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The Manufacture of Yttrium Aluminium Garnet (YAG) Fibres by Blow Spinning from a Sol–Gel Precursor

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Abstract

Three different systems consisting of a yttria sol and alumina sols were investigated, and gel fibres were successfully spun which on subsequent heating produced ceramic fibres of yttrium aluminium garnet (YAG). The fibres were characterised by various techniques. The fibres were found to begin forming YAG between 700–750°C and it was present as a single phase between 750–800°C, the lowest reported temperature for the crystallisation of this material. The fibres had no discernible grain structure and the average crystallite size was calculated to be only 20 nm at this temperature; however, the fibres were estimated to remain 20% porous up to 1200°C. The fibres were handleable after YAG crystallisation, but more investigation is required into sintering and the development of high temperature properties. © *1998 Elsevier Science Limited. All rights reserved*

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 present paper represents a first essay into the preparation of polycrystalline fibres of yttrium aluminium garnet (YAG). YAG is now established as a most suitable material for high temperature structural applications. It is simply unaffected by the oxidising conditions which degrade other creep resistant carbide, boride and nitride ceramics, and Corman[6] has identified single crystal YAG as the best oxide for creep resistance at high temperatures.

Parthasarathy[7] compared the high temperature properties of polycrystalline and single crystal YAG and suggested that polycrystalline YAG would be a potential reinforcing fibre constituent. Although single crystal materials show the highest properties, their superiority over polycrystalline material in creep being most strongly demonstrated by 'Saphikon' single crystal sapphire fibre,[8] there is still considerable merit in polycrystalline fibres, preferably of textile dimensions with diameters 20 μm or less.

The attractions of YAG have been recognised in patents by 3M[9] and Babcock.[10] The first of these described the preparation of a mixed amorphous and polycrystalline fibre from aqueous precursors and was filed before the work of Parthasarathy. More recently Morscher[11] has investigated the creep behaviour of fibres made from alkoxide sol–gel precursors. King[8] prepared and characterised coarse fibres from commercially available aqueous alumina and yttria sols, whilst Sporn[12] has presented general methods of preparing YAG and other ceramics from alkoxide precursors.

King[13] showed that the temperature of formation of fully crystalline YAG depends strongly the type of sol–gel precursor. His aqueous sols became segregated by flocculation during preparation, and as a consequence YAG was not fully crystallised until over 1300°C. YAG was formed at 900°C when atomically mixed carboxylates derived from organic solution were calcined.[13,14]

The object of this work was to investigate the preparation of non-segregated YAG spinning solutions from the simplest aqueous precursors, and to demonstrate the spinning of fibres of textile

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dimensions in commercially viable spinning equipment.

2 Experimental

2.1 Preparative methods

All chemicals and solvents used were commercially available ACS grade, except for the aluminium chlorohydrate solution which was Hoechst 'Locron-L'.

2.1.1 Sol preparation

Three different alumina sols were investigated:

2.1.1.1. Alumina sol from an aqueous precursor An aluminium nitrate nonahydrate solution ($2\,mol\,l^{-1}$) was titrated to pH5 with the addition of 4% ammonia solution at room temperature. The precipitate was then filtered and washed with 2×200 ml of distilled water, acidified to pH5. The resulting cake, consisting of 6·4% AlOOH ($1{\cdot}1\,mol\,Kg^{-1}$), was of a fine, smooth, creamy consistency and was easily liquidised on spreading with a spatula. 0·25 M nitric acid in a ratio of 1:2 HNO_3:Al was added to the cake, and the mixture mixed at room temperature for 1 min before being peptised at 95°C and under a vacuum of 95 kPa on a rotary evaporator. Distilled water was added when the mixture started to cling to the sides of the vessel, and then it was further digested under the previous conditions until it had formed a clear sol some 15 min later, of 18·5% AlOOH, pH 3 ($3{\cdot}08\,mol\,l^{-1}$).

2.1.1.2. Alumina sol from an organic precursor Aluminium tri-sec-butoxide was diluted to a 10% by weight solution in anhydrous iso-propoxide. A mixture of concentrated nitric acid (1:2 HNO_3:Al) and distilled water (6:1 H_2O:Al) were mixed to from a 4·6 M nitric acid solution, and this was added dropwise to the alkoxide solution whilst stirring at 600 RPM at room temperature, resulting in simultaneous hydrolysis and peptisation of the alkoxide. Immediately after addition the thick mixture was further digested at 95°C under a vacuum of 95 kPa, to form a clear sol within 15 min of 8·5% AlOOH, pH 3 ($1{\cdot}42\,mol\,l^{-1}$).

2.1.1.3. Commercially available alumina sol - Hoechst 'Locron-L' aluminium chlorohydrate, $Al_2(OH)_5Cl$ solution in water, was used (Al:Cl = 1·95–2:1, 23·5% Al_2O_3, Al = $4{\cdot}61\,mol\,l^{-1}$).

The yttria sol was produced via the peptisation of yttrium hydroxide. A yttrium salt solution ($0{\cdot}25\,mol\,l^{-1}$) was titrated to pH9·5 with 4% ammonia solution at room temperature, and the gelatinous precipitate was filtered and washed with distilled water which had a pH of 5. The resulting firm but fondant-like cake, which was only 10% $Y(OH)_3$ by weight, was then peptised at room temperature with 0·5 M nitric acid in a ratio of yttrium:acid of 2:1. The precipitate began to digest immediately, and within an hour a sol had started to form. After stirring at room temperature for 12 h all of the solid had been peptised to form a slightly milky yttria sol of pH7 ($0{\cdot}70\,mol\,l^{-1}$, 9·79% $Y(OH)_3$).

2.1.2 Fibre preparation

Stoichiometric amounts of alumina sol were added to the yttria sol and filtered through a 0·7 μm filter. The mixed sol was then rendered spinnable by the addition of a small amount of polyethylene oxide spinning aid and further concentration. The fibres were produced by a modified proprietary blow spinning process[15] 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 both in a basket as a random staple and on a rotating drum as an aligned blanket. After collection the fibres were removed and stored in a circulating oven at 110°C to await subsequent heat treatment.

2.1.3 Heat treatments of fibres

The gel fibres were fired at $100°C\,h^{-1}$ to 400°C and kept at this temperature for 2 h to remove any organic or nitrate components, and then further heated at $300°C\,h^{-1}$ to 600, 700, 750, 800, 900, 1000 and 1200°C, where they were maintained for 3 h unless otherwise stated.

2.2 Characterisation

2.2.1 Photon correlation spectroscopy (PCS)

The particle sizes of the sols were measured on a Malvern Instruments Lo-C Autosizer and series 7032 multi-8 correlator, using a 4 mw diode laser, 670 nm wavelength, after filtering through a 0·45 μm filter. This has been certified by the manufacturers to measure inorganic sol species of 3 nm diameter and above, provided the difference between the refractive indexes of the solvent and particle are sufficiently large. This was the case with our samples, the refractive indexes used being 1·33 for the solvent (water) and 1·60, 1·73 and 1·70 for the alumina, yttria and mixed sols, respectively. This piece of equipment conforms to the Methods of Particle Size Determination Standards ISO 13321, part 8—PCS (1996) and BS3406, part 8—PCS (1997) for determination of the Z Average, which is calculated from the intensity distribution. The volume distribution particle size was calculated using the Malvern PCS software version 1·32 in multimodal mode.

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 $2\theta = 10$–$80°$ with a scanning speed of $0{\cdot}25° \text{ min}^{-1}$ on a Philips PW1710 diffractometer using CuK_α 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:

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

where D = average size of the crystallites, K = Scherrer constant ($0{\cdot}9 \times 57{\cdot}3$), λ = wavelength of radiation (1·5405 Å), $h_{1/2}$ = peak width at half height and θ 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.

2.2.4 Porosity and sintering calculations

The weight loss and shrinkage in length of the fibres was measured over a range of temperatures from 100 to 1200°C. The ultimate shrinkage from sol to gel, then to fully dense refractory, can be calculated from the concentration of ceramic at different stages of the process and reasonably accurate estimates of sol and gel densities. The porosity of fibres during a firing sequence can then be inferred from the linear shrinkage of an aligned sample of fibre.

We have found that the density of simple salt solutions can be calculated to within a few percent from the salt and water densities by simple law of mixtures and that of alumina sols and gels from the mixed densities of $Al(OH)_3$, water and anion, to within 2% over a wide range of concentrations. The same methods were applied to shrinkage in the YAG system giving a linear shrinkage of 40%, from the gel fibres at 100°C (49·8% refractories, density = $1{\cdot}96 \text{ g cm}^{-3}$) to the fully dense ceramic (density = $4{\cdot}55 \text{ g cm}^{-3}$).

To calculate the porosity it was assumed that the shrinkage occurred uniformly in all three dimensions of the fibre. The porosity was then calculated from the equation:

$$P = 1 - \left(\frac{1 - S}{1 - S_T}\right)^3$$

Where S_T = % linear shrinkage measured at a given temperature, S = total % linear shrinkage calculated for fully sintered material (40 %) and P = % calculated porosity.

3 Results and Discussion

In all the sols the size of the sol particles were found to be sensitive to the preparative techniques and conditions employed, and 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.

The yttria sol was found to have a Z average of 131·2 nm and a volume average of 96·7 nm with an upper limit of over 1000 nm immediately after formation. However it continued to peptise upon standing to give a Z average of 41·9 nm, a volume average of 37·2 nm and an upper limit of 150 nm after standing at room temperature for 1 week. After this period no further improvement was observed, and the sol remained stable for over 2 months.

3.1 Addition of alumina sol prepared from an aqueous precursor to yttria sol

The alumina sol was measured as Z average = 18·4 nm, volume average = 16·8 nm and a volume tail of 22 nm, an unusually sharp peak with a small range of sizes. However, the sol was found to be thixotropic on standing, exhibiting evidence of some internal structuring which could interfere with the spinning process. Upon addition to the yttria sol the resulting combined sol (0·0509 mol total metals = 0·00637 mol YAG) had a Z average of 49·9 nm and a volume average of 43·1 nm with an upper limit of 300 nm, very similar to the yttria sol except for the increase in maximum size, which could cause problems during spinning.

The mixed sol also looked more cloudy, and could not be concentrated beyond 5 mol l^{-1} of total metals ($0{\cdot}63 \text{ mol l}^{-1}$ YAG) without precipitation occurring, despite the sol being only slightly viscous at that point. Gel fibres were successfully spun and collected, but they were of a poor quality, having uneven sides, containing shot and with a small diameter of around 3 μm, all symptoms of the spinning solution lacking viscosity. The fibres

were fired at various temperatures, but YAG was not formed and instead only mixtures of cubic $AlYO_3$ and monoclinic yttrium aluminate (YAM) were produced even after firing at 1200°C for 12 h, indicating that the two sols may have not formed a homogenous mix on the small scale. King reported the flocculation of mixed commercial alumina and yttria sols and a similar delayed crystallisation of YAG[8].

3.2 Addition of alumina sol from an organic precursor to yttria sol

The alumina sol produced from the alkoxide precursor was found to have a Z average of 86·6 nm and a volume average of 82·4 nm with an upper limit of 300 nm. This large particle size threatened to cause problems upon mixing with the yttria sol and spinning, and indeed this proved to be the case. Upon addition to the yttria sol (0·0667 mol total metals = 0·00834 mol YAG) the combined sol instantly became turbid, and a rubbery jelly-like mass precipitated out of the cloudy sol at only 1·1 mol l^{-1} total metals (0·14 mol l^{-1} YAG), a state which proved to be irreversible and rendered the sol totally unspinnable.

3.3 Addition of aluminium chlorohydrate sol to yttria sol

The aluminium chlorohydrate solution was clear and slightly viscous, with a particle size below the resolution of the PCS equipment (< 3 nm) but which has been previously estimated as 1–2 nm.[16] This was then diluted to 10% aluminium chlorohydrate solution in distilled water, and added to the yttria sol, resulting in a slightly cloudy, viscous sol (0·1333 mol total metals = 0·0167 mol YAG).

This mixed sol had a measured Z average of 48·6 nm and a volume average of 63·8 nm, but on analysis of the volume distribution 97% fell within an area which had an upper limit of 110 nm and 3% of the volume fraction registered as much larger particles around 400–500 nm. The low signal-to-noise ratio and very high polydispersity of the data, combined with the discrepancy between the Z average and volume average figures lead us to conclude the particle size results for this mixed sol to be unreliable. However, it is thought that the small amount of large particulate material might have resulted from contamination of the sol sample, as no there were no adverse effects observed during the spinning of the sol, as would have been expected from even a few particles of this size, and that the Z average probably represents the true particle size better than the larger volume average.

This mixed sol became too viscous to spin on concentration beyond 4·5 mol litre $^{-1}$ total metals (0·56 mol l^{-1} YAG). At high concentrations it became a hard, glassy gel, but no precipitation was observed and the process was reversible on dilution. The gel fibres collected were straight, even sided fibres with no visible internal structure and a diameter of between 7–10 μm. At 100°C the refractory content of the gel fibre was equivalent to a theoretical porosity of 78·4%. Compared to previously reported YAG fibres[17], a notable feature of the gel and spinning process was that the fibres were generated at 9 m s^{-1} and set within 1 s.

The gel fibres were heated between 100 and 1200°C, and their weight loss and linear shrinkage recorded at 200°C intervals. At 700°C the XRD pattern of the fibres still only indicated a large unidentified amorphous hump between $2\theta = 17$–38°, reaching maximum height around 33° [Fig. 1(a)]. However, by 750°C the YAG was present in the XRD as the major phase [Fig. 1(b)], with just a small amount of the amorphous material present, and at 800°C the YAG was present as a single phase [Fig. 1(c)].

This is the lowest reported formation temperature for this material, which has previously only been reported to begin to crystallise between 800–900°C, and not appear as the single phase until over 900°C.[17–19] As can be seen in the SEM micrograph in Fig. 2, the ceramic fibres have retained the smooth and even sided nature of the unfired gel fibres, and any microstructure is below the resolution of the micrographs, with a grain size of less than 0·1 μm. The average crystallite size

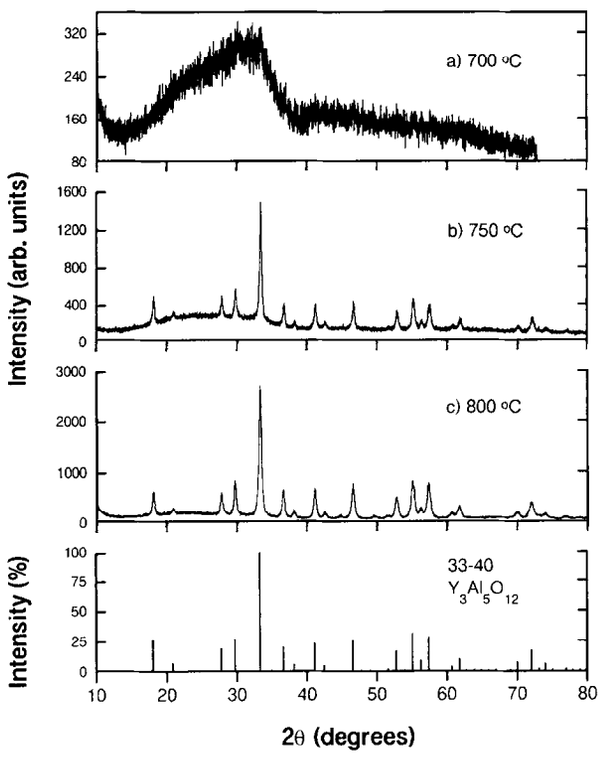

Fig. 1. XRD pattern of YAG fibres heated at (a) 700, (b) 750 and (c) 800°C for 3 h.

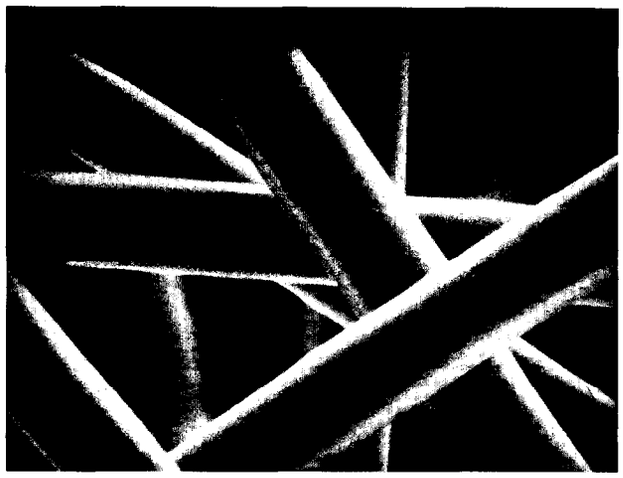

Fig. 2. SEM micrograph of YAG fibres fired at 800°C for 3 h.

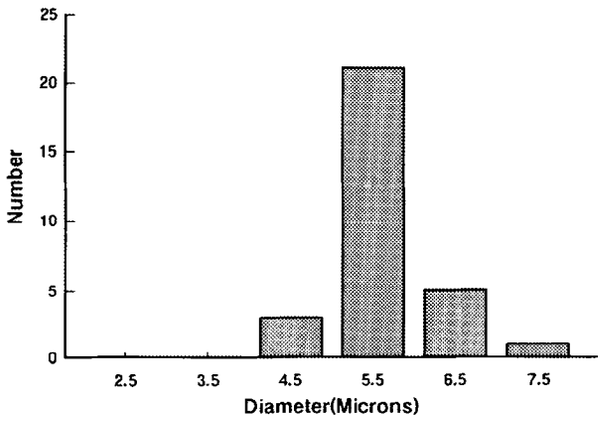

Fig. 3. Graph of the diameter distribution of YAG fibres fired to 800°C for 3 h.

calculated from the 100% peak gave an average crystallite size of 20 nm at 800°C, and the ceramic fibres were found to have an average diameter of 5·5 μm over a narrow spread between 4·5 and 7·5 μm (Fig. 3). This is a great improvement on the smallest previously reported diameter of 30 μm for YAG fibres.[17] The iso-electric points of yttria and alumina sols are both around pH 9, and the early crystallisation combined with the measurements of sol particle sizes before and after mixing suggest that the coarse yttria sol is effectively coated by small polycations in the chlorohydrate solution.

Table 2. Some properties of YAG fibres produced from mixed yttria and alumina chlorohydrate sols over a range of temperatures

	Average crystallite size	*Weight loss (%)*	*Longitudinal shrinkage (%)*	*Calculated porosity (%)*
800°C	20 nm	47·0	34·2	24·2
1000°C	24 nm	49·6	35·0	21·3
1200°C	47 nm	50·2	35·3	20.3

Between 800–1000°C there was very little change in the appearance or grain size of the fibres, with the crystallite size increasing slightly to 24 nm. However, the material was shown to be undergoing a steady sintering process, as the porosity was calculated to be 24·2% at 800°C, decreasing to 21·3% at 1000°C. By 1200°C the average crystallite size had grown to 47 nm, but the fibres were still had a calculated porosity of 20·3%, and despite the relative crudity of the porosity calculations this demonstrated that the fibres were not fully sintered even at this temperature. The difficulty in sintering is observed by other workers and sintering studies on the fibres will be reported in future work.

4 Conclusions

Three different mixed systems of a yttria sol and alumina sols were investigated, and an attempt was made to spin gel fibres from them which could subsequently be heated to produce ceramic fibres of yttrium aluminium garnet (YAG). The alumina sol produced from an alkoxide precursor contained the largest particles, and produced an unspinnable jelly-like gel when added to the yttria sol.

The alumina sol produced from an aqueous precursor produced a stable sol, but upon concentration of the spinning solution insufficient viscosity could be obtained and as a result the fibres were of poor quality. They also failed to produce YAG on heating up to 1200°C, indicating that the components were not intimately mixed sufficiently.

Table 1. Comparison of stoichiometric mixtures of different alumina and yttria sols and their subsequent formation of YAG fibres

	Sol characteristics	*Fibre characteristics*	*YAG crystallisation*
Y + Al(nitrate) sols	Clear, thixotropic, but not very viscous	Uneven, full of shot, small diameter (3 μm)	No YAG formed up to 1200°C/12 h
Y + Al(alkoxide) sols	Cloudy, forms a jelly-like mass	Totally unspinnable	—
Y + $Al_2((OH)_5Cl)$ sols	Slightly cloudy, viscous upon concentration	Smooth, even gel fibres 7–10 μm diameter	Single phase YAG fibres at 750–800°C, 4·5–7·5 μm

The commercially available aluminium chlorohydrate sol contained the smallest particles of all the alumina sols, and produced a viscous spinning solution on mixing with the yttria sol which enabled the spinning of good quality gel fibres. On subsequent heating these were found to produce YAG between 700–750°C and form as single phase fibres between 750 and 800°C, the lowest reported temperature for the crystallisation of this material. These results are summarised in Table 1.

The YAG fibres were averaging 5·5 μm in diameter, had no discernible grain structure and an average crystallite size of only 20 nm at this temperature, but they were estimated to be 24·2% porous, and this was only reduced to 20·3% with firing up to 1200°C. Some of the properties of the YAG fibres over a range of temperatures are summarised in Table 2.

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