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Inorganic sol gel synthesis of zirconium titanate fibres

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This note describes the preparation of zirconium titanate gel fibres from an aqueous mixed zirconia titania sol. The fibres are well formed and free of shot. Heat treatment to 750 °C produces a crystalline porous zirconium titanate fibre which shows a good (1%) strain to break. Further firing to 1100 °C causes a deterioration in properties, with retention of some porosity and a reduced strain to break. Recommendations for improving the material are suggested.

1. Introduction

Ceramic fibres have a number of advantages over bulk ceramics. Brittle materials can develop higher strengths and moduli in fibrous form [1] and also fine fibres are reasonably flexible and can be manipulated on a large scale without risk of breakage. Potential areas of application for ceramic fibres, extend beyond the structural duties implied by their superior mechanical properties. Ceramic materials are also used in electronic applications, usually as thin films or small components. Mechanical performance can become an issue in larger devices with linear dimensions greater than about 2 cm and the introduction of the ceramic component as a fibre is an obvious solution to this problem. Comparisons of the effects of composite phase geometry on material properties have been reviewed by Hale [2], and it is apparent from this work that the critical point for applications is that the best electronic properties are realized when the ceramic is in a fibrous form [3].

This work on zirconium titanate is part of a programme which shows how a number of refractory and electronic fibres can be made by entirely aqueous sol–gel routes. The paper reports the preparation of a spinning dope and its conversion to highly crystalline $ZrTiO_4$ fibre which shows good strain to break after firing up to 750 °C.

2. Experimental procedure

2.1. Solution

2.1.1. Materials

Zirconia was obtained as zirconium carbonate paste (44% ZrO_2) from Magnesium Electron Ltd (MEL, Stockport, UK) who quote the following impurities levels;

Na	< 0.11% Target 0.025% on ZrO_2
Sulphate (as SO_3)	0.25–0.5% on zirconia.
SiO_2	0.2% on zirconia

Tioxide UK Ltd supplied a titanium oxychloride solution that had a nominal composition $TiOCl_{2.8}$. Materials sourced by this route are reported to contain 50 p.p.m Fe and 100 p.p.m Sn on titanium.

2.1.2. Preparation

A zirconia solution was prepared by dissolving the zirconium carbonate paste in nitric acid. A reactive zirconium hydroxide was precipitated by adding ammonium hydroxide and the precipitate washed free of anions. A sol, containing approximately 300 g per l TiO_2, and with 0.9 per l anion per TiO_2 ratio was prepared by extracting Cl^- ions from the aqueous titanium oxychloride. The zirconium hydroxide precipitate was slurried with a small amount of water, mixed with an equimolar amount of the TiO_2 sol and digested at 80–90 °C. After about 2 h a transparent zirconia/titania mixed sol was formed.

The mixed sol was filtered through a Whatman GF/B glass fibre filter, then mixed with a filtered 2% solution of polyethylene oxide spinning aid (Union Carbide Polyox WSR-N-12K) which had been adjusted to pH 3 with a small amount of dilute HCl. The aid was used at a level of 2% on $ZrTiO_4$ ceramic.

The clear mixture was again filtered and concentrated by vacuum evaporation until the viscosity measured on a paint cone and plate viscometer at 1000 per s was 5–10 poise. At this stage the sol was ready for spinning.

2.2. Spinning

The fibres were made using a proprietary blow spinning process [4] in which the spinning dope is extruded through a row of holes (in this case 5) on either side of which are slits directing impinging jets of humidified air at near ambient temperature. The fibres are drawn by the high velocity primary slit jets and set by mixing in hot dry secondary air, in this present work at 75 °C. The fibre air mixture passed down

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a short diverging section into a parallel duct to be collected as a blanket in a stainless steel gauze basket.

2.3. Heat treatment

The fibre was dried overnight at 100 °C and then ramped to 750 °C at 200 °C per h. A small sample was removed at 350 °C for X-ray diffraction analysis. The firing of the bulk of the material was completed by holding at 750 °C for 6 h. A small sample was further treated at 1100 °C for 2 h.

2.4. Characterization

2.4.1. Optical fibre diameter measurements

The fired fibre blanket could be delaminated into thin layers. A thin layer was taken from the centre of the sample fired at 750 °C and viewed through a calibrated graticule with an Olympus transmitted light microscope at a 400X magnification. The fibre sample was traversed and the diameters of 60 fibres measured to the nearest 0.5 μm as each came into focus.

2.4.2. Strain measurement

A technique is being developed in our laboratory which estimates average strain to break in a fibre mat by combining wire indentation of a sample with acoustic emission "ring down" counts. Measurements are made with an available 750 kHz transducer and equipment from the AECL 2100M modular range, and a sample of fibre is impressed with wires ranging from 1.2–0.2 mm diameter. The technique can be applied rapidly and can discriminate between good quality and reject ICI Saffil alumina (S, (strain to break), = 0.8–1% and 0.4–0.5% respectively) and Sumitomo [5] textile mullite fibre (S > 1%).

2.4.3. Scanning electron microscopy (SEM) and energy dispersive X ray spectroscopy (EDX)

Morphology and elemental analysis of the fibres were carried out on a Philips Stereoscan equipped with an energy dispersive X-ray analyser as used in earlier work reported on $ZrTiO_4$ powder [6]. Conducting samples were prepared by either carbon coating or gold sputtering of the fired fibre specimens.

2.4.4. Thermal analysis

Simultaneous differential thermal analysis and thermogravimetric analysis (DTA-TGA) were performed for a sample of gel fibres on an STA1500 (PL Polymer Laboratories) in static air up to 1000 °C at a ramp rate of 10 °C per min.

2.4.5. X-ray diffraction measurement

X-ray powder diffraction patterns for fibre samples fired to 350 and 750 °C were recorded on a Philips diffractometer (Model PW1710) with Cu K_α radiation using a nickel filter. The scans were measured over the region of $2\theta = 10$–$80°$ with a scanning speed of 0.25° per min, using silicon as an internal standard. Crystallographic information was processed by an automated Philips APD 1700 software package and analysis procedures were applied to the measured peak positions of all major reflections up to $2\theta = 80°$.

2.4.6. Surface area and porosity measurements

Surface area and pore size distribution measurements were performed on a Micromeritics ASAP 2000 using nitrogen as the adsorption gas. Samples were degassed at 320 °C for 6 h prior to analysis.

3. Results and discussion

The diameter distribution of fibre fired to 750 °C is shown in Fig. 1 and an electron micrograph of the same material is shown in Fig. 2. The fibres are of good quality and totally free from shot and other non fibrous material. Fig. 1 shows a bimodal distribution with ~ 25% of the fibres between 2 and 3 μm and the rest grouped between 5 and 7 mm. The finer fibres are probably caused by minor flocculation in the spinning solution leading to the obstruction of a spinning hole. The ability to spin a shot free fibre indicate a solution

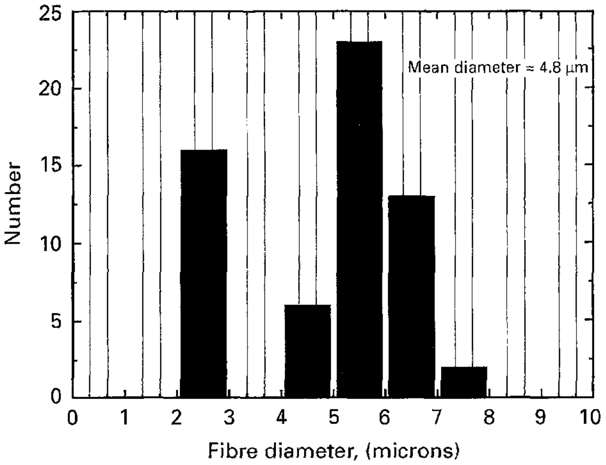

Figure 1 Fibre diameter distribution after firing at 750 °C.

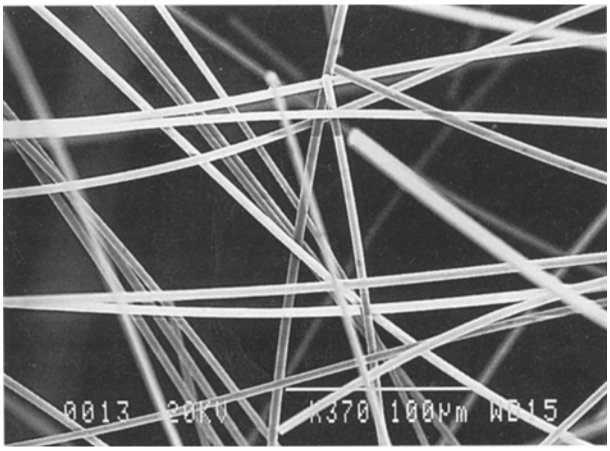

Figure 2 SEM Photomicrograph of $ZrTiO_4$ fibres after firing to 750 °C.

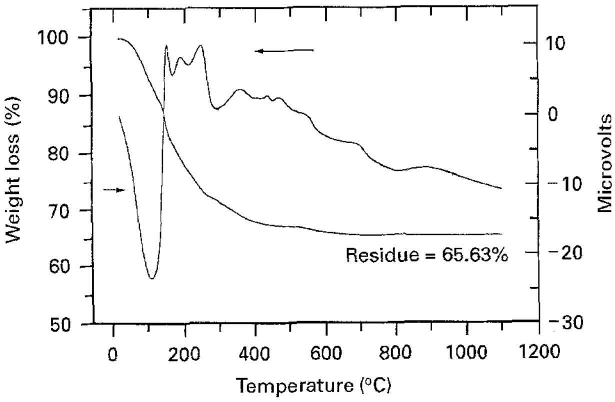

Figure 3 Simultaneous DTA-TGA plots of as-prepared $ZrTiO_4$ gel fibres.

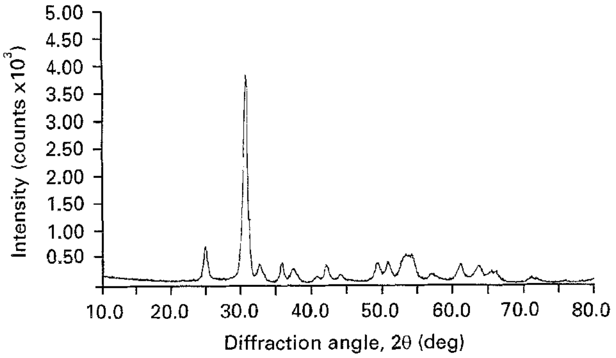

Figure 5 X-ray diffraction patterns of fibres fired to 750 °C.

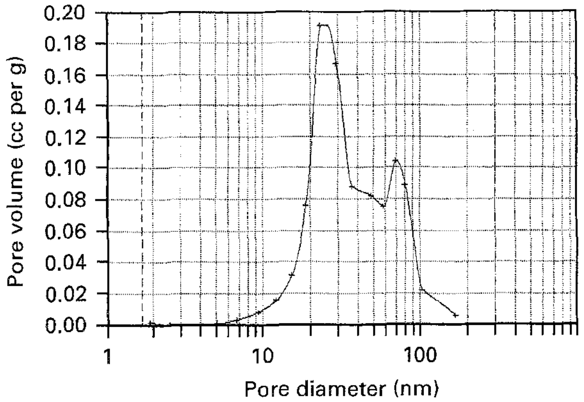

Figure 4 Pore size distribution of fibres fired at 750 °C.

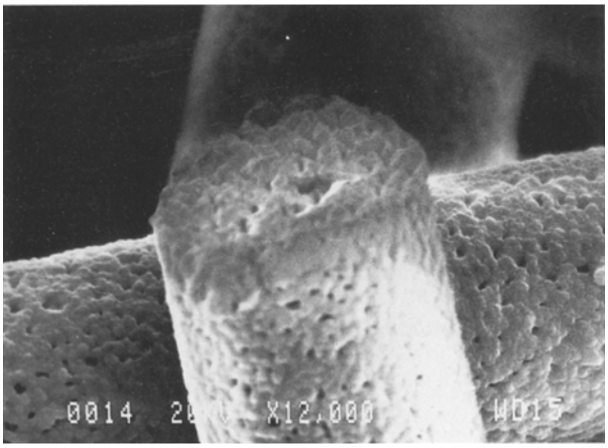

Figure 6 SEM photomicrograph of $ZrTiO_4$ fibres after firing to 1100 °C.

of reasonable colloidal stability free from particulate matter above 1 μm and the fine fibre fraction could probably be eliminated by filtering after the solution was concentrated.

A higher molecular weight spinning aid was required compared to earlier work [7] and this is thought to be due to polyethylene oxide degradation in the more acid precursor solutions.

DTA-TGA plots are shown in Fig. 3 and pore size distribution after firing to 750 °C in Fig. 4. X-ray diffraction patterns of fibres fired to 350 and 750 °C are shown in Fig. 5. Fig. 6 is an electron micrograph of the fibre after firing to 1100 °C. Fibre pore volumes were 0.093 and 0.048 cc per gm after firing to 750 and 1100 °C, respectively. It is worth noting that the density of zirconium titanate is about 5 gm per cc so that the fibre pore volumes represent porosities of 32.5 and 19% respectively. The results may be compared with those of our earlier work on $ZrTiO_4$ powder [6].

The DTA plot on fibre shows a strong endotherm at 100 °C followed by exotherms between 180–260 °C and 360–560 °C. The TGA plot shows a weight loss of 35% from the gel to calcined fibres. The powder showed a broad endothermic peak at about 170 °C and the more acute peak in the fibre at 100 °C is due to free water, either present in the gel or picked up from the atmosphere during transfers. The lower temperature exotherm of Fig. 3 is absent in the powder samples and is due to the exothermic decomposition of the spinning aid. The higher temperature exotherm is present in both the fibres and powder although somewhat more pronounced in the powder and is associated with the crystallization of $ZrTiO_4$. This is confirmed by the X-ray diffraction pattern shown in Fig. 5 which shows the crystalline material fired to 750 °C.

The fibre pore volume is 0.096 ccs per gm compared to less than 0.03 ccs per gm in the original powder sample. Although the weight loss on firing the powder gel from ambient was only 22% compared to 35% in this present work the weight losses above 170 °C are nearly identical (~ 9% in either case). This implies that the gel structures are similar at 170 °C and that the presence of polyethylene oxide and extra chloride has little overall affect at this stage. The increased porosity is not attributable to a more dilute gel structure and could be generated by the exothermic decomposition of the spinning aid between 180–260 °C.

After firing to 750 °C the fibre shows at least as good a strain to break as commercial staple Saffil alumina. The pore size distribution shown in Fig. 4 extends towards 0.2 μm. Fibres fired to 1100 °C show coarser grains around 0.25 μm and longer surface fissures.

With regard to the fibre mechanical properties and the estimates of average breaking strain, we have used the approximate relationship:

$$C = K_{IC}^2/\pi s^2 E^2 \qquad (1)$$

to give an order of magnitude estimate of the critical flaw size [8]. (C is the critical flaw size causing fracture,

K_{IC} the plain strain intensity factor, E Young's modulus and s the strain to break).

After firing to 750 °C the fibres are homogeneous and the equation should be applicable if the flaw size is much less than the fibre diameter. If we assume that the solid modulus of the fibres to be near that for bulk zirconia [9] ($E = 220$ GPa), we should expect the modulus of fibres of 32.5% porosity to be about 160 GPa [10]. Taking a modest value for $K_{IC} = 1$ MPa $m^{0.5}$, 1% strain to break gives a critical flaw size of 0.125 μm and suggests that critical imperfections are probably derived from the coarser porosity in the fibres.

The fibre structure certainly deteriorates on heating to 1100 °C with an estimated flaw size of 0.5 μm. Rapid grain growth is not a new phenomenon in crystallized zirconia fibres, since Kelly [11] has reported rapid grain growth in zirconia calcia fibres at 1000 °C. Fusible impurities particularly, sodium and sulphate are believed to have caused grain growth. These impurities still exist in reduced quantities in MEL zirconia but should be further investigated if improvements are to be made.

As a final point, the steam treatment of alumina gel fibres at intermediate temperatures decomposes the spinning aid and removes chloride and improves the strength of the final product [7]. Steaming might usefully be tried with $ZrTiO_4$.

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