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# Blow spun strontium zirconate fibres produced from a sol-gel precursor

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A zirconium sol was produced from the hydrolysis and immediate peptization of a zirconium alkoxide, which was found to be stable with the addition of a large proportion of a strontium salt, even up to equimolar amounts. Gel fibres were successfully blow spun from this doped sol, which on subsequent heating produced ceramic fibres of orthorhombic strontium zirconate. The fibres were characterized by various techniques. The fibres were found to begin forming $SrZrO_3$ at 400°C and were present as single phase orthorhombic strontium zirconate at 800°C and above. The ceramic fibres had no discernible grain structure and the average crystallite size was calculated to be only 20 nm at this temperature, but the fibres contained small surface pores ( $< 0.2$ μm) which continued to increase in size on subsequent heating, resulting in a weak and brittle fibre. Therefore, more investigation is required into sintering and the development of high temperature properties.

## 1. Introduction

In previous work we have described the preparation of zirconium titanate [1], mullite [2] and several hexagonal ferrite [3–5] fibres in a demonstration programme to show how refractory and effect fibres can be made by aqueous sol-gel routes. This work on strontium zirconate fibres is an off-shoot of a broader investigation into the preparation and properties of zirconia fibres made from aqueous precursor solutions.

An alkaline earth metal zirconate fibre has two features of special interest. The first derives from the chemical, especially alkali, resistance of zirconia which makes it more suited to operation in high temperature corrosive environments than alumina. Compounds of zirconia with the alkaline earth metals are expected to show even higher resistance to alkali and are also very refractory, the strontium melting at a higher temperature than calcium zirconate. The second feature of interest is in spinning solution preparation where the fundamental spinning property is derived from either a basic zirconia solution or a zirconia sol. These materials will, on concentration, follow Brinker's [6] criterion and transform continuously from a viscous solution to a homogeneous glassy gel without phase change. In the simplest preparations the additional metal component is conveniently added as a simple salt solution, which both induces flocculation and agglomeration of polymeric species in the basic solution or sol, and reduces the solution vapour pressure thereby making it more difficult to set the fibre. (Polymeric and sol species in solution are thought to be stabilized by a combination of positive charge and hydration barriers, in which case the salt acts both by dehydrating and supplying a high concentration of anions.)

Whatever the precise mechanism of destabilization there is a limit to the amount of salt that can be added to a particular sol or basic solution. The limit is easily recognized when attempts are made to prepare a spinning formulation since, on concentration, the solution destabilizes to form a non-coherent, unspinnable, slurry.

As a practical consequence it has not been possible to make spinel fibres of general composition $MO.Al_2O_3$ or $MO.Fe_2O_3$ by simple salt addition to available alumina or iron(III) spinning solutions, the highest levels of simple salt having been achieved when making the Y hexagonal ferrite $Ba_2Co_2Fe_{12}O_{22}$ [4].

The object of this work was to investigate the preparation of non-segregated strontium zirconate spinning solutions from the simplest aqueous precursors, and to demonstrate the spinning of fibres of textile dimensions in commercially viable spinning equipment. The preparation of strontium zirconate by the addition of a strontium salt solution to a zirconia sol is a particularly rigorous test of sol stability, other attempts using the aqueous zirconium carbonate paste [1] having been unsuccessful.

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## 2. Experimental

### 2.1. Preparative methods

All chemicals and solvents used were commercially available ACS grade.

### 2.1.1. *Zirconium sol preparation*

Zirconium iso-propoxide (0.1 mol, 32.76 g) was diluted to a 10% solution in iso-propanol which had previously been dried with molecular sieve, and this solution was then stored under a nitrogen blanket. An excess of three times the amount of distilled water (21.6 ml, 1.2 mol) needed to fully hydrolyse the zirconium alkoxide was mixed with 6.2 ml of concentrated nitric acid (0.1 mol $HNO_3$), and this was added to 50 ml of iso-propanol. This acidic solution was then added dropwise over 30 min to the zirconium alkoxide solution, which was stirred at 600 r.p.m. and was no longer kept under a nitrogen atmosphere. The pale yellow alkoxide solution immediately turned slightly cloudy upon addition of the acidic solution, and after a third of this had been added a thick white precipitate formed.

After the addition was complete, a cream coloured suspension (350 ml, 0.29 mol $l^{-1}$ zirconium) resulted, which had already begun to undergo some peptization. This was then immediately concentrated on a rotary evaporator at 90°C and under a vacuum of 95 kPa to the minimum volume required to keep the suspension in solution, which was around 100 ml (1 mol $l^{-1}$). The solution was then rediluted with approximately 300 ml of distilled water to form a suspension of 400 ml (0.25 mol $l^{-1}$) and reconcentrated under the same conditions as above. This process was repeated twice, by which point a pale yellow solution had been produced of 50 g (2 mol $l^{-1}$). On standing and cooling, it was apparent that a sol had formed, which was allowed to stand at room temperature for a further 24 h to complete peptization.

### 2.1.2. *Addition of strontium to zirconium sol*

Strontium nitrate (21.16 g, 0.1 mol) was dissolved in distilled water and added to the zirconium sol (50 g, 0.1 mol) to give a doped sol of 173.74 g, 0.2 mol total metals (1.15 mol $l^{-1}$ total metals = 0.58 mol $l^{-1}$ $SrZrO_3$).

### 2.1.3. *Fibre preparation*

The mixed sol was filtered through a 0.7 μm filter, and concentrated after the addition of a small amount of polyethylene oxide spinning aid. The fibres were produced by a modified proprietary blow spinning process [7] in which the spinning solution was extruded through a row of holes, on either side of which impinge parallel jets of humidified attenuating air. The fibres were gelled by mixing in a stream of hot secondary air and then collected in a basket as a random staple. After collection, the fibres were removed and stored in a circulating oven at 110°C to await subsequent heat treatment.

### 2.1.4. *Heat treatments of fibres*

The gel fibres were fired at 100°C $h^{-1}$ to 400°C and kept at this temperature for two hours to remove any organic or nitrate components, and then further heated at 300°C $h^{-1}$ to the required firing temperature, where they were maintained for three hours, unless otherwise stated.

### 2.2. Characterization

### 2.2.1. *Photon correlation spectroscopy (PCS)*

The sol was filtered through a 0.45 μm filter, and the particle size measured above the 3 nm diameter range with a Malvern Instruments Lo-C autosizer and series 7032 multi-8 correlator, using a 4 mW diode laser, 670 nm wavelength.

### 2.2.2. *X-ray powder diffraction (XRD) measurement*

X-ray powder diffraction patterns of the samples treated at various temperatures were recorded in the region of $2\theta = 10\text{–}80°$ with a scanning speed of 0.25° $\min^{-1}$ on a Philips PW1710 diffractometer using $CuK_\alpha$ radiation with a nickel filter. Cell parameters were calculated and further refined using linear regression procedures applied to the measured peak positions of all major reflections up to $2\theta = 90°$ with the Philips APD 1700 software. This software was also used to calculate the average size of the crystallites in a sample using the well known Scherrer equation:

$$D = K\lambda / h_{1/2} \cos\theta$$

where $D$ = average size of the crystallites, $K$ = Scherrer constant ($0.9 \times 57.3$), $\lambda$ = wavelength of radiation (0.15405 nm), $h_{1/2}$ = peak width at half height and $\theta$ corresponds to the peak position.

### 2.2.3. *Scanning electron microscopy (SEM)*

Scanning electron micrographs and analysis of the morphology of the samples was carried out on a Cambridge Instruments Stereoscan 90 SEM operating at 10 kV. Conducting samples were prepared by gold sputtering fibre specimens.

## 3. Results and discussion

In all the sols the size of the sol particles was found to be sensitive to the preparative techniques and conditions employed. In a system near the limits of colloidal stability, PCS enabled us to measure and control the properties of the sol to a certain extent. The volume distribution of the sol particles has a direct effect on the spinning process, and even a small number of large particles can severely impede or even nullify the spinnability of the sol. Therefore, volume distribution, especially the upper limit, was considered a more relevant measure than the $Z$ average. Also, it must be considered that the technique is unable to detect particles below the 3 nm threshold, and therefore these measurements may be higher than the true figures.

The zirconium sol appeared to have finished peptizing after 24 h, and remained stable for at least a month. The $Z$ average was found to be 23.5 nm, with a volume average of 33.2 nm and an upper limit of 70 nm. This zirconium sol, produced by immediate peptization following hydrolysis, appeared to be superior to other sols produced from either slower digestion at 35 °C or filtration and subsequent digestion of the precipitate [8]. Removing as much alcohol as possible from the solution during the peptization process also seemed to give a smaller particle size than when the sol was left to digest without any IPA removal.

Whilst the addition of a very high proportion of strontium nitrate solution (1:1 Zr:Sr), did not destabilize the dilute sol, it could only be concentrated to a limited extent before precipitation occurred between 2.5 and 3.0 mol $l^{-1}$ total metals. The spinning solution was therefore concentrated to 2.5 mol $l^{-1}$, and the PCS of this gave a $Z$ average of 41.6 nm and a volume average of 58.9 nm with an upper limit of 130 nm. This is on the limit of acceptable particle size for a successful spinning solution, but despite this, and the lack of viscosity of the spinning solution, gel fibres were successfully spun and collected as a random staple. These fibres were between 8–13 μm in diameter, but they contained a high proportion of shot, a symptom of the low concentration and lack of viscosity of the spinning solution.

Following the criterion discussed in the introduction these observations are an indication of a spinning formulation on the limit of acceptability. The gel fibres contained the equivalent of only 46.2% by weight of refractory material, compared to up to 60% expected for a typical zirconia precursor, and this is a further indication of the loose structure of a gel formed near the limits of flocculation.

The gel fibres were heated between 200 and 1450 °C and their XRD pattern taken at 200 °C intervals. Tetragonal zirconia and orthorhombic strontium zirconate had both crystallized by 400 °C, with the $SrZrO_3$ as the major phase. The fibres had a rough and lumpy appearance, with crystalline growths around 3 μm in diameter on the surface of the fibre. The zirconia remained as a minor product until 800 °C, when single phase orthorhombic $SrZrO_3$ fibres had been formed (Fig. 1). The average crystallite size calculated from the XRD data was 28.2 nm, and, as can be seen in Fig. 2, the fibres were now much smoother and even-sided with only a few small crystalline surface features, but the surface was pockmarked with pores less than 0.2 μm in diameter. The ceramic fibres had diameters between 6 and 10 μm.

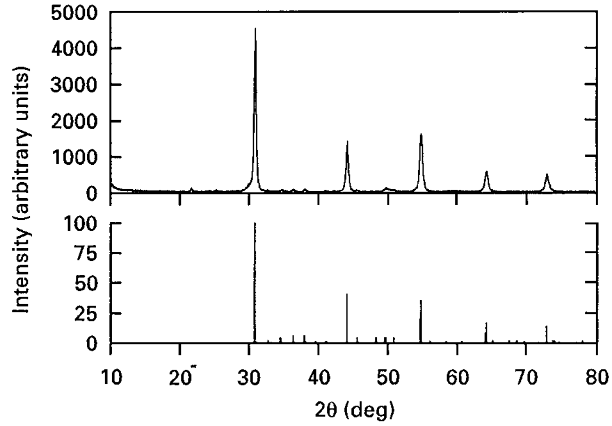

*Figure 1* XRD pattern of strontium zirconate fibres (10–268) heated to 800 °C for 3 h.

Between 800–1450 °C there was very little change in the morphology of the fibres, except for a steady increase in the size of the surface pores to over 1 μm at 1450 °C. The fibres had begun to gain a slightly pink tint at 1000 °C while the crystallite size had increased to 34 nm, and at 1250 °C the fibres were the characteristic pale pink colour of orthorhombic strontium

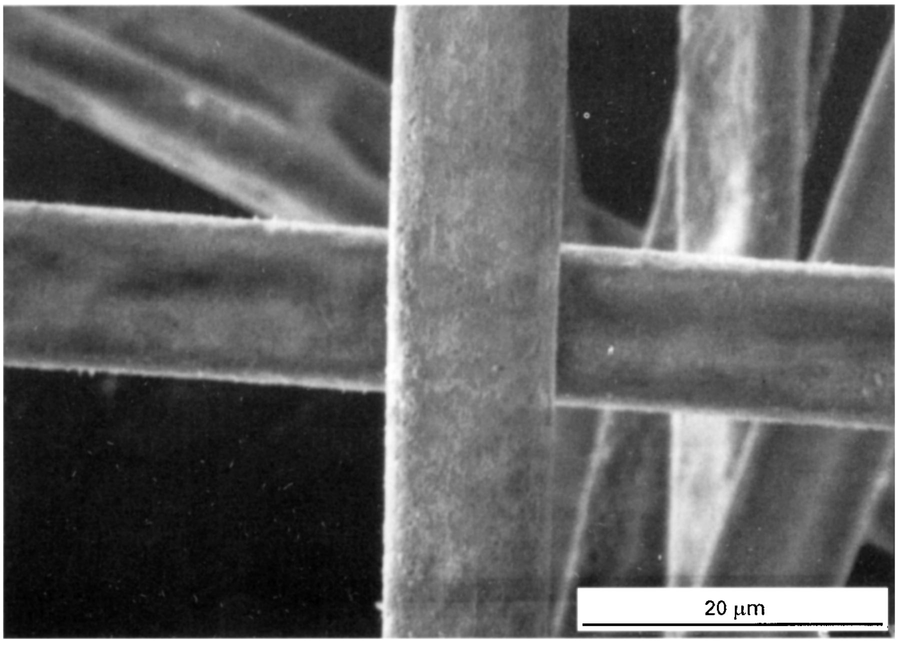

*Figure 2* SEM micrograph of strontium zirconate fibres fired at 800 °C for 3 h.

zirconate, with an average crystallite size of 47 nm. At 1450 °C the fibres were still orthorhombic strontium zirconate, but the average crystallite size was calculated now to be 57 nm and the fibres were extremely brittle and powdery.

## 4. Conclusions

A stable zirconium sol with a relatively small particle size was successfully produced from the hydrolysis and immediate peptization of a zirconium alkoxide. This sol remained stable even with the addition of a large amount of strontium nitrate solution as a dopant, up to equimolar amounts. Gel fibres were successfully spun and they had begun to form orthorhombic strontium zirconate at temperatures as low as 400 °C. By 800 °C the ceramic fibres were single phase orthorhombic strontium zirconate, and the fibres were smooth and even-sided in appearance with no observable grain structure. However, the surface of the fibres contained small pores of between 0.1–0.2 μm in diameter, and these persisted and grew until they were over 1 μm wide at 1400 °C, resulting in a weak and brittle fibre. The ultimate deterioration of the fibre is probably derived from the open gel structure indicative of a sol-gel precursor near the limit of colloid stability.

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