viscosity of the solution exceeds 20 P.

### 3.1.3. Influence of the drying environments on precursors

The drying conditions determine whether or not the precursors of alumina fibre will crack. Temperature and humidity of the environment, in particular, are two key points for successful drying of alumina fibre. The following interesting tendencies can be generalized from Table V.

1. The suitable drying conditions change with the starting raw materials. The different precursors of the starting raw materials required different drying conditions.

2. As seen from Samples 1–4 of Table V, the appearance of the dried precursor and the drying time show that the appropriate relative humidity (RH) for different starting raw materials has the following tendencies: aluminium nitrate system > aluminium chloride system > aluminium chloride system which contains boric acid > aluminium chloride system which contains silicic acid. This is probably because the starting raw materials containing additives have different moisture contents in air.

TABLE III Effect of different acids on the aluminium chloride system

Sample	H <sub>2</sub> O (mol) <sup>a</sup>	Al (mol) <sup>a</sup>	Reflux time (h)	Additive (mol) <sup>b</sup>	Initial state of sol <sup>c</sup>	Ageing conditions	Spinnability	Gelation time (h)	Appearance of gel
1	22.2	1.8	3	–	Silver–grey opaque (19.5 P)	RT	Yes	457	Translucent
2	22.2	1.8	3	–	Silver–grey opaque (19.5 P)	60 °C (3.66 h) (3013 P)	Yes	44(RT)	Opaque
3	22.2	1.8	3	0.15 acetic acid	Silver–grey opaque (19.5 P)	60 °C (5.038 h) (> 4000 P)	Yes	80(RT)	Yellow opaque
4	22.2	1.46	3.25	0.328 silicic acid	Silver–grey clear sol (2.6 P)	RT	Yes	> 1050	Translucent
5	22.2	1.36	2.5	0.168 silicic acid	Silver–grey clear sol (2.8 P)	–	–	–	–
6	22.2	1.46	3.25	0.328 silicic acid	Silver–grey clear sol (2.6 P)	60 °C (13 h) (> 4000 P)	Yes	164(RT)	Translucent
7	22.2	1.46	3.25	0.328 silicic acid + 0.15 acetic acid	Silver–grey clear sol (2.6 P)	60 °C (23.08 h) (> 4000 P)	Yes	> 758(RT)	Yellow opaque
8	22.2	1.424	3	0.025 boric acid	Silver–grey clear sol (4.9 P)	RT	Yes	> 864	Translucent
9	22.2	1.424	3	0.025 boric acid	Silver–grey clear sol (4.9 P)	60 °C (5.05 h) (3320 P)	Yes	192(RT)	Opaque
10	22.2	1.424	3	0.025 boric acid + 0.15 acetic acid	Silver–grey clear sol (4.9 P)	60 °C (11.75 h) (> 4000 P)	Yes	> 503(RT)	Yellow opaque
11	22.2	1.3348	2.5	0.0554 boric acid	White opaque (> 4000 P)	RT	Yes	> 76(RT)	White opaque

<sup>a</sup> Mol ratio to AlCl<sub>3</sub>.<sup>b</sup> Mol ratio to Al<sup>3+</sup>.<sup>c</sup> After reflux at 100 °C.

TABLE IV Characterization of sol–gel conversion from the aluminium nitrate system

Sample	H <sub>2</sub> O (mol) <sup>a</sup>	Al (mol) <sup>a</sup>	Additive acid (mol) <sup>b</sup>	Initial state of sol	Ageing conditions	Spinnability	Gelation time (h)	Appearance of gel
1	20	0.59	–	White opaque	85 °C	No	5.66	Transparent
2	10	2.29	–	Slightly yellow clear sol (0.6 P)	60 °C (8.83 h)	Yes	82(RT)	Slightly yellow, transparent
3	10	1.87	–	Slightly yellow clear sol	60 °C (10.33 h)	Yes	100(RT)	Slightly yellow, transparent
4	10	1.63	0.3 TEOS + 0.01 HCl + 1.22 C <sub>2</sub> H <sub>5</sub> OH	White opaque	RT (1.41 h)	Yes	25 min(RT)	Transparent

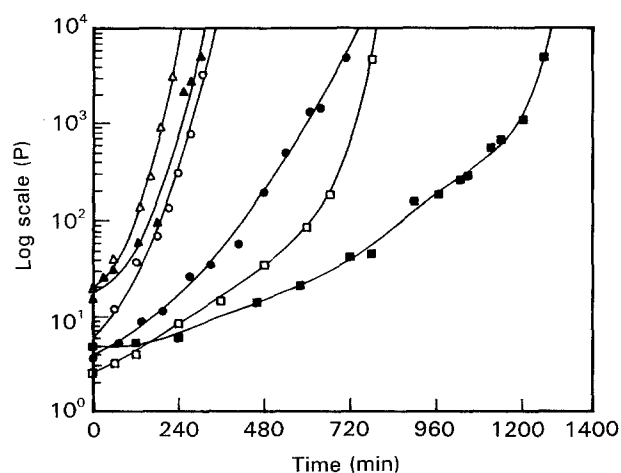
<sup>a</sup> Mol ratio to Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O.<sup>b</sup> Mol ratio to Al<sup>3+</sup>.

Figure 3 Gelation effect of acetic acid on various sols. Table III, Samples: (Δ) 2, (▲) 3, (□) 6, (■) 7, (○) 9, (●) 10.

3. Each precursor should dry at the following relative humidities at room temperature: (a) aluminium nitrate system should be dried below 55 % RH; (b) aluminium chloride system should be dried below 45 % RH; and (c) aluminium nitrate and aluminium chloride should be dried at less than the above mentioned RH if they contain either boric acid, silicic acid, or acetic acid.

4. The fibres would crack or produce bubbles, as shown in Samples 6–8 of Table V, if the precursor evaporates too fast or dries at a higher temperature than it can stand.

### 3.1.4. Polymerized sol for aluminium isopropoxide system

Silica fibres were prepared in the same manner as described previously [12]. The solution [13] showing

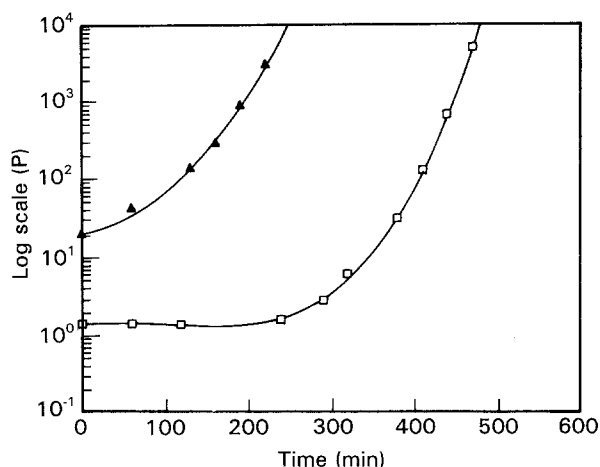


Figure 4 Gelation of two different systems: (▲) Table III, Sample 2, aluminium chloride system; (□) Table IV, Sample 2, aluminium nitrate system.

no spinnability during the course of hydrolysis, solidified into an agar-like mass when the molar ratio of water to alkoxide was larger than 4. According to the above description, the fibre synthesized from the alkoxide should limit the water content of the solution into the range of slow hydrolysis. This implies that the alumina fibre prepared from the aluminium isopropoxide system should contain a small amount of water. Table VI shows the characterization of sols synthesized by heating the suspension of  $\text{Al}(\text{OC}_3\text{H}_7)_3/\text{C}_3\text{H}_7\text{OH}/\text{H}_2\text{O}/\text{HCl}$  at 78–80 °C in reflux. The following interesting tendencies can be seen from Table VI.

1. When the  $\text{H}_2\text{O}/\text{Al}(\text{OC}_3\text{H}_7)_3$  molar ratio is more than 40, e.g. Sample 5, the solution is soupy and its viscosity is too low to produce a fibre after refluxing and ageing.

2. When the  $\text{H}_2\text{O}/\text{Al}(\text{OC}_3\text{H}_7)_3$  molar ratio is between 10 and 30, e.g. Samples 2–4, the solution is spinnable after refluxing and ageing. However, the dried precursors have no bond strength and yield powdery particles after contact. The spinnability of the solution is probably due to the partial attraction

between the particles that precipitated in the solution. After the precursor dried, the attraction between particles becomes less.

3. Sample 1 of Table VI shows that the isopropyl alcohol and water contents were too low to dissolve the aluminium isopropoxide completely and yielded partially powdery particles.

The above discussion indicates that isopropyl alcohol is not a suitable solvent for aluminium isopropoxide. Isopropyl alcohol cannot dissolve  $\text{Al}(\text{OC}_3\text{H}_7)_3$  into a clear solution with a small amount of water. It is impossible to synthesize alumina fibres with  $\text{Al}(\text{OC}_3\text{H}_7)_3/\text{C}_3\text{H}_7\text{OH}/\text{H}_2\text{O}/\text{HCl}$  solution unless an appropriate solvent, which can dissolve  $\text{Al}(\text{OC}_3\text{H}_7)_3$ , instead of  $\text{C}_3\text{H}_7\text{OH}$ , can be found, or unless  $\text{Al}(\text{OC}_3\text{H}_7)_3$  can be modified into a liquid solution [8].  $\text{Al}(\text{OC}_3\text{H}_7)_3/\text{C}_3\text{H}_7\text{OH}/\text{H}_2\text{O}/\text{HCl}$  is not suitable for producing alumina fibres, but is suitable for producing monoliths as shown in Fig. 5, membranes [14], powders, and multicomponent ceramics.

### 3.2. Characterization of precursors by infrared spectroscopy and TEM

Infrared spectroscopy has been used to examine the specimens made of the three distinct alumina hydroxide solutions. All spectra were obtained from the Bomem–Michelson Model 100 infrared spectrometer.

The clear sol [15] was prepared by hydrolysing 1 mol  $\text{Al}(\text{OC}_3\text{H}_7)_3$  with 100 mol water and peptizing with 0.2 mol  $\text{HNO}_3$  at 85 °C. The clear sample was placed on a potassium bromide plate, and then infrared spectra were obtained by scanning the sample from 360–4000  $\text{cm}^{-1}$  to identify the alumina hydroxide solutions from the OH vibrations in the stretching and bending regions. Fig. 6 shows all the infrared spectra of alumina hydroxide solutions and some standards. Frederickson [16] indicated that the OH stretching vibrations observed for boehmite are at 3079 and 3262  $\text{cm}^{-1}$ , and its OH bending vibrations are at 1073 and 1145  $\text{cm}^{-1}$ . According to Frederickson's studies, and subtracting the standard infrared spectrum of isopropyl alcohol, it is implied that the

TABLE V Influence of drying environments on various precursors

Sample	Species of sample	Relative humidity (%)	Temperature	Drying time	Appearance of dried precursor
1	$\text{AlCl}_3$ (Sample 8 of Table II)	55	RT	24 h	Wet but non-drop-like
2	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sample 2 of Table IV)	55	RT	< 30 min	Translucent dried fibre
3	$\text{AlCl}_3$ (Sample 10 of Table III)	55	RT	2 h	Wet and drop-like
4	$\text{AlCl}_3$ (Sample 7 of Table III)	55	RT	5 min	Wet and drop-like
5	$\text{AlCl}_3$ (Sample 8 of Table II)	45	RT	6 h	Slightly yellow, translucent dried fibre
6	$\text{AlCl}_3$ (Sample 8 of Table II)	–	60 °C	20 min	Translucent dried fibre but cracking into several pieces
7	$\text{AlCl}_3$ (Sample 8 of Table II)	30 ↓	RT	5–10 min	Clear dried fibre with blowhole
8	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sample 2 of Table IV)	30 ↓	RT	2–4 min	Clear dried fibre with blowhole

TABLE VI Characterization of sol-gel conversion from aluminium isopropoxide system

Sample	Al(OPr <sup>i</sup> ) <sub>3</sub> :C <sub>3</sub> H <sub>7</sub> OH:H <sub>2</sub> O:HCl <sup>a</sup>	Reflux condition	Initial state of post-refluxing sol	Ageing condition	State of sol after ageing	Appearance of dried precursor
1	1:5:3.33:0.02	80 °C, 3.91 h	White opaque sol with some precipitation	–	–	–
2	1:10:10:0.1	80 °C, 3.33 h	White opaque sol	80 °C stirring 50 min	White opaque sol with spinnability	No cracking but without bonding strength
3	1:10:20:0.1	78 °C, 8.5 h	White opaque sol	80 °C stirring 1.25 h	White opaque sol with spinnability	No cracking but without bonding strength
4	1:10:30:0.1	80 °C, 5 h	White opaque sol	80 °C stirring 1.43 h	White opaque sol with spinnability	No cracking but without bonding strength
5	1:10:40:0.1	80 °C, 5 h	White translucent sol	80 °C stirring 1.66 h	White translucent soupy sol without spinnability	–
6	1:10:20:0.4	78 °C, 21.3 h	White opaque sol	70 °C stirring 3.5 h	White opaque sol with spinnability	No cracking but without bonding strength

<sup>a</sup> Mol ratio.

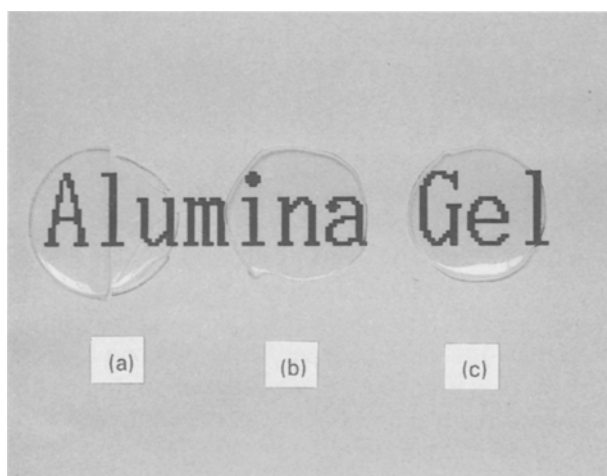


Figure 5 As-dried alumina monolith.

clear sol [15] contained the pseudoboehmite contents for the OH vibration peaks at 1070, and 3079 cm<sup>-1</sup>, as shown in Fig. 6. This was subsequently proved by TEM observations. Fig. 7 shows a transmission electron micrograph and diffraction pattern of the clear sol after drying on a copper mesh. The diffraction pattern clearly shows that the needle-like microstructure is the boehmite phase.

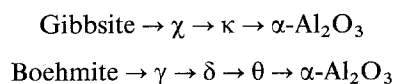
By comparing hydrolysed aluminium chloride solution and post-refluxed solution, the post-refluxed solution possesses more absorption peaks at 980, 1070, and 1155 cm<sup>-1</sup>, and its OH bending vibrations at about 3000 cm<sup>-1</sup> shifted to a higher wave number. These OH absorption peaks at 980, 1070 and 1155 cm<sup>-1</sup> probably result from the OH stretching vibrations of pseudogibbsite overlapping that of pseudoboehmite. The OH bending vibrations of pseudogibbsite probably cause the vibrations of post-refluxed solution to shift to a higher wave number. This is also proved by TEM. Fig. 8 shows a transmission electron micrograph and diffraction pattern of post-refluxed solution dried on a copper mesh. The

diffraction pattern illustrates the weakly crystalline phases are boehmite and gibbsite. This indicates that the post-refluxed solution contained pseudoboehmite and pseudogibbsite contents.

### 3.3. Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of these as-dried precursors were performed in flowing air at 10 °C min<sup>-1</sup> to 1370 °C. Fig. 9 shows the TGA and DTA curves of the as-dried precursors of aluminium chloride and aluminium nitrate systems. Curves 1 and 2 indicate that there is a weight loss between 30 and 655 °C and exothermic peaks, respectively, at 770 and 1090 °C without weight loss in the aluminium chloride system. Curves 3 and 4 indicate that there is a weight loss between 30 and 480 °C and exothermic peaks, respectively, at 816 and 1050 °C without weight loss in the aluminium nitrate system. These exothermic peaks without weight loss imply that the phase transformation takes place at these temperatures, and they are confirmed by the following XRD analysis.

X-ray diffraction was used to study these calcined precursors at different temperatures in air. Tables VII and VIII show the results of the phase transformation of these precursors prepared from the aluminium chloride and aluminium nitrate systems. Not only  $\gamma$ ,  $\delta$ , and  $\theta$  but also  $\chi$  and  $\kappa$  could be detected by XRD in the range 850–1050 °C, as shown in Table VII. Although XRD did not find peaks of boehmite, gibbsite and bayerite phase below 500 °C, according to Gitzen's study [17] and the previous infrared, TEM discussion, we deduce that the phase transformation of calcined precursors in the aluminium chloride system obeys the following route



By bringing the above data from infrared, TEM and XRD together, we can deduce the following sol-gel

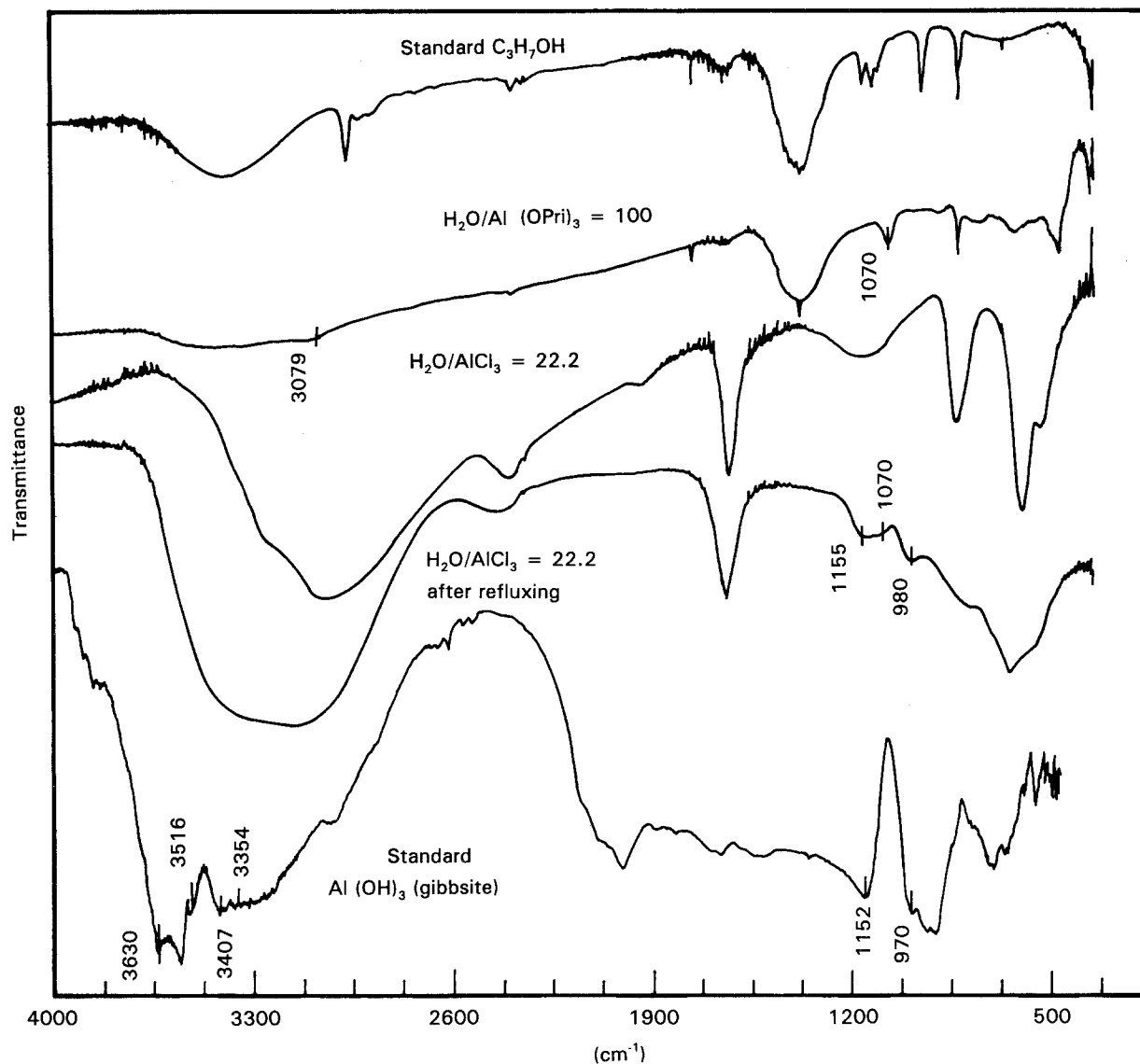


Figure 6 Infrared spectra of different aluminium hydroxide solutions and some standards.

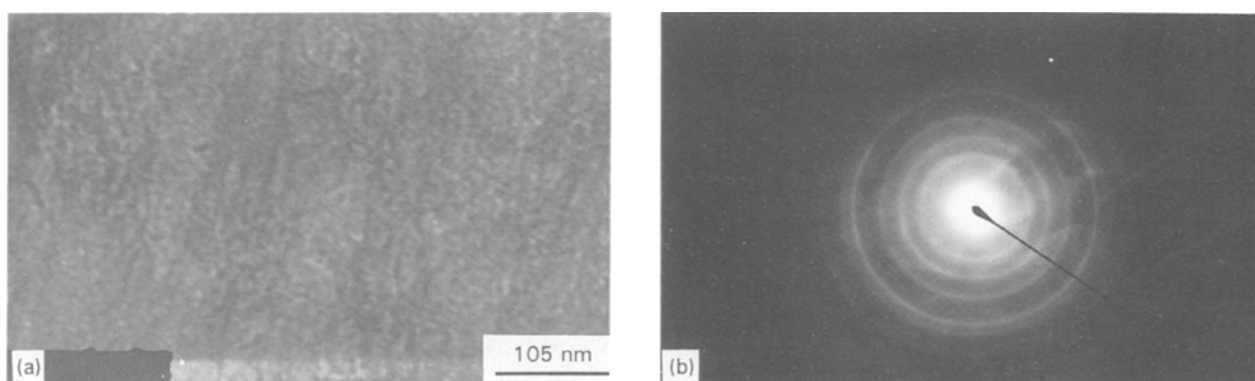


Figure 7 (a) Transmission electron micrograph and (b) diffraction pattern of  $\text{Al}(\text{OC}_3\text{H}_7)_3/\text{H}_2\text{O}/\text{HNO}_3$  solution.

reaction of the aluminium chloride system. Aluminium chlorides hydrolyse with water and form aluminium hydroxides in hydrochloric acid solutions. To increase the  $\text{Al}^{3+}$  content of the solution, aluminium pellets dissolve in hydrochloric acid solution during refluxing. Their chemical reaction equation is



The aluminium hydroxides will convert into pseudoboehmite and pseudogibbsite in hydrochloric acid solutions after refluxing, as confirmed previously by infrared spectra and TEM. With increasing contents, these pseudoboehmite and pseudogibbsite particles aggregate with each other in the solution. With increasing viscosity, the sol finally converts into gel.



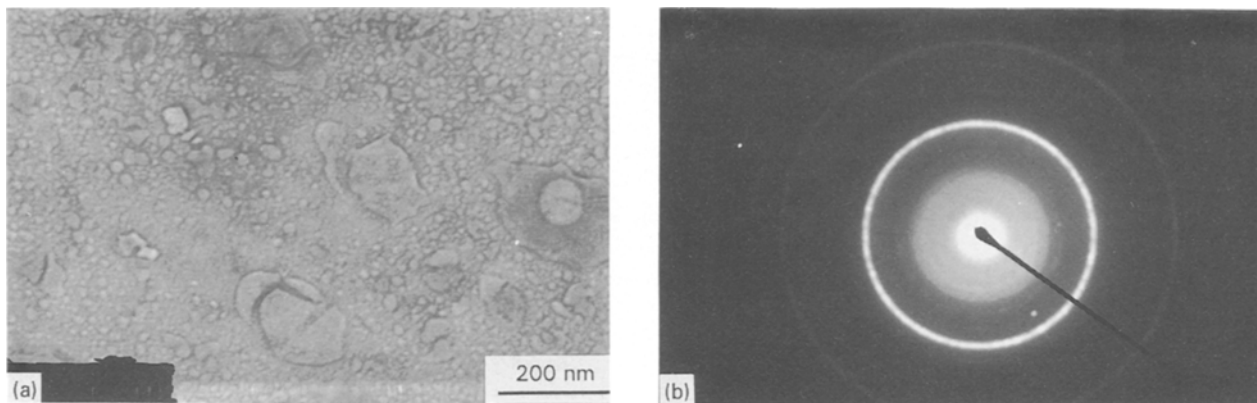


Figure 8 (a) Transmission electron micrograph and (b) diffraction pattern of as-dried precursor prepared by the aluminium chloride system.

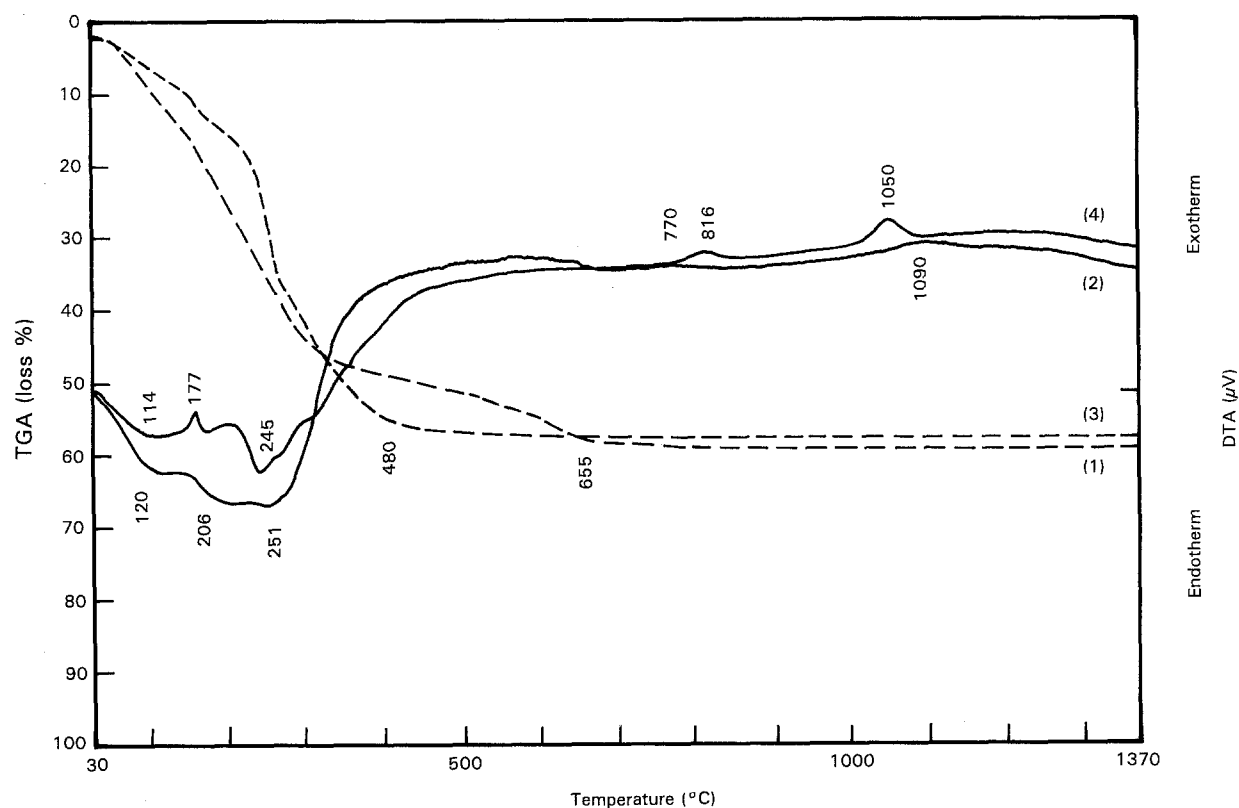


Figure 9 TGA and DTA curves of the as-dried precursors of aluminium chloride (1,2) and aluminium nitrate (3,4) systems.

TABLE VII Phase transformations of the precursors prepared by the aluminium chloride system under different calcining conditions

Calcining conditions	Crystallographic phase
25 °C	Amorphous
500 °C, 4 h	Amorphous
700 °C, 2 h	Trace of $\gamma$ and $\chi$ phase
850 °C, 2 h	$\gamma$ , $\chi$ phase mainly and trace of $\delta$ phase
900 °C, 2 h	$\delta$ , $\chi$ phase
1000 °C, 1 h	$\delta$ , $\kappa$ phase
1050 °C, 1 h	$\theta$ , $\kappa$ phase and trace of $\delta$ , $\alpha$ phase
1085 °C, 1 h	$\alpha$ phase and trace of $\theta$ , $\kappa$ phase
1150 °C, 1 h	$\alpha$ phase

TABLE VIII Phase transformations of the precursors prepared by the aluminium nitrate system under different calcining conditions

Calcining conditions	Crystallographic phase
25 °C	Amorphous
800 °C, 4 h	Amorphous
900 °C, 4 h	$\gamma$ , trace of $\delta$ , $\theta$ , $\alpha$ phase
1000 °C, 4 h	$\alpha$ phase

### 3.4. Sintering

The as-dried precursors of aluminium chloride, as shown in Fig. 10, and aluminium nitrate, as shown in Fig. 11, were heated to 800 °C for 4 h, and then to

1300 °C for 4 h in flowing air. The heating rate of the whole process was maintained at 3 °C min<sup>-1</sup>. Their SEM microstructures are shown respectively, in Figs 12 and 13. It is obvious that the porosity developed in the aluminium chloride system is bigger than that in the aluminium nitrate system in/ between the grains. This implies that the precursors of the

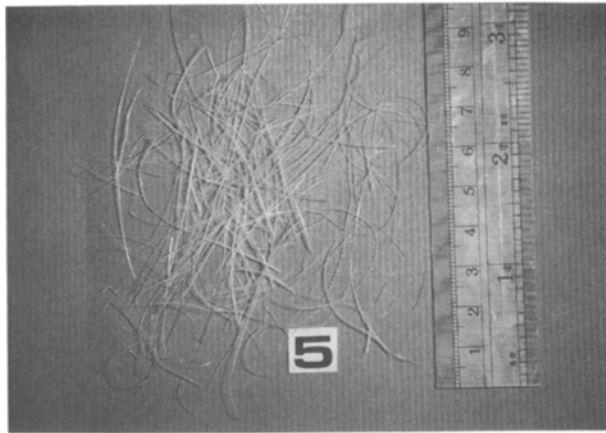


Figure 10 As-dried alumina fibre prepared by the aluminium chloride system. (1–4) See text.



Figure 11 As-dried alumina fibre prepared by the aluminum nitrate system.

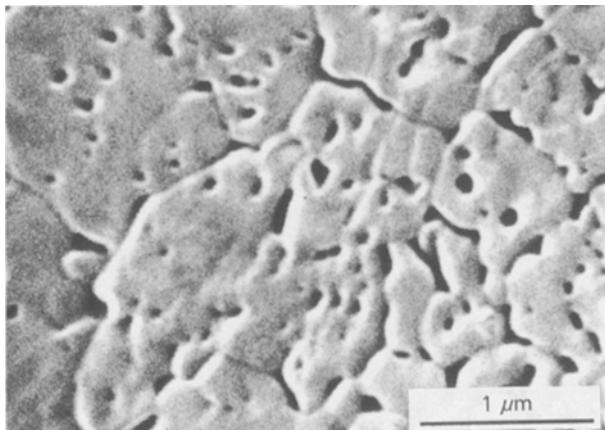


Figure 12 SEM microstructure of alumina fibre prepared by the aluminium chloride system.

aluminium nitrate system have a better sintering behaviour than those of the aluminium chloride system. The following results of previous thermal analysis may be the main contributions to the above phenomenon.

1. From Tables VII and VIII, the  $\alpha$ -phase transformation of the precursors synthesized from the

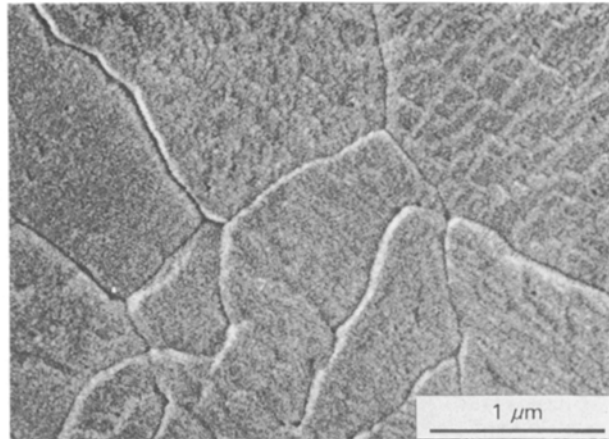


Figure 13 SEM microstructure of alumina fibre prepared by aluminium nitrate system.

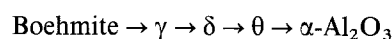
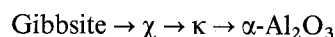
aluminium nitrate system is completed at lower temperature than that in the aluminium chloride system.

2. The precursors of the aluminium chloride system do not show any weight loss until 655 °C, but those of the aluminium nitrate system cease to lose weight at above 480 °C, because the aluminium chloride is moister in air than is aluminum nitrate, and the thermal decomposition of  $\text{Cl}^-$  is more difficult than that of  $\text{NO}_3^-$ .

#### 4. Conclusions

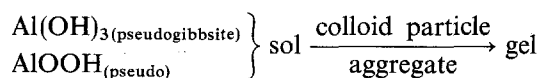
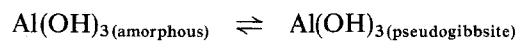
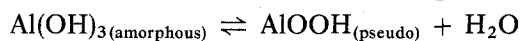
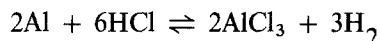
In previous work, various raw materials have been successfully used to prepare alumina fibre. It is known that alkoxide methods are very popular for producing alumina fibre, but they either require several steps to synthesize and modify the raw materials, or much time is required for exposure to moisture in air. Thus the polymerized alkoxide method requires a long time and much money to synthesize alumina fibre. Therefore, it is not suitable for mass production of alumina fibre in industry. Fortunately, aluminium chloride or aluminium nitrate are much more economical than alkoxide and do not require a long period of time for the synthesis of a spinnable sol. They are thus potential methods for the mass production of alumina fibre, but the characteristics of sol–gel conversion and drying conditions change with the raw materials. More detailed considerations is required in choosing raw materials to prepare alumina fibres. In this study, the sol–gel process has been characterized and some important conclusions can be drawn.

1. Infrared, TEM, and XRD were used to analyse the precursors of the aluminium chloride system that induces the following phase transformation of thermally decomposing precursors



2. The chemical reaction of the sol–gel process in the aluminium chloride system may be written as follows





3. Because the sintering of the aluminium nitrate system is better than that of the aluminium chloride system, the aluminium nitrate system seems to be more suitable for preparing alumina fibres.

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