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Preparation of continuous zirconia fibres from polyzirconoxane synthesized by the facile one-pot reaction

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A one-pot reaction of zirconium oxychloride octahydrate (ZOC) with ethyl acetoacetate (Hetac) in the presence of triethylamine was investigated. The reaction was carried out in molar ratios of Hetac/ZOC = 1.0, 1.5, 2.0 to give highly viscous solutions with good spinnability and stability to self-condensation. Polyzirconoxanes (PZOs) were isolated as white powders by reprecipitation of the solutions with tetrahydrofuron (THF)-hexane that were soluble in acetone, methanol and THF. The molecular weight of PZO was Mn = 1000–2000, and was dependent on the molar ratio and the reaction time. Dry spinning of the solution (Hetac/ZOC = 1.5) containing 3 mol % tris(acetylacetonato)yttrium [Y(acac)$_3$] gave continuous precursor fibres (3.0Y–PZO). Yttria stabilized zirconia fibres of 12–18 μm diameter with a tensile strength of 1.4 GPa were obtained by heat treatment of the 3.0Y–PZO at 1100 or 1200 °C. The fibre consisted of submicrometre-sized particles of tetragonal crystallites. © *1998 Chapman & Hall*

1. Introduction

Zirconia (ZrO_2) has been known as an excellent ceramic with high melting point and mechanical properties at high temperature in addition to acid and alkali resistance. In particular, yttria-stabilized zirconia is expected to be applied not only as an insulating material but in composite materials because of its high strength and toughness. Zirconia fibres have been prepared by the following processes:

1. impregnation of organic polymer fibres with zirconium salt solutions followed by sintering [1, 2],
2. spinning of the precursor fibres from organic polymer solutions containing zirconium salts or fine zirconia powders followed by sintering [3, 4] and
3. dry spinning of sol solutions prepared by sol–gel processing of zirconium acetate or alkoxide followed by sintering [5–7].

In the impregnation method, the high content of organic residues and/or low zirconia content results in large volume contraction to form fibres with a low tensile strength. The organic polymer fibre method is reported to provide continuous zirconia fibres with a tensile strength of 1.5 GPa, but the process does not seem to be practical because of the complicated steps of the preparation of submicrometre-sized zirconia particles and subsequent homogeneous polymer solution followed by spinning. The sol–gel process, on the other hand, is a potential method for preparing various oxide fibres by dry spinning of polymetalloxane sol solutions obtained by hydrolytic polycondensation of metal alkoxides followed by the addition of additives and then sintering. Usually, this method forms a sol solution of relatively high oxide content that gives densely sintered fibres with high strength. However, the process is often encountered with the gelation of sol solutions, which makes it difficult to spin fibres. Acetylacetone is realized to be an effective additive for increasing the stability of the sols to gelation [8, 9].

Thus, no reports have been published on the synthesis of sols and, moreover, precursor polymers that are stable for the preparation of zirconia fibres by self-condensation except for PZO, which has appreciable stability and good spinnability [10, 11]. This PZO is synthesized by acid-catalysed hydrolytic polycondensation of zirconium chelates and provides zirconia fibres by dry spinning with the addition of a yttrium chelate followed by steam treatment and then sintering. This method may be a new route for the preparation of continuous zirconia fibres, but it is not practical because PZO has to be prepared via the synthetic processes of zirconium tetraalkoxide and then zirconium chelate complex. Recently, we have briefly reported the convenient one-pot synthesis of PZO by reaction of zirconium oxychloride with ethyl acetoacetate in the presence of triethylamine and preparation of the zirconia fibre from a precursor [12]. In this paper, the results of the detailed investigation will be described.

2. Experimental procedure

2.1. A one-pot synthesis of PZO

Into 130 ml of methanol containing 9.7 g (0.03 mol) of ZOC, Hetac and then 6.1 g (0.06 mol) triethylamine were added dropwise below 5 °C at molar ratios of Hetac/ZOC = 1.0, 1.5, 2.0 and Et_3N/ZOC = 2.0. The reaction mixture was stirred at room temperature for 2 h and then concentrated *in vacuo* to give white solids. Addition of THF (50 ml) and filtration of the precipitate followed by concentration of the filtrate gave a highly viscous solution. Reprecipitation of the solution with hexane, followed by drying *in vacuo* for 6 h, gave PZO as a white powder.

After reaction at room temperature for 2 h, the mixture was further subjected to reflux for various periods of times ranging from 1, 2, 4 to 8 h to give a higher molecular weight PZO.

2.2. Synthesis of silylated PZO

The PZO obtained above was dissolved in THF. Hexamethyldisilazane (HMDS) was added dropwise to the solution in the molar ratio HMDS/ZOC = 3.0, and then the reaction mixture was stirred at room temperature for 24 h. Filtration of the reaction mixture and removal of solvent followed by drying *in vacuo* at 80°C for 6 h gave the silylated PZO as a white powder.

2.3. Preparation of zirconia fibres by dry spinning of PZO followed by steam treatment and heat treatment

Tris(acetylacetonato)yttrium $Y(acac)_3$ was added into a methanol solution of PZO of composition $Y_2O_3:ZrO_2 = 3:97$ to give a homogeneous solution. Evaporation of the solvent gave a highly viscous yttrium-containing PZO solution (abbreviated as Y–PZO solution). The solution was fed into the spinning nozzle of a laboratory-made dry spinning apparatus (Fig. 1) from which precursor fibres were extruded by means of N_2 pressure and were wound with a spinning dram. Under suitable conditions of nozzle size (0.15 mmlϕ × 0.9 mm or 0.10 mmϕ × 0.6 mm), temperature, N_2 pressure and winding rate, fine continuous $3.0Y_2O_3$–$97ZrO_2$ precursor fibres were obtained.

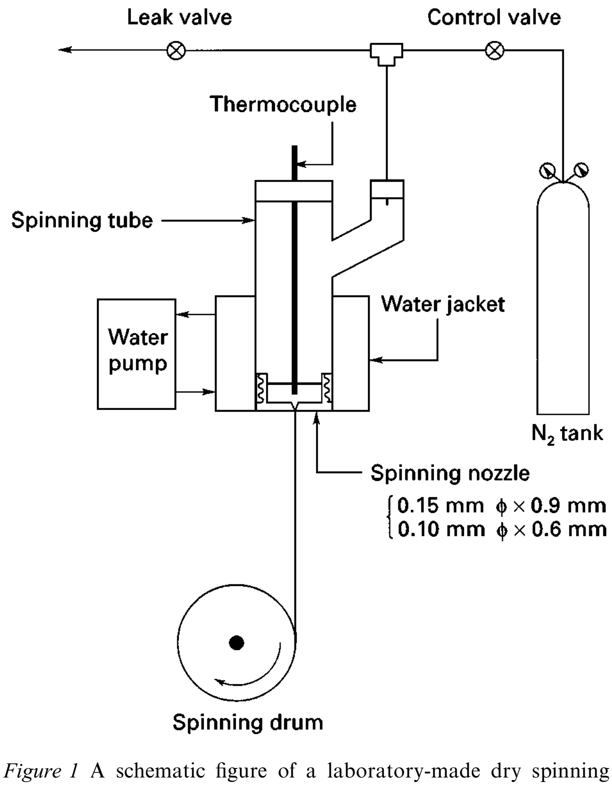


Figure 1 A schematic figure of a laboratory-made dry spinning apparatus.

Steam treatment of the $3.0Y_2O_3$–$97ZrO_2$ precursor fibres at 70°C for 1 h followed by heat treatment up to 1100 or 1200 °C at a heating rate of 2 °C min^{-1} provided continuous $3.0Y_2O_3$–$97ZrO_2$ fibres.

2.4. Instruments and analysis

^1H nuclear magnetic resonance (NMR) spectra were measured using a Jeol PMX60SI spectrometer in chloroform-*d* or carbon tetrachloride.

Infrared (i.r.) spectra were measured using a Hitachi 260–50 i.r. spectrophotometer by the KBr disc method.

Molecular weight was measured by means of vapour pressure osmometry (VPO) using a Corona 117 molecular weight apparatus in benzene at 40 °C.

Scanning electron micrograph (SEM) photographs were taken with a Jeol JSM-T330A. X-ray diffractograms (XRD) were measured using a Rigaku Denki model CN-2013. Elemental analysis was carried out using a Hereus CHN-O-RAPID.

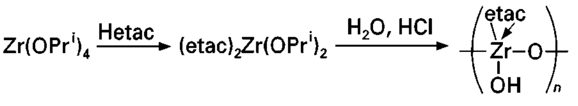
The zirconium content of PZO was measured as follows. A PZO–methanol solution (10 ml, 1.14×10^{-2} mol l^{-1}) was boiled at 100 °C for 5 min in the presence of 61% concentration of nitric acid (11.23 ml) and ion-free water (38.77 ml). Ion-free water (100 ml) was added to the solution, and the solution boiled at 100 °C and titrated with an aqueous ethylenediaminetetraacetic acid (EDTA) in the presence of a xylenol orange indicator.

The tensile strength of the fibres was measured with a single fibre of 25 mm in length using an ultimate tensile machine UTM-II-20) at a loading speed of 1 mm min^{-1}. The tensile strength was calculated by dividing the maximum load by the cross-sectional area of the fibre.

3. Results and discussion

3.1. Synthesis and properties of PZO

In ceramic synthesis by the sol–gel process or precursor method, the key step is the preparation of the sol or polymetalloxanes as the precursor. We have reported that continuous zirconia fibres were prepared from PZO [10, 11]. However, PZO is not a precursor for practical use, because it has to be provided via several processes: i.e. syntheses of zirconium tetraisopropoxide, zirconium chelate compound by the conventional method, and then acid-catalysed hydrolytic polycondensation of the chelate according to Equation 1.

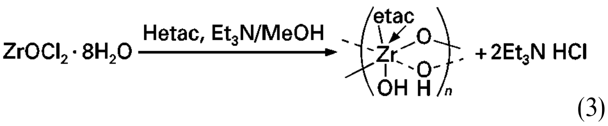


$$Zr(OPr^i)_4 \xrightarrow{Hetac} (etac)_2Zr(OPr^i)_2 \xrightarrow{H_2O,\ HCl} \left(-\underset{OH}{\overset{etac}{Zr}}-O- \right)_n \qquad (1)$$

In this work, therefore, a more convenient method of obtaining PZO was investigated using a versatile starting material of zirconium oxychloride. It is reported that zirconium tetraalkoxides are prepared by the reaction of zirconium oxychloride pyridine adduct with alcohol in the presence of triethylamine (Equation 2) [13, 14].

$$ZrOCl_2\cdot 8H_2O \xrightarrow{C_5H_5N,\ HCl} (C_5H_5N)_2ZrCl_6 \xrightarrow{ROH,\ Et_3N} Zr(OR)_4 \qquad (2)$$

This method was applied to prepare zirconium chelate or PZO with ethyl acetoacetate, acetylacetone, methoxyethanol and lactic acid, but the reaction resulted in the formation of heterogeneous solutions or gels. On the other hand, reaction of zirconium oxychloride hydrate with Hetac in the presence of triethylamine, (Equation 3)



(3)

was found to give a homogeneous and viscous solution that showed good spinnability and stability to self-condensation, while a spinnable but turbid solution or a transparent solution with no spinnability was obtained by reaction with acetylacetone or lactic acid, respectively [12]. In the present work, the reaction with ethyl acetoacetate was investigated in detail.

Table I shows the result of the synthesis of PZO. The isolation yield of PZO was 57–74% for the reaction at room temperature and it increased with increasing reflux time, regardless of the molar ratio of Hetac/ZOC (= r). The number average molecular weight (M_n) of PZO, given in the margin of Table I, was not so high as 1380 ($r = 1.0$), 1980 ($r = 1.5$), 990 ($r = 2.0$), but the concentrated methanol solution showed excellent spinnability of more than 100 cm ($r = 1.0$, 1.5) and high stability to self-condensation to form gels for more than four months. PZO (Run No. 6, $r = 1.5$; no reflux) was soluble in acetone, methanol and THF, but insoluble in hexane. The molecular weight of PZO seems to increase with increasing reflux time, as is suggested analytically by the increase of Zr content, although it was not confirmed by means of gel permiation chromatography and VPO because of the low solubility in THF and benzene for the PZO obtained by the reaction under reflux. The elemental analysis data of PZO (Run No. 6–10) are summarized in Table II. The carbon and hydrogen content decreased while the zirconium content increased with increasing reaction time. The molar ratio of the etac group to zirconium also decreased from 1.0 (Run No. 6) to 0.82 (Run No. 10) as the reflux time increased, suggesting the formation of a high molecular weight PZO by condensation due to elimination of the etac group.

TABLE II Elemental analysis of PZO (Runs No. 6–10)

Run No.	Reflux time (h)	Elemental analysis (%)			Molar ratio etac/Zr
		C	H	Zr	
6	0	26.6	4.2	33.6	1.00
7	1	25.6	4.0	35.3	0.92
8	2	24.5	3.9	36.8	0.84
9	4	24.2	3.8	37.1	0.83
10	8	24.1	3.8	37.1	0.82

Figs 2 and 3 show the i.r. and the ^1H NMR spectra of PZO (Run No. 6 in Table I). The i.r. spectrum of PZO exhibits absorption peaks at 3400 (ν_{OH}), 3000 (ν_{CH}), 1620 ($\nu_{C=O}$), 1520 ($\nu_{C=C}$), 1280 (δ_{CCH_3}) and 450 cm^{-1} (ν_{Zr-O}). The ^1H NMR spectrum of PZO indicates the signals due to the ethyl acetoacetato group at 1.2 (CH_3CH_2O–), 1.8 (CH_3CO– enol form),

TABLE I Yield, Zr content, and solubility of PZO

Run No.	Molar ratio of Hetac/ZOC[a]	Reflux time (h)	Yield (%)[b]	Zr content (%)	Solubility[c]			
					Methanol	Acetone	THF	Hexane
1	1.0	0[d]	74.3	35.2	+ +	+ +	+ +	−
2		1	84.5	37.7	+ +	+ +	−	−
3		2	90.7	39.1	+ +	+	−	−
4		4	90.8	39.3	+ +	+	−	−
5		8	89.8	39.2	+ +	+	−	−
6	1.5	0[e]	63.1	33.6	+ +	+ +	+ +	−
7		1	87.0	35.3	+ +	−	−	−
8		2	89.2	36.8	+ +	−	−	−
9		4	92.4	37.1	+ +	−	−	−
10		8	88.0	37.1	+ +	−	−	−
11	2.0	0[f]	57.6	34.6	+ +	+ +	+ +	−
12		1	84.1	37.2	+ +	+ +	+	−
13		2	89.9	38.2	+ +	+ +	+	−
14		4	90.8	38.4	+ +	+ +	+	−
15		8	90.3	38.6	+ +	+ +	+	−

[a] Reaction conditions: $ZrCl_2O\cdot 8H_2O$ 9.7 g (0.030 mol), methanol 130 ml, Et_3N 6.1 g (0.06 mol), $Et_3N/ZOC = 2.0$.
[b] Isolated yield by means of reprecipitation with THF and hexane.
[c] + +, easily soluble; +, soluble; −, insoluble.
[d] $M_n = 1380$ (VPO method).
[e] $M_n = 1980$ (VPO method).
[f] $M_n = 990$ (VPO method).

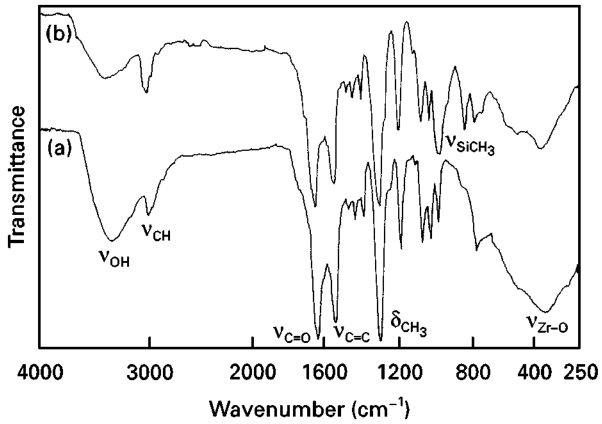


Figure 2 Infrared spectra of (a) PZO (Run No. 6 in Table I) and (b) its silylated PZO (KBr disc method).

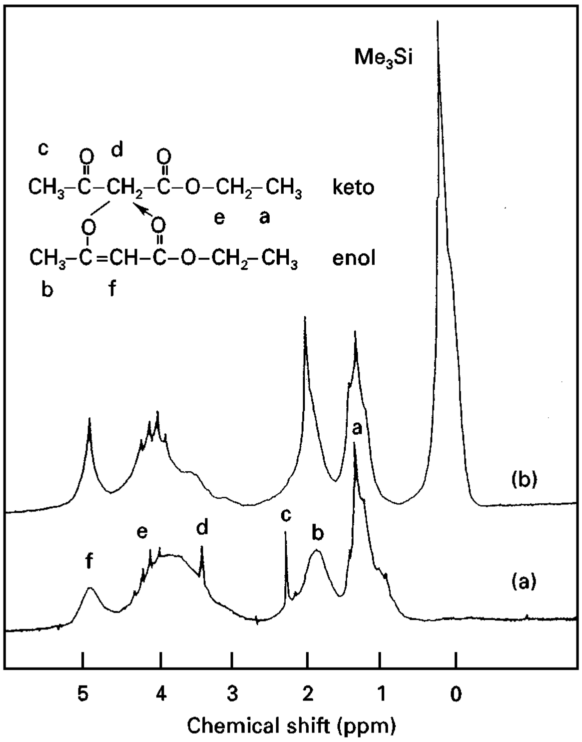
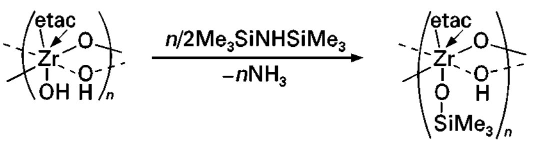


Figure 3 ^{1}H NMR spectra of (a) PZO (Run No. 6 in Table I) and (b) silylated PZO (solvent $CDCl_3$).

2.2 (CH_3CO–, keto form), 3.3 (–CH_2–, keto form), 4.0 (CH_3CH_2O–) and 4.8 p.p.m. (=CH– enol form) together with a signal at 4.0 p.p.m., which may be ascribed to the signal due to the OH group. Consequently, PZO consists of a main chain of Zr–O bonds with etac and OH groups as a pendant. The molar ratio OH/etac was determined to be 2.8 based on the ^{1}H NMR spectrum (Fig. 3).

3.2. Silylated PZO

In order to confirm the structure, PZO was silylated with hexamethyldisilazane in THF to form silylated PZO according to Equation 4.



(4)

Concentration of the reaction mixture followed by reprecipitation with hexane gave silylated PZO as a white powder. It is clear from the solubility results shown in Table III that PZO, when silylated, becomes more soluble in non-polar solvents such as benzene and carbon tetrachloride. However, no spinnability was observed when PZO was silylated, which implies that the spinnability results from interaction based on co-ordination between the hydroxy group and zirconium. The i.r. and ^{1}H NMR spectra of the silylate are also shown in Figs 2 and 3. In the i.r. spectra, the peak intensity at 3400 cm^{-1} is due to the OH group decreases compared with that of PZO, and new peaks appear at 2900 and 830 cm^{-1} due to the Si–CH_3 group. The ^{1}H NMR spectrum of silylate is essentially identical with that of PZO except for the disappearance of the signals at 2.2 and 3.2 p.p.m. due to the keto form of the ligand group. The molar ratio OH/etac calculated, based on the proton ratio, was 1.9. In the case of PZO, on the other hand, the proton ratio was determined to be 2.8. Therefore, a difference of 0.9 equivalent OH should result from the silylation of PZO. This is also supported by the result that the proton ratio of the methyne (f) to the silylmethyl group is 1:6.6 for 1:9 as calculated, i.e. 0.9 mole equivalent proton is silylated.

3.3 The structure of PZO

Table IV shows the analytical data of PZO and the silylate. The data are in fairly good agreement with the values calculated for the structure shown in Fig. 4a. The spectral data and the results of silylation clearly indicate that PZO has OH groups. No free OH groups attached to metal should be present but should be co-ordinated in between molecules; by which condensation to form metalloxane bonds and/or the formation of a metal oxide gel is prevented. PZO, therefore, is stable to condensation and soluble in methanol, acetone and THF. Because there is no evidence concerning the co-ordination number of zirconium and subsequently no confirmation of the backbone linkage, the structure of PZO is estimated to be as shown in Fig. 4b.

3.4. The dry spinning condition of $3.0Y_2O_3$–$97ZrO_2$ precursor fibre and steam treatment

We have already reported on the preparation of zirconia fibres according to Equation 5

$$\text{PZO} \xrightarrow[\text{Dry spinning}]{\text{Y(acac)}_3\text{/MeOH}} \text{Precursor fibres} \xrightarrow[\text{Heat treatment}]{\text{Steam treatment}} Y_2O_3\text{–}ZrO_2 \text{ fibres} \qquad (5)$$

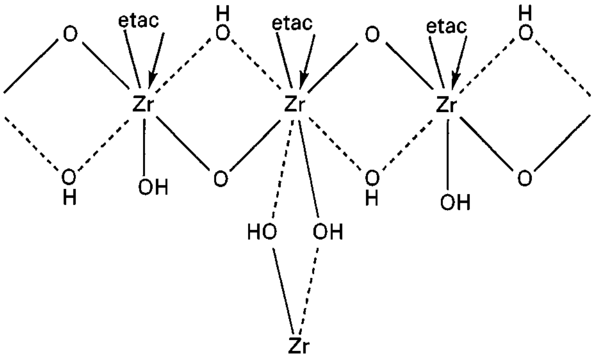
from PZO synthesized by hydrolysis of a zirconium chelate compound. The $3.0Y_2O_3$–$97ZrO_2$ precursor fibres were prepared by dry spinning a Y–PZO solution using a spinning machine where the dry spinning conditions were confirmed to depend especially on the concentration and temperature [11]. In this work, the conditions in addition to N_2 pressure and spinning rate were also investigated.

TABLE III Solubility[a] of PZO[b] before and after silylation[c]

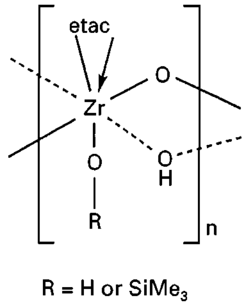
Solvent	PZO	Silylated PZO
Water	− −	− −
Methanol	+ +	+ +
Acetone	+ +	+ +
THF	+ +	+ +
Benzene	+	+ +
Carbon tetrachloride	+	+ +
Hexane	−	−

[a] + + , easily soluble; + , soluble; − , insoluble.
[b] Run 6 in Table I
[c] HMDS/etac = 3, M_n = 3080 (VPO method).

Table V shows the results of spinning conditions of the precursor fibres from the Y–PZO solution. At relatively low concentration, PZO can easily be spun at a low temperature and N_2 pressure at a rather fast spinning rate (Run Nos 1 and 5). While at higher temperature and N_2 pressure, a lower spinning rate has to be applied, because PZO could hardly be spun out from the spinning nozzle when the concentration was high (Run No. 3). As a result, precursor fibres can preferably be prepared under the following conditions: 76.0–76.4 wt %, 31–33 °C, 5–9 kg fcm^{-2}, 50–60 m min^{-1}.



(a) PZO



(b) Silylated PZO

Figure 4 The possible structure of (a) PZO (Run No. 6 in Table I) and (b) silylated PZO.

The green fibres are so brittle that they cannot be handled, and also the oxide fibres obtained by heat treatment of the fibres have no tensile strength or are so brittle that they cannot retain the shape of fibres. As described in previous papers [11], however, steam treatment of green fibres is very effective in obtaining oxide fibres with an appreciable tensile strength because hydrolysis of the ligand group leads to a reduction of the stress evolved on combustion of the organics. This is confirmed by the i.r. spectra of $3.0Y_2O_3$–$97ZrO_2$ precursor fibres before and after hydrolysis (Fig. 5) indicating the disappearance of peaks at 3000, 1620 and 1520 cm^{-1} due to the ligand group. In fact, even precursor fibres can be handled just after steam treatment.

3.5. The preparation of $3.0Y_2O_3$–$97ZrO_2$ fibres

Table VI shows the colour of the fibres and the crystal form on heating $3.0Y$–$97ZrO_2$ precursor fibres. The

TABLE IV Results of the analyses of PZO[a] and the silylate[b]

Product			Observed	Calculated
PZO[a]	M_n (VPO method)		1980	1827 (n = 7) 2088 (n = 8)
	Analysis, %	Zr	33.6	33.6
		C	26.6	26.6
		H	4.6	4.4
	Etac/Zr, molar ratio		1.0[c]	1.0[e]
	OH/etac, molar ratio		2.8[d]	2.0[e]
Silylated PZO	M_n (VPO method)		3080	2345 (n = 7) 2680 (n = 8) 3015 (n = 9)
	Analysis, %,	Zr	28.6	28.4
		Si	6.1[f]	6.0
		C	29.6	30.1
		H	5.2	5.4
	Me_3Si/etac, molar ratio		0.7[d]	1.0[e]
	OH/etac, molar ratio		1.9[d]	2.0[e]

[a] Run 6 in Table I
[b] HMDS/etac = 3.
[c] etac/Zr = (26.6/72.0)/(33.6/91.2).
[d] Calculated from the proton ratio of ^1H NMR.
[e] Based on the structure in Fig. 4.
[f] Wet method.

TABLE V Results of spinning experiments

No.	Concentration (wt %)	Spinning temperature (°C)	Pressure ($kg f cm^{-2}$)	Spinning rate ($m min^{-1}$)
1	76.0	32–33	5.5	53
2	76.8	33–34	8.0	43
3	77.9	34–35	11.5	22
4	76.3	32–33	6.0	53
5	76.0	32–33	5.5	53
6[a]	76.0	31–32	9.0	61

[a] Spinning nozzle size: 0.1 mm ϕ × 0.6 mm.

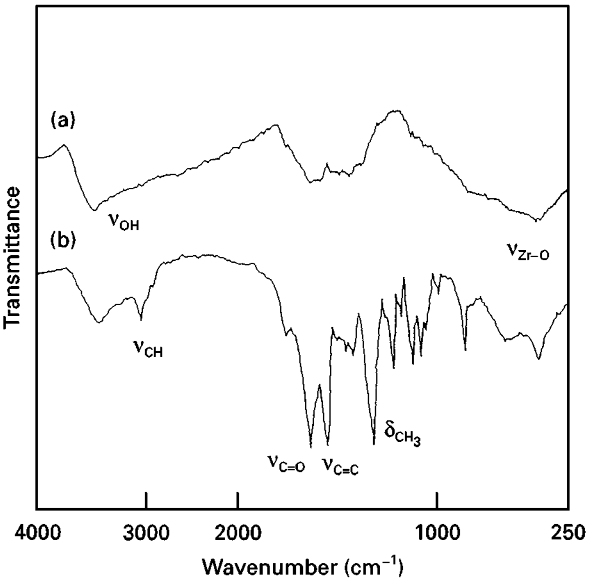


Figure 5 Infrared spectra of $3.0Y_2O_3$–$97ZrO_2$ precursor fibres (a) with and (b) without steam treatment.

TABLE VI Results of heat treatment of 3.0Y–$97ZrO_2$ precursor fibres

Heat treatment temperature (°C)	Crystal form	Colour
200	Amorphous	Golden-yellow
400	Amorphous	Dark-brown
600	Tetragonal	Black
800	Tetragonal	White
1000	Tetragonal	White
1200	Tetragonal	White
1400	Tetragonal	White

fibres became golden-yellow (200 °C), dark-brown (400 °C), black (600 °C) and white (800 °C) when heated. Thus, organic residues are removed at 800 °C. The crystal form of zirconia was amorphous below 400 °C and tetragonal above 600 °C. The results of the tensile strength measurements of the oxide fibres obtained by heat treatment of precursor fibres at 1100 and 1200 °C are summarized in Table VII. Dry spinning of a Y–PZO solution of high concentration (Run Nos 2 and 3) provided fibres with a large diameter for a high viscosity which made it difficult to extrude out PZO from the spinning nozzle. In the same concentration (Run Nos 1 and 5), fibres with a high tensile strength were prepared by heat treatment at 1200 °C compared with that at 1100 °C. Continuous zirconia fibres with a tensile strength ranging from 780 and 1450 MPa were obtained.

Fig. 6 is a plot of tensile strength versus elongation of fibres for Run Nos 4–6 from Table VI. Elongation almost linearly increases with increasing tensile strength regardless of the fibres. The dependence of tensile strength on heat treatment temperature is more clearly revealed in Fig. 7. Tensile strength increases with increasing temperature up to 1200 °C and then decreases on further heat treatment. This is ascribed to crystal growth, as represented in Fig. 8. The crystal diameter increases gradually up to 1200 °C and then critically above that temperature. Therefore, the marked decrease in the tensile strength may result

TABLE VII Preparation conditions and tensile strength of 3.0Y–$97ZrO_2$ fibres[a]

No.[b]	Pyrolysis temperature (°C)	Fibre diameter (μm)	n[c]	Tensile strength (MPa)		
				Maximum	Average	σ[d]
1	1100	14	23	1020	550	23
2	1100	17	17	740	500	19
3	1100	18	7	690	350	17
4	1200	15	23	1310	730	28
5	1200	14	17	1400	780	32
6[e]	1200	12	17	1450	780	29

[a] PZO (Hetac/ZOC = 1.5, reaction for 2 h at room temperature).
[b] Corresponding to sample No. in Table V.
[c] Number of samples for the tensile strength test.
[d] Standard deviation.
[e] Spinning nozzle size: 0.1 mm ϕ × 0.6 mm.

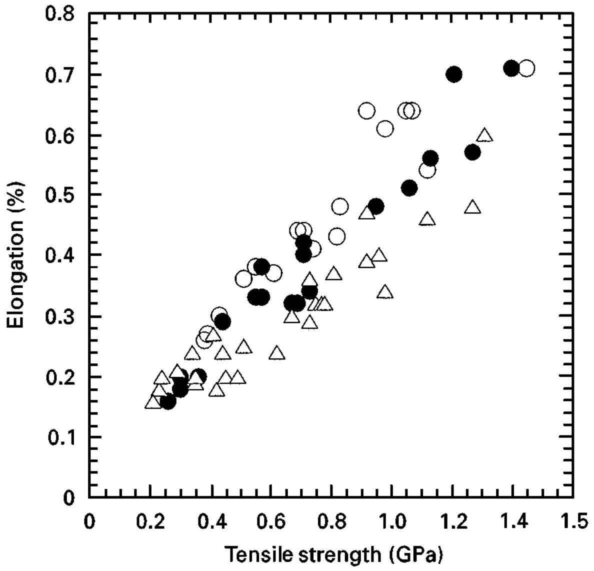


Figure 6 Relationship between elongation and tensile strength (Runs No. 4–6): (○) maximum 1450 MPa, Run No. 6; (●) maximum 1400 MPa, Run No. 5; (△) maximum 1310 MPa, Run No. 4.

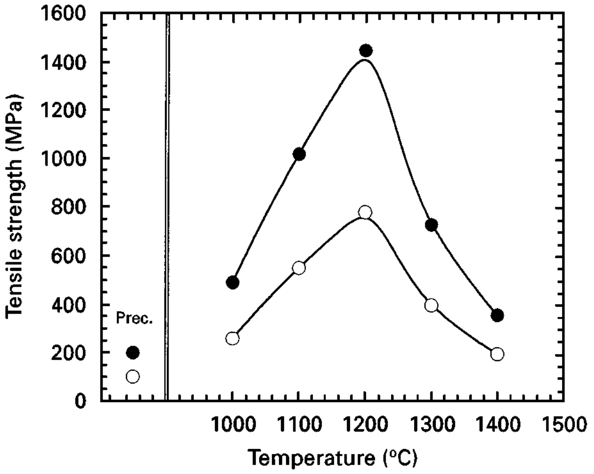


Figure 7 Relationship between temperature and tensile strength: (—●—) maximum, (—○—) average.

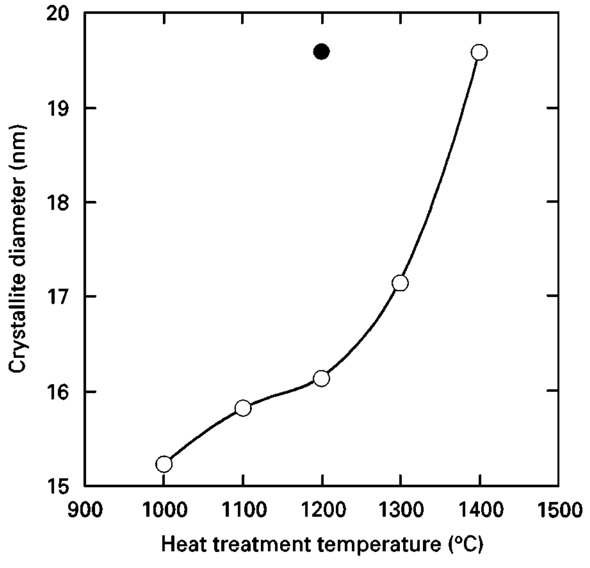


Figure 8 Relationship between heat treatment and diameter of a particle: (a) for hold time of (—○—) and (●) 10 h, respectively.

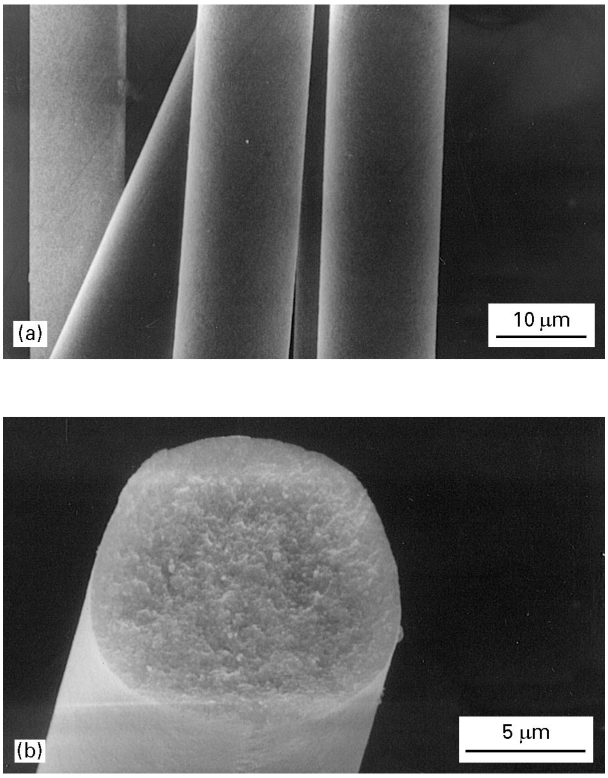


Figure 9 Scanning electron micrographs of oxide fibres obtained by heat treatment of $3.0Y_2O_3$–$97ZrO_2$ precursor fibres: (a) fibre surface, and (b) cross-section. Heat treatment condition: heating up to 1200 °C (2 °C min^{-1}) and standing for 1 h.

from crystal growth. It was observed that the crystallite diameter of fibres increased by 20% compared with those fibres heat treated for 1 h and, furthermore, the tensile strength also decreased from 1450 to 100 MPa when the fibres were heat treated for 10 h.

Fig. 9 shows SEM photographs of $3.0Y_2O_3$–$97ZrO_2$ fibres prepared by heat treatment of $3.0Y_2O_3$–$97ZrO_2$ precursor fibres at 1100 and 1200 °C. An individual consists of a submicrometre-sized grain sintered body with a smooth surface and a diameter of 10–24 μm.

4. Conclusions

The one-pot reaction of zirconium oxychloride hydrate with Hetac in the presence of triethylamine formed highly viscous solutions having good spinnability and high stability to self-condensation. PZO was isolated as white powders by precipitation with THF–hexane, which are easily soluble in acetone, THF, and methanol and have a molecular weight, $M_n = 1000$–2000. It was confirmed that PZO consisted of a back-bone Zr–O linkage with the pendant etac and OH groups.

The continuous precursor fibres were prepared by dry spinning of the concentrated PZO solution containing 3 mol % $Y(acac)_3$. Heat treatment of the precursor fibres at 1100 and 1200 °C provided fibres having a tensile strength of 1.4 GPa. Individual fibres were constructed of submicrometre-sized grain sintered bodies having smooth surfaces and diameters of 10–24 μm.

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