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Sol/gel-based precursors for manufacturing refractory oxide fibres

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Several kinds of mixed refractory oxide fibres containing the oxides of Zr, Ti, Al, Cr and Ce were produced from sol/gel precursors via a melt spinning process from 50 to 110 °C. For the synthesis of precursor sols the *n*-propoxides of Zr and Ti were reacted with chelating agents acetylacetone, ethyleneglycole, acetic acid and hydrolysis water. The surplus of solvents was distilled off, to adjust the viscosity. The viscosity and spinnability were improved by the use of *N,N*-dimethylformamide (DMF) as drying control chemical additive (DCCA) and different organic polymers as plastifiers. The elements Al, Cr and Ce were added to the precursor sols as chlorides, basic chlorides or basic acetates. The precursors were spun into bundles of thin gel-fibres with minimum diameters of ca. 45 μm by extrusion though multifilament spinnerets. The gel fibres were cured in air at 105 °C and converted into fine grained ceramic fibres by pyrolysis at 1450 °C. The decomposition process was investigated by thermogravimetric measurements (TG/DTA) and thermomechanical analysis (TMA).

1. Introduction

For economic production of refractory fibres it is very important to use a fibre spinning process that works at temperatures considerably lower than the melting temperature of the refractories. In the case of oxide fibres, in particular, the problem of corrosion of the spinning equipment and the orifices limit the process temperature.

For the production of such oxide fibres the conversion of primary fibres, the slurry process and gel spinning processes are the most frequently used methods. As an exception, the unidirectional freeze drying of aquasols consisting of metal alkoxide or hydroxide colloidal particles is used for the production of short fibres [1–3].

Prior to the conversion to the final oxidic fibre, primary (green) organic fibres are impregnated with metal salts and pyrolysed to burn off the organics and decompose the metal salts. A typical example is a Zr/Al-oxide fibre, based on Zr- and Al-chlorides on a cellulose fibre [4], or the Zr/Y-oxide short fibres produced by Union Carbide [5]. As a result of the high content of organics to be burned off, dense and endless fibres cannot be produced by this process.

For the slurry process, highly concentrated and viscous mixtures of colloidal metal oxide particles and organic binders are used as precursors to be extruded through the orifices. Usually these fibres have to be stabilized thermally or by passage through a precipitate bath. On an industrial scale the FP fibre [6, 7] (99.9% α-Al_2O_3), derived from a colloidal suspension of α-Al_2O_3, Al-salts and spinning additives and the fibre PRD 166 [8] (80% Al_2O_3, 20% *t*-ZrO_2) (E.I. du Pont de Nemours), are produced following this route.

The gel spinning process is based on the sol/gel method, which was originally developed for the synthesis of fine oxide powders exhibiting excellent sintering properties [9]. Gel spinning seems to be the most promising process to produce continuous fibres. It is used for the production of 3M Corporation's Nextel fibres (320, 440 and 480) [10] containing Al_2O_3, SiO_2 and B_2O_3, based on a silica hydrosol, aluminium formoacetate and boric acid, respectively. The fibre Nextel Z11 (32% ZrO_2, 68% SiO_2) is synthesized [11] using a similar process. Sumitomo produces Al_2O_3 fibres using an $Al(OEt)_3$- and $Al(Et)_3$-based sol/gel process [12, 13]. Even for SiO_2 fibres, commonly produced by melt spinning, a sol/gel process has been introduced by Akzo Company [14]. The objective of the investigation described in this paper was to develop sol/gel precursors for a gel spinning process to produce continuous fibres composed of varying mixtures of refractory oxides such as ZrO_2/Al_2O_3, TiO_2/Al_2O_3, $ZrO_2/TiO_2/Y_2O_3$, ZrO_2/

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CeO_2 and Cr_2O_3/Al_2O_3. Emphasis was placed on the synthesis of stable precursor sols, i.e. sols that could be stored for several days and which could be heated in the spinning machine without the risk of premature gelation.

2. Experimental Procedure

2.1. Preparation of the precursor solutions

The molar compositions of the precursors cited in this paper are listed in Tables I and II. For the tetravalent elements Zr and Ti the alkoxides ($Zr(OPr^n)_4$ in $HOPr^n$ solution, and $Ti(OEt)_4$ and $Ti(OPr^n)_4$) were used, respectively. Among the trivalent metals $Al_2(OH)_5Cl \cdot 2.5H_2O$ (basic aluminium chloride), $CeCl_3 \cdot 6.6H_2O$ (cerium chloride) and $Cr_3(OAc)_7(OH)_2$ (basic chromium acetate) were used due to the high cost of the Cr- and Ce-alkoxides. In some experiments Al was added as its iso-propoxide ($Al(OPr^i)_3$).

The alkoxides were first mixed with an adequate amount of acetylacetone (AcAc), which is known to act as a stabilizing agent [15, 16] by forming a chelate complex [17], and reacted in an open glass beaker at 80 °C for 30 min. Subsequently, the solution was mixed with a second solution comprising the other metal salts, hydrolysis water and organic additives, such as the drying control chemical additives (DCCA) [18], *N,N*-dimethylformamide (DMF) and ethyleneglycol ($Et(OH)_2$). In the case of the Cr/Al precursors, no means of hydrolysis and condensation control was necessary, so the Al- and Cr-salts were dissolved in a mixture of ethanol and water.

The amount of plastifying organic polymers polyvinylpyrrolidone (PVP) and polyethyleneglycole were 3 wt% of the oxide mass for the Ce/Zr-precursors and 1 wt% for the Cr/Al-precursors. During the fibre spinning process the viscosity of the precursor sol needed to range from ca. 1 to 50 Pas. For this reason it was necessary to remove the excess solvent by distillation.

2.2. Gel-spinning process

The main system of the piston spinning unit used in this investigation (see Fig. 1) consisted of a sample chamber with two heating zones, the spinning nozzle and a bronze piston. To start fabrication of the gel fibres the spinning precursor was melted at a temperature in the range of 50–100 °C and pressed with constant feed through the orifices (diameters 100 or 200 μm, numbers 20–100) and finally wound on a spool. Between the orifices and the spool the fibres passed a free distance of 1 m. Here the ductile fibres were stretched in order to minimize the diameter by increasing the winding speed of the pick-up unit. They solidified on the way to the pick-up unit and were collected as bundles of individual monofilaments.

2.3. Heat treatment and characterization of the gel fibres

After the spinning step, the gel fibres were cut off the spools and subjected to an ageing treatment at 105 °C for at least 5 days in air. During calcination these dried gel fibres were heated in several steps in the temperature range of 180–400 °C at a heating rate of 1–3 K min^{-1}. Sintering temperatures ranged from 1300 to 1450 °C, depending on the chemical composition of the precursor.

TABLE I Molar composition of the precursors

Number	$Zr(OPr^n)_4$ $Ti(OPr^n)_4$	$Al(OPr^i)_3$	$Al_2(OH)_5Cl \cdot 2.5H_2O$	AcAc	Spinnability
ZA 2	2	–	1	2	Poor, fast gelling
ZA 3	1	1	–	1	Good, from solution
TA 4	1	1	–	0.4	No, monolithic gels
TA 7	1	–	1	0.4	Good
	$Ti(OEt)_4$	$Zr(OPr^n)_4$	$Y(NO_3)_3 \cdot 6H_2O$	AcAc	Spinnability
TZ	1	1	–	1.2	Good
TZY	1	0.35	0.035	0.6	Good
	$CrCl_3 \cdot 6H_2O$	$Cr_3(OAc)_7(OH)_2$	$Al_2(OH)_5Cl \cdot 2.5H_2O$	DMF	Spinnability
CA 11	0.32		1		Poor, hygroscopic
CA 63[a]		0.16	1	1.1	Very good
CA 76[b]		0.16	1	1.1	Very good

[a] contained 1% PEG and 1% SiO_2; [b] contained 1% PVP and 1% SiO_2.

TABLE II Molar composition of the Zr/Ce-precursors based on $Zr(OPr^n)_4$ and $CeCl_3 \cdot 6.6H_2O$ in the molar ratio 1:0.2

Number	H_2O	AcAc	$Et(OH)_2$	HOAc	DMF	Others	Spinnability
CZ 1	1.3	0.6	0.18	0.5	–	–	Good
CZ 4	1.3	0.5	0.09	1	–	–	Good
CZ 3	1.3	0.75	0.9	–	–	–	Good
CZ 53	1.32	0.6	2	–	–	–	Good
CZ 60	1.32	0.75	–	–	2	–	Good
CZ 62	1.32	0.4	–	–	2	–	Good
CZ 611	1.4	0.75	–	–	2	PVP 3%	Very ductile
CZ 615	1.4	0.75	–	–	2	PEG 3%	Very ductile

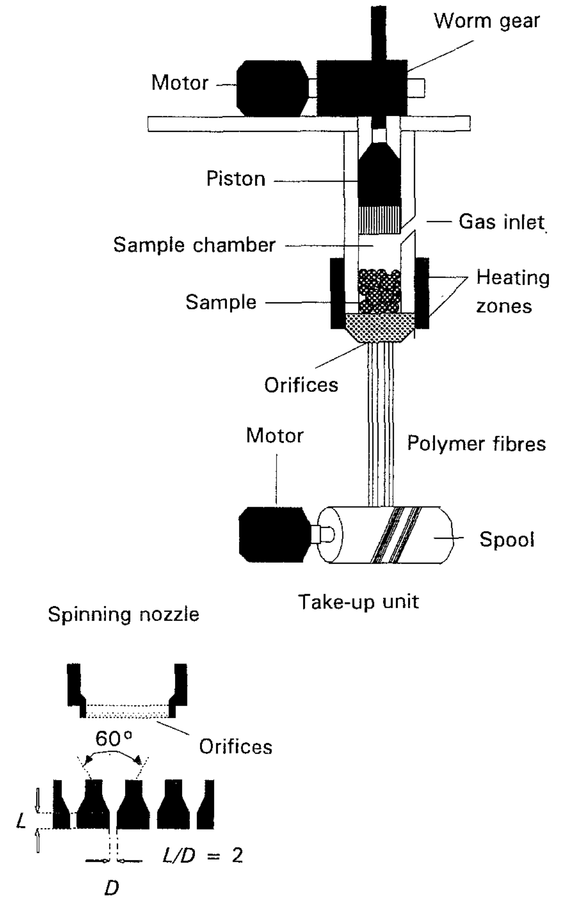

Figure 1 Piston spinning unit.

To obtain detailed information about the decomposition processes of the gel fibres, thermogravimetric investigations (TG) and thermomechanical analysis (TMA) of the crushed fibres were applied. The crystallization was investigated by X-ray diffraction with a CuK_α-source.

The chemical compositions of the spinning sols were determined by analysing the volatile products escaping during distillation using a gas chromatograph (GC).

3. Results

3.1. Spinning properties of Zr/Al-precursors

When basic aluminium chloride $[Al_2(OH)_5Cl \cdot 2.5H_2O]$ and Zr-*n*-propoxide (ZA 2, Table 1) were used, a minimum ratio $H_2O/Zr = h$ of only 10 could be realized, due to the poor solubility of the Al component in dry organic solvents. The use of AcAc to slow down the rate of the hydrolysis of the Zr-*n*-propoxide was limited to a ratio of $AcAc/Zr = r$ of ca. 1 due to the high thermodynamic stability of the $Al(AcAc)_3$ complex against hydrolysis and condensation reactions, and its poor solubility in alcoholic media. Since these precursors showed fast gelling of monolithic gels (within a few minutes) their use as spinning precursors was not possible.

Using the Al-isopropoxide instead of the basic Al-chloride, stable sols with adjustable gelling times could be prepared. Sols with $h = 2$ and $r = 1$ that were narrowed to 70% of their initial volume showed excellent spinning properties is (ZA 3, Table 1). Thin gel fibres with diameters of ca. 100 μm and a length of up to 1.5 m were spun by pulling a glass rod out of the solution.

Experiments with the spinning machine showed that the thermal and long-time stability of these precursors was not sufficient for the applied gel spinning process. Spinning from the solution, however, seemed to be a suitable method for the production of Zr/Al-oxide fibres.

3.2. Spinning properties of Ti/Al-precursors

Using a mixture of Ti- and Al-alkoxides ($Ti(OEt)_4$, $Al(OPr^i)_3$) and AcAc as chelating agent, sols were produced that formed transparent monolithic gels upon hydrolysis (TA 4, Table I). The major problem of poor solubility and inertness of the $Al(AcAc)_3$ against hydrolysis limited the addition of AcAc, as described above. Thus, the sols could not be sufficiently stabilized for storage over a period of at least 2 days or heated during the spinning process. This problem was solved by replacing the Al-alkoxide by the basic aluminium chloride.

The time for the formation of well spinnable precursors based on $Ti(OEt)_4$ and basic aluminium chloride by hydrolysis with water ($H_2O/Ti = h = 12$) could be adjusted from several minutes to seven days just by varying the molar ratio of $AcAc/Ti = r$ from 0.2 to 1. Sols with $r > 1.5$ did not show any tendency to form gels.

The gel spinning experiments were performed using sols with a AcAc/Ti ratio of 0.4 (TA 7, Table I), since this composition was sufficiently stabilized to avoid gelation in the spinning machine at spinning temperatures (50–80 °C). The as-spun fibres underwent gelation on exposure to air on their way from the orifice to the pick-up unit. Gel fibres with minimum diameters of 113 μm were produced using spinnerets of 300 μm diameter. After drying and heat treatment at a sintering temperature of 1700 °C short ceramic fibres (2–5 mm in length) with diameters of ca. 100 μm were obtained.

3.3. Spinning properties of Zr/Ti-precursors

Using precursors with equimolar amounts of $Zr(OPr^n)_4$ and $Ti(OEt)_4$ a minimum molar ratio of $AcAc/Zr > 1.2$ was found to be necessary for the formation of spinnable sols. Sols with molar ratios $AcAc/Zr = r$ of 1.2 and $H_2O/Zr = h$ of 2.5 (TZ, Table I) showed good spinning properties at moderate temperatures (58 °C), but the minimum diameter of the gel fibres was not significantly lower than the diameter of the spinnerets (100 μm).

Using these types of precursors it was shown to be possible to vary the composition of the final fibres within wide limits. For example, a precursor leading to the oxide composition $TiO_2 \cdot 0.35ZrO_2 \cdot 0.035Y_2O_3$ (TZY, Table 1) was spun to gel fibres ($d_{min} = 90$ μm) under conditions comparable to those for the spinning of the equimolar Ti/Zr-sols. The final ceramic fibres (sintering temperature 1450 °C) consisted of a mixture of TiO_2 (rutile) and $ZrTiO_4$.

Due to the high spinning pressure (up to 1.8×10^7 Pa, which was near to the maximum pressure of the machine) a further optimization for lowering the viscosity of the spinning solution, preferably by the addition of organic spinning additives, would be advisable.

3.4. Stabilization and spinning properties of Zr/Ce-precursors

For these precursors, detailed investigations on the role of chelating agents like AcAc and acetic acid (HOAc) and drying control chemical additives (DCCA) like DMF and $Et(OH)_2$ were carried out. For all precursors based on Zr-*n*-propoxide and $CeCl_3 \cdot 6.6\,H_2O$ as raw materials the $H_2O/(Zr,Ce)$ ratio for the formation of spinnable sols ranged from ca. 1.2–2.4. For $H_2O/(Zr,Ce)$ ratios (h) higher than 2.4 the hydrolysis and condensation reactions were too fast to handle or spin the sols.

The minimum AcAc/(Zr,Ce) ratio for the formation of stable solutions was found to be $h_{min} = 0.4$. For $h > 0.75$ no gelation was observed, regardless of the water content.

According to GC measurements the following stoichiometric composition of the spinning solution in the metal concentration range 2.35–2.7 $mmol\,g^{-1}$ was found:

$$Zr(AcAc)_{0.6}(OPr^n)_{0.76}O_{1.32}Ce_{0.2}Cl_{0.6} \cdot 3.5\text{–}5HOPr^n \qquad (1)$$

The additional use of $Et(OH)_2$ as DCCA introduced the possibility of increasing the sol viscosity, and thus improving its spinnability. The formation of Zr-glycolates, which can be insoluble products [19], was avoided by adding the $Et(OH)_2$ after the AcAc.

In Fig. 2 the precursor's properties are shown as a function of the content of water, AcAc and $Et(OH)_2$. Three distinct areas of different behaviour can be recognized. The range of compositions leading to the best spinning properties can be seen in the hatched region, where h ranged from 1.3 to 2.4 and the $[Et(OH)_2 + AcAc]/(Zr, Ce)$ ratio ranged from 1 to 4.2. From these precursors thin gel fibres with diameters ranging from 70 to 90 µm, with a length of several metres, were obtained at moderate spinning temperatures below 100 °C (see Table III).

The composition determined by GC-measurements in the metal concentration range of 2.35–2.7 $mmol\,g^{-1}$ was:

$$Zr(AcAc)_{0.6}(O\text{–}Et\text{–}O)_{0.38}O_{1.32}Ce_{0.2}Cl_{0.6} \cdot 2.6\text{–}4.8HOPr^n \cdot 1\text{–}1.6Et(OH)_2 \qquad (2)$$

With an increasing water content (black zone, Fig. 2) the viscosity increased too rapidly during solvent removal of the precursor sol to obtain precursors suitable for a spinning process.

With an increasing content of stabilizing agents (dotted region, Fig. 2) the precursor sols could not be drawn to thin fibres since the resulting gels were very brittle and crumbly.

The use of small amounts of HOAc as a chelating agent did not lead to stable sols unless AcAc was also

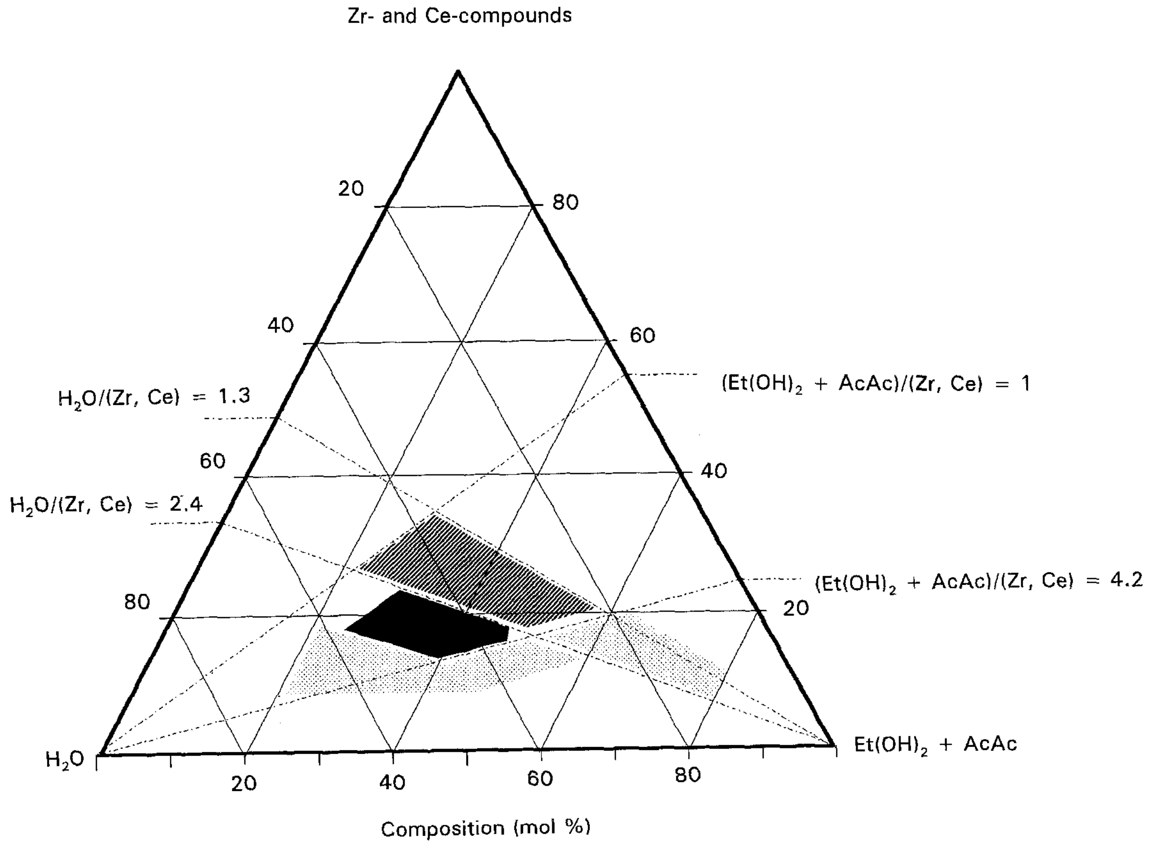

Figure 2 Regions of stability and spinnability of CZ precursors containing AcAc and $Et(OH)_2$. ▨, good spinnability; ▦, stable sol, no gelling; ■, instable gel, fast gelling.

TABLE III Parameters and results of spinning experiments

Number	Spinneret nd [µm]	T (°C)	Flow (cm^3 min^{-1})	$d_{\min}$ (µm)	p (Pa)
TA 7	20·300	80	2	113	8.0×10^6
TA 5	20·100	58	1	100	1.8×10^7
TA 35	20·100	64	1	90	1.8×10^7
Z 1	20·300	98	5	160	3.5×10^6
Z 13	20·100	80	2	91	8.0×10^6
Z 38	100·100	58	8	75	2.3×10^6
CA 20	20·100	105	2	80	1.5×10^7
CA 63	20·100	52	2.5	40	2.0×10^6
CA 76	100·100	62	3	42	2.5×10^6
CZ 1	20·100	75	2	70	8.5×10^6
CZ 4	20·100	60	2	70	8.0×10^6–1.2×10^7
CZ 3	20·100	89	2	90	4.0×10^6
CZ 53	20·100	60	1	72	7.0×10^6
CZ 46	20·100	52	1.5	80	5.5×10^6
CZ 60	20·100	80	2.1	91	8.0×10^6
CZ 62	20·100	79	4	93	1.07×10^7
CZ 611	100·100	105	3	70	5.7×10^6
CZ 615	100·100	58	8.1	75	2.3×10^6

added. For all precursors with HOAc/(Zr,Ce) ratios > 0.5 a phase separation of the sol was observed into a HOAc-rich phase that slowly formed a white precipitate and a *n*-PrOH-rich phase that did not show any tendency of gelation. The rate of phase separation increased with increasing HOAc content.

Only for HOAc/(Zr,Ce) ratios < 0.5 and AcAc/(Zr,Ce) ratios ranging from 0.5 to 0.6 could the phase separation be oppressed, or at least sufficiently slowed so that well spinnable precursors were obtained (see Table II). Spinning temperatures and the diameters of the resulting gel fibres were comparable to those observed for the precursors mentioned above (see Table III).

Additions of DMF significantly improved the chemical stability and the spinning properties. The hydrolysis and condensation reactions were significantly retarded during storage or heating. During the spinning process the DMF evaporated smoothly from the gel fibres. The as-spun gel fibres showed remarkably few defects and were very flexible. The metal concentration of the DMF-containing spinning solutions was relatively high, ranging from 3.5 to 3.7 mmol g^{-1}.

The resulting chemical composition was determined by GC-measurements as follows:

$$\mathrm{Zr(AcAc)_{0.75}(OPr^n)_{0.45}O_{1.4}Ce_{0.2}Cl_{0.6}}$$
$$0.05\text{–}0.4\mathrm{HOPr^n} \cdot 1.4\text{–}1.8\mathrm{DMF} \qquad (3)$$

The addition of viscosity controlling additives like tetraethyleneglycol (tetra), polyethyleneglycols with different molecular weights (PEG 300, PEG 10 000) and polyvinylpyrrolidone (PVP) led to a further improvement of the spinning properties (precursors CZ 611 and 615, Table II). With these additives very flexible gel–fibre bundles with a length of hundreds of metres and monofilament diameters of ca. 70 µm were obtained (see Table III).

3.5. Spinning properties of the Al/Cr-precursors

For the preparation of fibres composed of Al_2O_3/Cr_2O_3 with 10 wt% Cr_2O_3 a route for the synthesis avoiding alkoxides was chosen. In order to improve the sintering properties of the oxide mixture, 1 wt% of SiO_2 was added as $Si(OEt)_4$ (TEOS) to selected precursors. Changes in physical and spinning properties of the precursors due to this addition were not observed.

In the case of the basic aluminium chloride used as a solution in an ethanol/water mixture a chemical stabilization against hydrolysis was not necessary because reversible formation of the gel could be performed by controlling the water content.

Chromium was added as a water soluble salt either as $CrCl_3 \cdot 6H_2O$ or as $Cr_3(OAc)_7(OH)_2$, but the spinning, drying and ageing properties of the precursors markedly depended on the Cr component. Spinning solutions based on Cr(III) chloride (CA 11, Table I), as well as the as-spun gel fibres, were very hygroscopic. For this reason a drying duct fed with hot air had to be attached to the spinning machine. The as-spun gel fibres had to be stored at temperatures above 100 °C to avoid the incorporation of water leading to swelling and crack formation.

The chromium acetate based precursors (CA 63 and CA 76, Table I) were considerably less hygroscopic, as the spun gel fibres rapidly hardened in air at 20 °C and their storage in air was possible without deterioration of the fibre quality.

The spinning pressures were markedly lower (ca. 2.5×10^6 Pa) compared to the pressure required for the spinning of the chromium chloride based precursors (ca. 1.5×10^7 Pa).

A typical chemical composition of the spinning solution at a metal concentration of 5.5 mmol g^{-1} was:

$$\mathrm{[(Al_{11.14}Cr_{1.86})O_4(OH)_{21.1}Cl_{2.89}(H_2O)_{12}]}$$
$$\mathrm{Cl_{2.65}(OAc)_{4.35} \cdot 68.3H_2O \cdot 8.9EtOH \cdot 0.67DMF} \qquad (4)$$

The notation was adapted to the basic structural units for Al-hydrogels proposed by Sopicka-Lizer and Pawlowski [20] consisting of $Al_{13}O_4(OH)_{24}(H_2O)_{12}$ polyhedra. It was assumed that the Cr^{3+}-ions could substitute Al^{3+}-ions without significant structural changes.

With the addition of viscosity controlling polymeric additives, as mentioned for the Zr/Ce-precursors, flexible fibre bundles with monofilament diameters ca. 45 µm and fibre lengths of several hundreds of metres were spun (see Table III; CA 63 and 76).

3.6. Changes at the heat treatment of the gel-fibres and formation of Zr/Ce- and Al/Cr-oxide fibres

The decomposition behaviour of a CZ-precursor containing the spinning additives DMF and a small amount of tetraethyleneglycol (tetra) before and after drying at 105 °C can be seen in the TG- and DTA-curves (Fig 3).

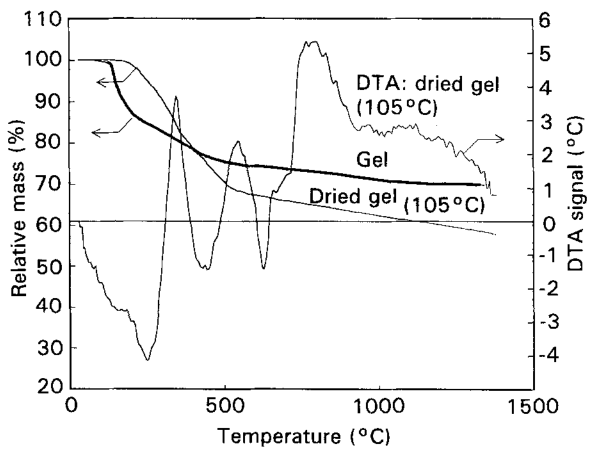

Figure 3 TG- and DTA-curves of CZ gel containing DMF.

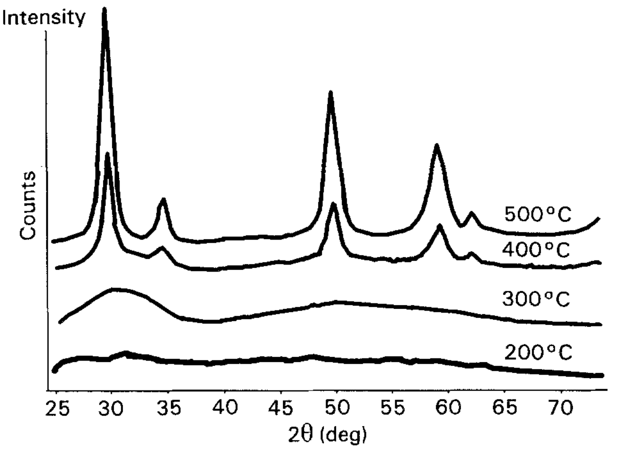

Figure 5 X-ray diffractogram of tempered (Zr, Ce)O_2-fibres.

The TG curve of the gel shows two distinct ranges of decomposition. The first, with a mass loss of 15% in the temperature range 120–230 °C, could be ascribed to the volatilization of residual *n*-PrOH and DMF. The ceramic yield of this gel was 70%. In comparison, the gel dried at 105 °C in air showed a lower ceramic yield of ca. 58%, but considerable mass loss did not start until 210 °C.

The exothermic DTA-peak with maximum at 750 °C indicated the crystallization of (Zr,Ce)O_2.

A very important characteristic of the gel fibres is the generally high shrinkage that accompanies the decomposition of gels upon thermal treatment. The as-spun CZ-gel fibre (Fig. 4a) showed considerable isotropic shrinkage of 53%. The two-step decomposition observed in the TG measurements was also reflected by the TMA-curve. After fibre drying at 105 °C, solute (*n*-PrOH) and spinning additive [Et(OH)$_2$] had both evaporated (Fig. 4b), so only the second range of shrinkage from ca. 350 to 450 °C was observed, resulting in a total of 30%.

Tempering the gel fibre at a temperature of 300 °C for 10 h had an important effect on the second range of shrinkage, as observed in the as-spun gel fibre. Although the heat treatment temperature was significantly lower than 350 °C, almost no shrinkage was observed until a small step of 7% at 550 °C, which was ascribed to the onset of crystallization of ZrO_2.

The thermal evolution of crystalline phases is shown in Fig. 5. Upon heating to 1450 °C the dark brown gel fibres changed colour to light yellow. The sintered ZrO_2/CeO_2-fibres showed a dense and crack-free morphology (see Fig. 8) of tetragonal and orthorhombic mixed oxide crystals [21].

Mass loss and thermal analysis of the decomposition of a Cr/Al-spinning precursor containing the additive DMF is shown in Fig. 6. The two-stepped mass loss started at a temperature of 100 °C, accompanied by a distinct endothermal DTA-peak with maximum at 150 °C, indicating the volatilization of physisorbed water and the DMF. At the second step, with an endotherm peak at 290 °C, which turned into a broad exotherm peak with maximum at 580 °C, chemisorbed water evaporated and residual organics were burned off. The ceramic yield of this spinning precursor was 66%. The weak exotherm peak at ca. 1220 °C, which was not accompanied by a mass effect, was attributed to the crystallization of the mixed α-Al_2O_3/Cr_2O_3.

A slightly hygroscopic behaviour of the gel fibres could be seen in the shrinkage that occurred during heating (see Fig. 7). In the temperature range from ca. 40 to 150 °C it was attributed to the loss of physisorbed water, a shrinkage of 10% takes place for the as-spun (Fig. 7a) and aged (Fig. 7b) gel fibres. The overall shrinkage was 35 and 41%, respectively. The fibres dried at 105 °C (Fig. 7c) did not show any contraction up to a temperature of ca. 150 °C, therefore the overall shrinkage at 850 °C of 28% was markedly lower than

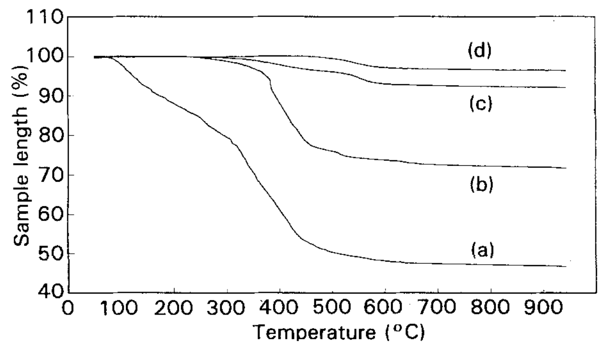

Figure 4 TMA-curve of CZ-gel fibres as spun (a), dried at 105 °C (b), heated at 300 °C (c) and 400 °C (d).

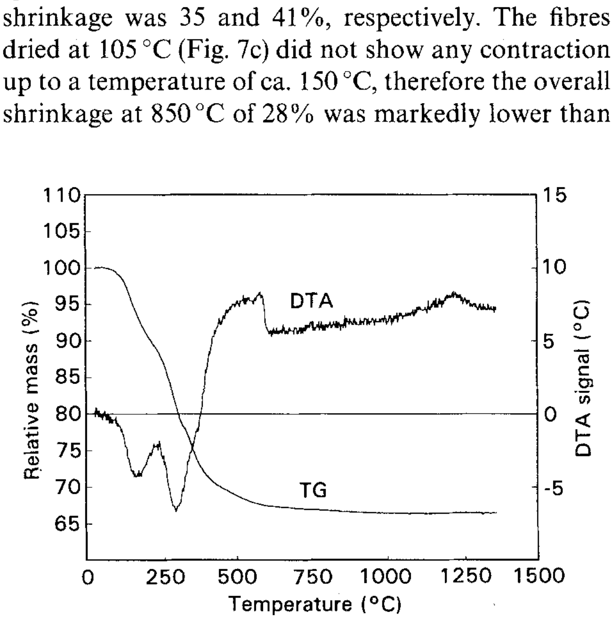

Figure 6 TG/DTA-curves of a Cr/Al-oxide spinning precursor containing the spinning additive DMF.

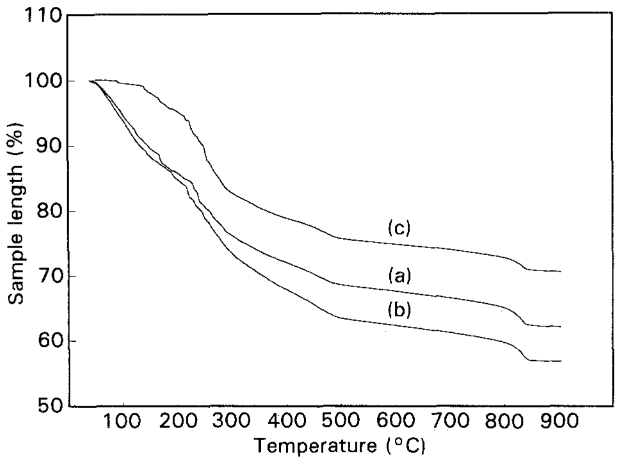

Figure 7 Dilatometric curves of CA gel fibres, as spun (a), aged for 1 day (b), dried at 105 °C (c).

for the other fibres. The distinct step of ca. 2% at 830 °C indicated the crystallization of some mixed oxide species. Upon heating, the fibres were glassy and transparent with a green colour up to ca. 1100 °C, thereafter they became opaque. At temperatures beyond 1200 °C the colour turned to red. From Figs 9 and 10 it can be seen that the sintered Cr_2O_3/Al_2O_3-fibres showed a very smooth surface without visible defects or cracks. The fracture surface of the oxide fibres showed a very dense structure with fine scaly and flaky crystals.

4. Discussion

To obtain spinnable solutions it was necessary to convert the monomeric metal species to polymetaloxanes, which preferably should be composed of linear chains. Strict control of the hydrolysis and polycondensation reactions was necessary to obtain precursors with suitable viscosity and melting points. According to the desired oxide composition either the alkoxides of Ti, Zr and Al, or inorganic metal salts of Cr, Al and Ce, were used to produce the precursors. It was found that sol stability and spinnability of the alkoxide-based precursors depended highly on the amount of hydrolysis water and organic additives. In the case of the (Zr,Ti)- and (Zr,Ce)-precursors a water/metal ratio of only 1.2–2.4 was found to lead to the best spinning sols. Since these alkoxides showed very high hydrolysis rates it was essential to retard this reaction by the addition of chelating agents. It was shown that the formation of partially AcAc-substituted Zr- and Ti-alkoxides was an appropriate way of retarding the hydrolysis reaction. Guinebretière *et al.* [22] reported that in Zr-*n*-propoxide/AcAc gels the particle size was reduced significantly with an increasing AcAc content.

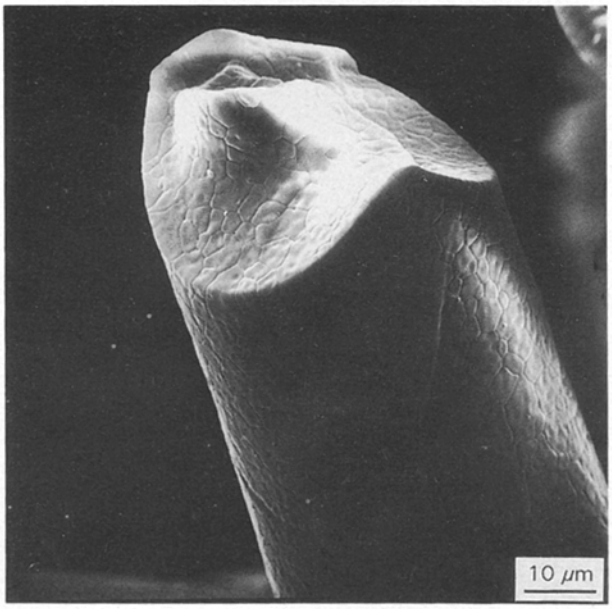

Figure 8 SEM micrograph of CZ-fibre sintered at 1450 °C.

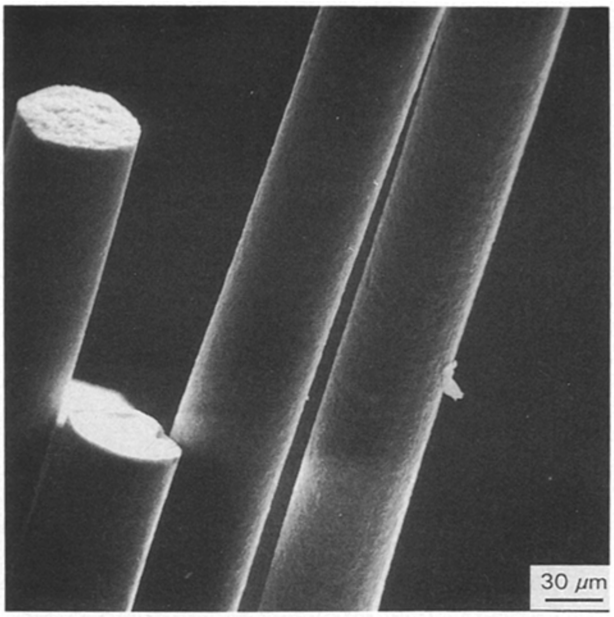

Figure 9 SEM micrograph of Cr_2O_3/Al_2O_3-fibres with 1% SiO_2, sintered at 1450 °C.

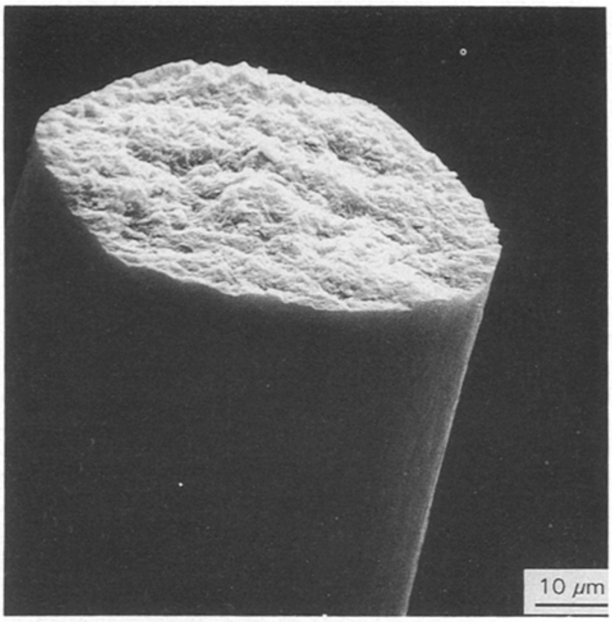

Figure 10 SEM micrograph of the surface of a Cr_2O_3/Al_2O_3-fibre, sintered at 1450 °C.

For both alkoxides a minimum AcAc/(metal alkoxide) ratio of ca. 0.2 was found to form precursors stable enough to permit the addition of the hydrolysis water and the other components without inducing spontaneous gelation. With increasing amounts of AcAc the stability of the sols was improved. This meant that the sols did not gel during the distillation of solvent, during storage for several days or at the elevated temperatures in the melt-spinning machine. Before solvent removal the gelling times of these precursors were in the order of several weeks.

For all investigated oxide compositions, stable sols and best spinning results were obtained when a AcAc/(metal alkoxide) ratio of about 0.5 was chosen. This meant that half of the metal alkoxide molecules were chelated by one AcAc molecule. Excessive amounts of AcAc deteriorated the spinning properties because the molecular weight of the metaloxane species became too small. In the case of the Zr/Ce-precursors this limit was found to be a AcAc/Zr ratio of 0.75. For AcAc/(metal alkoxide) ratios higher than ca. 1.2 most of the precursors did not show any gelation.

The high thermodynamic stability of the Zr–AcAc chelates was reflected by the fact that addition of $Et(OH)_2$ to AcAc-stabilized precursors did not lead to precipitates of insoluble Zr-glycolates as found for pure alcoholates [19]. Instead, the $Et(OH)_2$ was used as a viscosity and drying control chemical additive to improve the spinnability of the sols and the handability of the green fibres. The use of HOAc as DCCA in the Zr/Ce-precursors presented some specific problems because for HOAc/(Zr,Ce) ratios higher than 0.5 a phase separation was observed. This behaviour can be explained by the low solubility of the acetate species in *n*-PrOH solution, as this problem was not encountered in the $Zr(OPr^i)_4/H_2O/HOAc$ sol/gel system [23].

In the Cr/Al system the basic aluminium chloride could easily be transformed to a sol by the addition of water. The basic chromium acetate was more suitable than the chloride because the gel was less hygroscopic. Furthermore, the presence of some acetate seemed to inhibit the formation of dense three-dimensional network structures and to favour the formation of linear polymers, since the spinnability improved significantly.

An important improvement in precursor quality was achieved by the use of DMF as DCCA. The substitution of *n*-PrOH (Zr/Ce-precursors) and EtOH (Cr/Al-precursors) by DMF retarded the drying of the sol during the spinning process. Due to the lower vapour pressure of DMF the viscosity of the precursor remained almost constant during the spinning process. It was found that the spinning temperature was lower and the as-spun fibres were thinner and much more flexible than for precursors without DMF.

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