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The Sintering Behaviour, Mechanical Properties and Creep Resistance of Aligned Polycrystalline Yttrium Aluminium Garnet (YAG) Fibres, Produced from an Aqueous Sol–Gel Precursor

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Abstract

Continuous ceramic fibres are finding applications as reinforcements in ceramic matrix composites, and yttrium aluminium garnet (YAG) is a particularly attractive candidate material on account of its creep resistance at high temperatures. A continuous, aligned, 5·5 μm diameter polycrystalline YAG fibre was manufactured from an aqueous sol–gel precursor which contained chlorine, and compared to a similar nitrate containing YAG precursor fibre we have reported previously. The precursor sol was found to be stable at a higher concentration than the nitrate containing sol, and this resulted in denser gel fibres which demonstrated better sintering at equivalent temperatures, giving a 98·5% sintered YAG fibre at 1550°C with a grain size of only 1 μm. However, on firing in air, the fibres formed fully crystalline YAG between 800 and 900°C, a temperature 100°C higher than the fibres containing nitrate, and they were weakened by the presence of many hemispherical faults. It was shown that both of these features were due to the retention of chlorine until the onset of formation of the crystalline YAG phase, and a series of steaming experiments were devised to remove the halide before this process could occur. It was found that steaming the precursor fibre from 200 to 500°C over 3 h, followed by firing to the required temperature in air, removed the chlorine and the problems it caused in the formation of the YAG phase without any change in the sintering characteristics or grain size. The steamed fibres were of a strength and quality comparable to fibres drawn from organometallic precursors. Empirical friability measurements showed the strength was maintained after firing to 1550°C, although there was a deterioration in apparent strain to break of the aligned blanket product above 1200°C. Conversely, the creep resistance, measured using the BSR test, improved with increase in temperature. The fibres fired to 1550°C were fully relaxed at temperatures 100–150°C below that of coarser, larger YAG fibres previously reported with a 3 μm grain size and 120 μm diameter. However, when allowance was made for grain size, the difference in creep rates was within the range obtained by extrapolating previous data using lattice diffusion and grain boundary effect models. Fibres fired to 1400°C were much finer grained but only slightly inferior to the 1550°C fibre in terms of creep. The alumina sol used in this work contained a significant level of sodium, and this suggests that the creep rates are effected by grain boundary impurities, especially sodium. A sodium free sol has been procured and further work is recommended to clarify the effect of impurities and improve fibre properties. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: yttrium aluminum garnet (YAG), sol–gel process, fibres, creep sintering.

1 Introduction

Ceramics are constantly finding new applications as structural and engineering materials, especially in high temperature (> 1400°C) applications, but their inherent brittleness poses a problem. An established solution to this problem is the use of continuous fibre reinforcement in the ceramic matrix. Ceramic oxide fibres are a suitable candidate due to their high thermo-mechanical stability

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and resistance to both oxidising and reducing atmospheres at high temperatures.[1]

Of all the ceramic materials currently investigated, yttrium aluminium garnet (YAG) demonstrates the best all-round resistance to creep.[2] Single crystal YAG has a creep strength 10 times higher than single crystal alumina,[2,3] and a melting point of 1970°C.[4] Furthermore, the creep in YAG is very weakly dependent upon orientation,[5] unlike the strongly anisotropic creep in alumina, removing the complication of crystal alignment from any future manufacturing process. Although the exact mechanism of creep in single crystal YAG is still uncertain, it is suggested that it is largely a diffusion-controlled process,[6] as the large size of the cubic unit cell and large lattice parameters of the garnet dramatically reduces the number of dislocations, especially climb dislocations which are a key creep mechanism.[7] In polycrystalline YAG boundary diffusion will become an important process and reduce the creep resistance of the material, but never-the-less, at 1400°C polycrystalline YAG with a grain size of 3 μm is 3 times better than polycrystalline alumina of the same grain size.[8]

The previously reported YAG fibres have almost entirely been either spun from metalloorganic precursors,[9] or extruded from a melt;[10] those produced from aqueous sols have needed the addition of a large amount of organic polymer (20%) to stabilise the sol precursor, and have produced fibres only of a very large diameter (120 μm),[5] It would be preferable to manufacture thin fibres ($<20\,\mu$m) for optimum strength, flexibility and weavability,[11] to spin them as a truly continuous fibre and to collect these fibres in a dried form on a winding mechanism. Continuously spinnable YAG fibres have been produced and collected,[12] and Liu *et al.* have reported 20 μm fibres extruded from an organic precursor,[13] which crystallised to form YAG at 800–1000°C.

This research is part of a much wider, ongoing inorganic fibres development programme, in which a range of structural, magnetic and electronic ceramic fibres have been produced from an aqueous sol–gel based process. The advantage of using an aqueous precursor is that it can be made from air-stable starting materials, and contains only small amounts of organic compounds in the gel fibres to be removed during firing. In a previous publication[14] we reported the blow spinning of a stable, aqueous sol–gel precursor peptised with nitric acid, and its collection as a continuous, dried gel fibre in aligned form. This underwent a subsequent crystallisation to form single phase YAG fibres of 5·5 μm diameter between 700 and 800°C, the lowest reported crystallisation temperature for this material, and this indicated that the sol was an extremely homogenous mixture. Unfortunately these YAG fibres were found to remain ~20% porous even up to 1400°C, and therefore they had poor mechanical properties. This paper continues this investigation, focusing on the improvement of the sintering behaviour, mechanical properties and creep resistance of these YAG fibres. This was achieved by exploring the use of alternative counterions in the yttria sol, and varying other process parameters and the firing regimes used to obtain a better ceramic fibre.

2 Experimental

2.1 Preparative methods

2.1.1 Sol preparation

Previously a stable mixed sol was produced from a stoichiometric combination of a commercially available alumina sol and an aqueous yttria sol.[14]

The alumina sol used was Hoechst 'Locron-L' aluminium chlorohydrate, $Al_2(OH)_5Cl$ solution in water (Al:Cl = 1·95–2:1, 23·5% Al_2O_3, Al = 4·61 mol l^{-1}). The solution contains an average of 130 ppm by weight of sodium. (M. Smith, ICI Saffil Business, Widnes, UK, pers. comm.).

The yttria sol was produced via the peptisation of a precipitated 99·9% pure yttrium salt, using a variety of acids in a ratio of yttrium:acid of 2:1. Peptisation with 0·5 M nitric or hydrochloric acids were found to be the most successful. The resulting yttria–chloride sol (0·77 mol l^{-1}) and yttria–nitrate sol (0·70 mol l^{-1}) thus produced were virtually identical, both being slightly milky sols which were stable for several months when diluted to 0·4 mol l^{-1}. Typical assays of the yttrium salt were obtained from the manufacturer (I. Higgins, Johnson Matthey, Widnes, UK, pers. comm.). Rare earth metal impurities sum to 600 ppm. Other contaminants in decreasing molecular order are Si, Mg, Al, Ca, Pb, Fe and Zr at levels of 70, 20, 20, 20, 20, 2 and 1 ppm by weight.

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 (2% to YAG by weight) of PEO (polyethylene oxide, Union Carbide grade WSR-N-60K) 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 at 100°C, and then collected both in a basket as a random staple and on a rotating drum as an aligned blanket. 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. After collection the fibres were removed and stored in a circulating oven at 110°C to await subsequent heat treatment.

2.1.3 Firing of fibres in air

The gel fibres were fired in alumina vessels at 100 K 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 K h^{-1} to the desired temperature, where they were maintained for 3 h unless otherwise stated.

2.1.4 Steaming of fibres

The fibres were steamed in a fused silica tube furnace with a volume of 1018 cm^3. Water was injected into the tube through a 'Saffil' wick at a rate of 18 ml h^{-1}, which provided a gas flow of 38 744 cm^3 h^{-1} at 200°C and 87 891 cm^3 h^{-1} at 800°C, so the tube was flushed every 95 to 41 s. Numerous steaming regimes were investigated between 200 and 800°C, and four of particular interest are detailed below:

1. Heated to 200°C at 100 K h^{-1} in air, then steamed from 200 to 500°C for 3 h at 100 K hr^{-1}
2. Heated to 500°C at 100 K hr^{-1} in air, then steamed at 500°C for 3 h.
3. Heated to 200°C at 100 K h^{-1} in air. then steamed from 200 to 800°C for 3 h at 200 K h^{-1}.
4. Heated to 800°C at 100 K h^{-1} in air, then steamed at 800°C for 3 h.

After steaming the fibres were allowed to cool down in air and were then fired to any higher temperatures in air as above.

2.2 Characterisation

2.2.1 Characterisation of sols and spinning solutions

Particle size measurement of the sol above the 3 nm diameter range was measured on a Malvern Instruments Lo-C Autosizer and series 7032 multi-8 correlator, using a 4 mw diode laser, 670 nm wavelength. A more detailed experimental is given in Ref.14. Viscosity measurements were taken using a cone-and-plate paint shear viscometer.

2.2.2 Assessment of fibre alignment

The fibres were collected as a blanket on a high speed rotor, in a manner similar to that used for 'Safimax' alumina fibres[16], a development product which was an aligned blanket with 90% of the fibres within ±10° and all within ±20°.

A small proportion of fibres crossing the general alignment was estimated using an optical microscope at 40× magnification. The number of aligned fibres in a field was counted, together with the few crossing the alignment in the same field. Counts were made in up to five separate fields summing to several hundred generally aligned fibres and up to about 50 crossing the alignment.

The direction of the generally aligned fibres was analysed by traversing the electron micrographs with a protractor normal to the axis of alignment and measuring the deviations of at least 100 individual fibres. Two sets of data were taken from opposite sides of each micrograph.

2.2.3 X-ray powder diffraction (XRD) measurements

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 0·25° min^{-1} on a Philips PW1710 diffractometer using CuK_α radiation with a nickel filter. Philips APD 1700 software was used to calculate the average size of the crystallites in a sample using the Scherrer equation:

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

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

2.2.4 Differential thermal analysis (DTA) and thermogravimetric analysis (TGA)

Simulataneous differential thermal analysis and thermogravimetric analysis (DTA–TGA) was performed on gel fibres using a Rheometric Scientific STA 1500 in flowing air up to a temperature of 1000°C at a rate of 10°C min^{-1}.

2.2.5 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 5 kV. Conducting samples were prepared by gold sputtering fibre specimens.

2.2.6 Porosity and sintering calculations

The weight loss and shrinkage in length of the fibres was measured over a range of temperatures from 100 to 1550°C. The ultimate shrinkage from sol to gel, and 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. When the same methods were applied to shrinkage in the YAG system, the calculated density of the gel fibre = 1·96 g cm^{-3}, the gel fibres being 58·0% YAG and the density of the fully sintered ceramic = 4·55 g cm^{-3}.[17] The maximum linear shrinkage to the fully sintered state was calculated from the change in volume when the gel fibre shrinks to 1 g of fully dense ceramic.

$$\text{Gel volume} = \frac{1}{0{\cdot}58} \times \frac{1}{1{\cdot}96} = 0{\cdot}8797 \qquad (1)$$

$$\text{Volume of 1 g YAG} = \frac{1}{4{\cdot}55} \qquad (2)$$

$$\%\ \text{Change in volume} = 1 - \frac{(2)}{(1)}$$

Assuming that the shrinkage is equal in all three dimensions,

$$\%\ \text{Change in length} = 1 - \left(\frac{(2)}{(1)}\right)^{\frac{1}{3}}$$

Giving a total linear shrinkage of 37·02% from the chloride-containing gel fibres to the fully dense ceramic. 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 (37·02%) and P = % calculated porosity.

2.2.7 Friability assessment

This test was originally used by 3M[18] in the development of 'Nextel' continuous ceramic fibre. Taylor[19] found that this test gives reliable comparative results when applied to commercial staple fibres with defined properties, and could be used as a means of assessing the properties of blow spun products at an early stage of development.

In the friability test a sample of fibre was placed in a 0·51 glass jar containing 28 rubber stoppers of 11 mm diameter and a total weight of 118 g. The jar was rotated at 160 RPM for exactly 5 min, and then the contents of the jar (fibre and stoppers) were washed with a solution of ICI 'Hypermer C-6' surfactant (1% in water) in an 840 μm sieve, and the fibre thus collected dried and weighed. The percentage of fibre retained after this process is the friability index, and this can then be compared to commercially available fibres of known strength.

2.2.8 Estimation of strain to break

Wire indentation tests were done by gluing a thin strip of fibres on to the surface of transparent double sided adhesive tape which in turn was glued to a soft rubber pad. The blanket was indented with stainless steel wires of reducing diameter from 1·2 down to 0·3 mm. The wires were held in toolmakers clamps and pressed into the sample. The tape was then carefully removed with the adhering fibre strip from the rubber pad, mounted on a glass slide and the lines of indentation examined for fines of breakage under and optical microscope at 100× magnification. The technique is useful for a rough estimate but is not preferred in routine work because the wires stretch and break too easily.

2.2.9 Creep measurements using the bend stress relaxation (BSR) technique

High temperature creep behaviour may be sensitive to small changes in formulation and may also be optimised the early stages of a development. The Bend Stress Relaxation (BSR) technique was developed by Morscher[20] and has been used in other work[5] to rank the creep performance of polycrystalline YAG fibres. The test was carried out on strips of aligned YAG fibre 1×10 mm, with the longer dimension parallel to the axis of alignment. These fibres were prefired to a nearly or fully sintered state, so any observed effect was due to creep, and not a sintering effect.

In the test the fibre was sandwiched between a 5·6 nm alumina rod resting on two other larger rods of 8·0 mm diameter (Fig. 1). The fibre was therefore bent to a known initial diameter, d_0 (= 5·6 mm), imposing a surface strain given by d/d_0 where d = the fibre diameter. The fibre was then heated to various temperatures where it was held for 1 h, and then allowed to cool down immediately in air to room temperature and the strain inducing rod removed. If a stress relaxation has taken place and creep has occurred the fibre retains a residual curvature of diameter d_f. The stress relaxation ratio, M, can then be calculated from the equation:

$$M = 1 - \frac{d_0}{d_f}$$

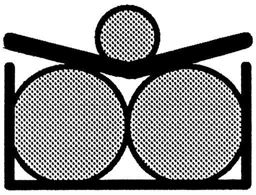

Fig. 1. Cross sectional diagram of the fibre–alumina rod sandwich in BSR test.

If $M=1$ this means that no creep has taken place, while $M=0$ indicates that the fibre has undergone total stress relaxation and crept around the diameter of the rod. These results can then be plotted against temperature and compared to previous results.[5] The rod size was chosen so that even the smallest fibres (4·5 μm diameter) were subjected to less than 0·15% strain, and the diameter of creep could be measured with a reasonable degree of accuracy (±0·4 mm). Morscher indicated that during the BSR test a sample undergoes a creep strain proportional to $(1/M)-1$ so that the technique may be used to make approximate quantitative comparisons.

3 Results and discussion

3.1 Precursor sols, spinning solutions and gel fibres

The yttria–nitrate sol has been characterised previously,[14] and the yttria–chloride sol was found to demonstrate a similar volume average particle size of around 40 nm, but with a smaller upper limit of 75 nm. When this was added to a stoichiometric amount of the alumina sol, the mixed sol was also virtually identical to that of the mixed sol using the yttria–nitrate sol. However, upon concentration of the spinning solution after addition of PEO the chloride containing solution was spun at a concentration of 0·84 mol l^{-1} YAG, and with a viscosity of only 0·32 Pa s. The spinning solution could have been concentrated further, and this was in contrast to the nitrate containing sol, which could not be concentrated beyond 0·56 mol l^{-1} YAG, and had a viscosity of 0·45 Pa s.[14] It would therefore appear that the presence of chloride counterions help stabilise the sol and aid the spinning process, a feature we have noted previously in the manufacture of ferrite fibres.[21] However, in work on ferrites the chloride ions were found to encourage thixotropic behaviour in the sol and delay the formation of some crystalline phases upon heating, and this indeed proved to be the case with the YAG precursor.

The gel fibres collected were straight, even sided fibres with no visible internal structure and a diameter of between 7 and 10 μm. At 100°C the theoretical refractory content of the gel fibre was 58·0%, compared to 49·8% for the nitrate containing fibre. Therefore the more concentrated chloride containing sol also resulted in denser gel fibres. As shown in Fig. 2 the alignment of the fibres was found to be reasonably good, 89·8% within 20° and 71·4% within 20° of the axis of alignment. This is comparable to ICI 'Safimax' a commercially developed fibre, and almost as good as the alignment of a range of hexagonal ferrite fibres produced previously by this group on the same apparatus, which have achieved alignments as high as 97% within 200° and 82% within 10°.[22,23] Therefore a similar degree of alignment should be possible with the YAG fibres after further refinement of the spinning process.

It should be noted that the 'nitrate containing fibre' also contains some chloride from the aluminium chlorohydrate, and that both this phrase and the phrase 'chloride containing fibre' are used only to differentiate between the fibres produced from the two different yttria precursor sols, as this appears to make a critical difference to the subsequent materials behaviour.

3.2 YAG fibres from firing in an air atmosphere

The chloride containing gel fibres were heated between 200 and 1550°C, and their weight loss and linear shrinkage recorded at 200 K intervals. Up to 700°C the XRD pattern of the fibres still only indicated a large unidentified amorphous hump between $2\theta=17$ and 38°, reaching maximum height around 33° [Fig. 3(a)]. However, by 800°C crystalline YAG had begun to form as a minor phase, although the rather indistinct peaks were nearly entirely masked by the major amorphous phase in the XRD pattern [Fig. 3(b)]. By 900°C the YAG had fully crystallised as a single phase [Fig. 3(c)], with a calculated crystallite size of 20 nm. The peaks of the XRD patterns became palpably sharper and narrower above 1000°C, with a corresponding increase in crystallite size to 44 nm at 1200°C and 68 nm at 1550°C [Fig. 3(d)].

With the chloride containing fibres, the YAG phase began to form and became fully crystalline at

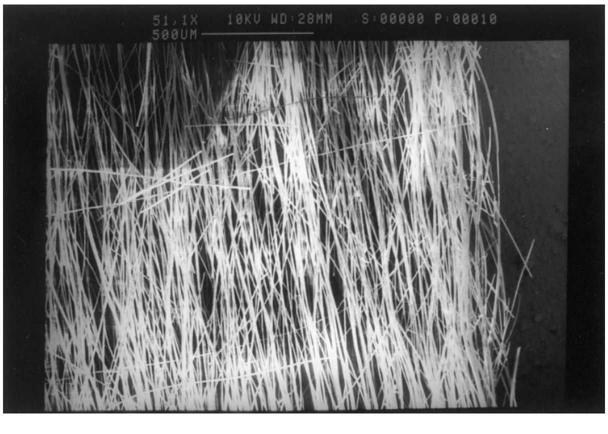

Fig. 2. Photograph of the aligned YAG fibres fired to 1000°C.

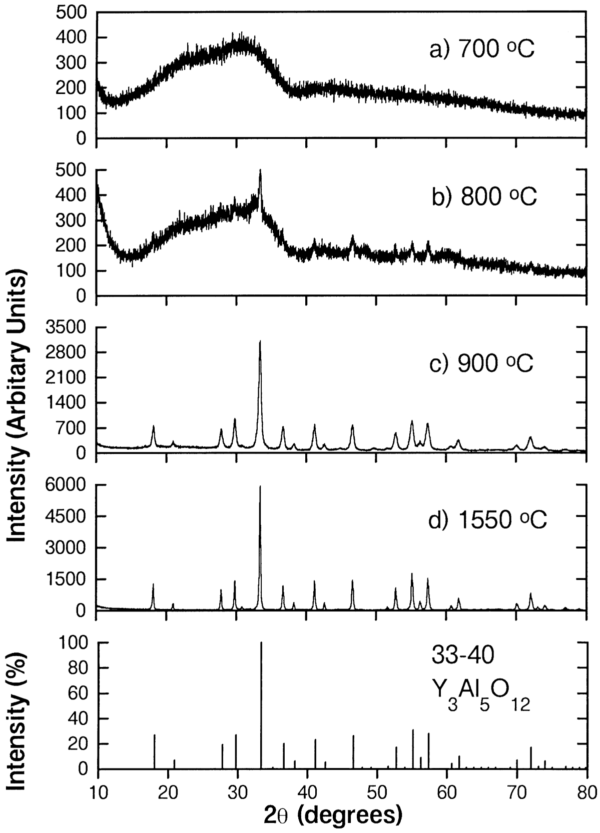

Fig. 3. XRD patterns of YAG fibres heated in air at (a) 700°C, (b) 800°C, (c) 900°C and (d) 1550°C for 3 h.

a temperature 100°C higher than that observed for the nitrate containing fibres, which had become single phase YAG between 750 and 800°C.[14] However, once the YAG phase had crystallited in the chloride containing fibres their crystallise size was exactly the same as that of those with nitrate from 900°C and over. This suggests that the chloride ions are delaying the formation of the YAG phase, until they are driven from the fibre at between 700 and 900°C. This parallels our findings based on halide containing ferrite fibres,[21] which have been shown by X-ray fluorescence studies to retain some of their chlorine up to 800°C, but to have lost all their halides at 1000°C, coincident with the formation of a hexagonal ferrite phase at a temperature 200°C higher than in halide free fibres.

There is further evidence for the retention of chlorine in the fibres in the DTA–TGA plots of the fibres between 25 and 1000°C. The plot for the precursor fibres with nitrate shows a steady weight loss of 10% up to 290°C, where a large exotherm occurs coincident with a very sudden weight loss of nearly 30% over only 10 K, or 1 min (Fig. 4). This is caused by both organic compounds and the nitrate combusting, and a peak in the DTA is observed around this temperature in all the fibres containing PEO spinning aid. It should be noted that the violence of this combustion has resulted in the slight drop in temperature after the extreme loss of weight, and that it probably also caused the ejection of some sample material (~ 13%) from the crucible, as the total weight loss is more than that observed during firings of larger amounts of material. After this burst of activity the fibre continues to slowly decrease in weight with a small corresponding thermal change until it reaches 44% at 500°C, after which there is virtually no further loss until the YAG crystallises. This crystallisation occurs at 830°C on the DTA–TGA and is accompanied by a large exothermic peak and another, small loss of weight. The discrepancy between the crystallisation temperature of YAG in the XRD data and the DTA–TGA can be explained by the fact that the XRD plots were of fibres fired for three hours at 750 and 800°C, allowing the YAG phase sufficient time to crystallise. The DTA–TGA's high ramp rate of 10 K min^{-1} leads to an artificially high temperature of crystallisation, as it covers the range of 750 to 830°C in only 8 min, and other workers have reported a time as well as a temperature dependency for the formation of YAG.[13] The 2–3% weight loss could be due to the chlorine held in the fibres which originated from the aluminium chlorohydrate sol, and an even lower crystallisation temperature may be achievable if a chlorine-free alumina sol was used as a starting material.

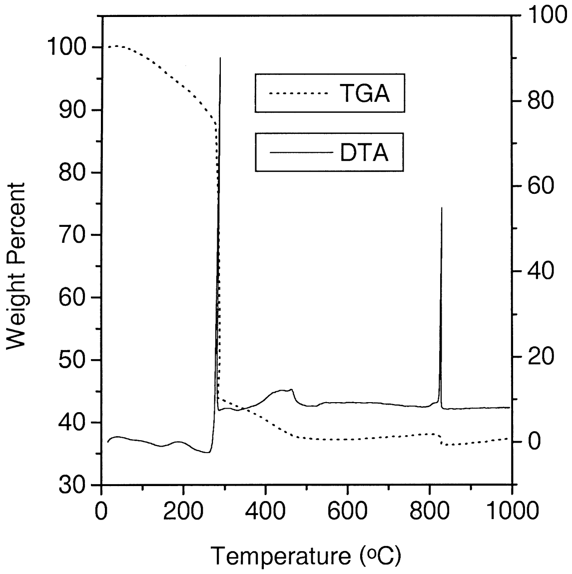

Fig. 4. DTA–TGA plot for the nitrate containing fibres between 25 and 1000°C, heated at 10°C min^{-1}.

By comparison, although the DTA–TGA plot of the chlorine containing fibres (Fig. 5) shows a similarly large exotherm, at 280°C as the organics combust, there is no large or sudden corresponding loss of material, and instead the weight uniformly decreases to 68% at 500°C. There is no further weight loss until a sudden exotherm occurs at 790°C, which is caused by the release of the retained chlorine and the start of YAG formation. The full crystallisation of YAG is signaled by a broader and less extreme exotherm peak around

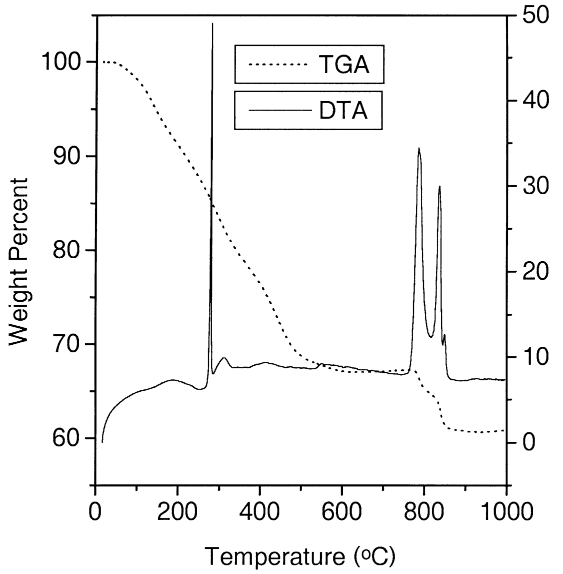

Fig. 5. DTA–TGA plot for the chloride containing fibres between 25 and 1000°C, heated at 10°C min^{-1}.

the higher temperature of 840°C, and the entire crystallisation process is accompanied by a large weight decrease of 7%, indicating the final release of the retained chlorine. Again it must be noted that the crystallisation temperatures indicated by the DTA–TGA plots may be artificially high due to the rapid heating rate involved in the technique.

This was not the only effect the chlorine was observed to have on the fibres. As can be seen in the SEM micrograph in Fig. 6 the ceramic fibres fired to 800°C have retained the smooth and even sided nature of the unfired gel fibres, and the ceramic fibres were found to have an average diameter of 5·0 μm over a narrow spread between 4·0–7·5 μm, similar to the 5·5 μm nitrate containing fibres. Any microstructure was below the resolution of the micrographs, with a grain size of less than 0·1 μm, except for the large, roughly circular features which were as wide as the actual fibre and sometimes wrapped around nearly the entire circumference of the fibre. These were not just surface features, but they appeared to be lose dome-shaped sections, and were observed to have sometimes come free of the fibre leaving symmetrical, hemispherical pits, sometimes with a depth of more than the fibre radius. These wedge-like gaps in the fibre were obvious weak points, and there were many short fibres observed with broken ends featuring these faults (see bottom left corner of Fig. 6). This was confirmed by the general weakness of the YAG fibre, which was extremely poor, the fibre readily breaking into short mm lengths upon handling or the application of the slightest pressure.

The nitrate containing fibre, while still weak, was much more handleable than the chloride containing fibre, and it had been assumed that the weakness was due to the 20% porosity remaining in the

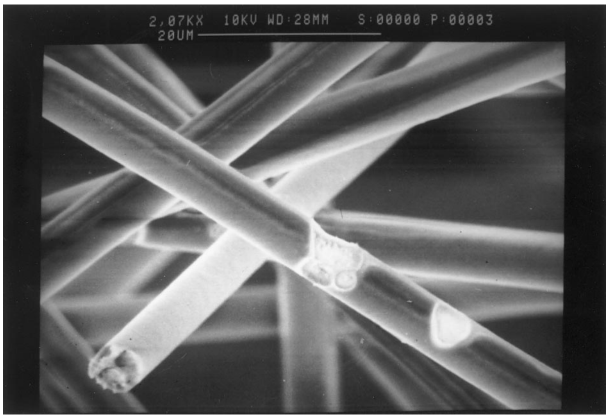

Fig. 6. SEM micrograph of chlorine containing YAG fibres fired at 800°C for 3 h.

YAG even at 1200°C. However, upon a careful inspection of the nitrate containing YAG fibres it was observed that there were a few of these features present even in these, although to a vastly lesser extent. It is suggested that these features are caused during the late release of the chlorine as HCl immediately prior to, or during, the formation of the crystalline YAG phase. They are not present in the amorphous fibres of either composition and remain unchanged at higher temperatures, they occur to a much lesser extent in the fibres produced from the yttria–nitrate sol, although some chlorine retained from the alumina sol must be responsible for the few which are present. Again, this problem could be avoided by using a halide–free alumina sol, or by removing the chlorine prior to YAG crystallisation.

Weight loss and linear shrinkage measurements were carried out on the chloride containing fibres fired at 500, 800, 1000, 1200, 1400 and 1550°C for 3 h. The porosity and shrinkage results are shown in Table 1 and are compared to those for the nitrate containing fibres.[14] The chloride containing fibres had experienced 21–22% less weight loss and 43–45% less linear shrinkage up to 800°C (when corrected for the differing starting densities), and this is further evidence for the retention of some chlorine in the fibres. Once the chloride had been removed from the fibres and the YAG phase formed, the actual weight loss and shrinkage was almost exactly the same in both fibres. However, the chloride containing gel fibres had been more dense from the start and they achieved a higher degree of sintering than the nitrate containing fibres immediately. Furthermore the rate of loss of porosity was much higher than that of the nitrate containing fibres, the chloride containing fibre having less than half the porosity at 1200°C. By 1400°C the fibres were 95% sintered and at 1550°C, the limit of the furnace range, they were nearly fully sintered at 98·5%, which agrees well

Table 1. The comparison of the weight loss, linear shrinkage and calculated porosity of YAG fibres produced from yttria–nitrate[14] and yttria–chloride sol precursors

	Yttria–nitrate sol precursor			*Yttria–chloride sol precursor*		
Temperature (°C)	*Weight (%)*	*Shrinkage (%)*	*Porosity (%)*	*Weight (%)*	*Shrinkage (%)*	*Porosity (%)*
500	45·19	32·91	28·47	41·46	17·97	54·74
800	47·04	34·18	24·25	42·94	19·53	52·06
1000	49·57	35·01	21·31	48·56	34·38	11·59
1200	50·24	35·25	20·43	48·60	35·16	8·36
1400	n/a	n/a	n/a	48·06	35·95	4·93
1550	n/a	n/a	n/a	48·09	36·68	1·60

with other reports of polycrystalline YAG fibres becoming fully densified between 1500 and 1600°C.[13] This was compared to the very slow decrease in porosity observed in the nitrate containing fibres, which suggested that they would never achieve maximum density.

The ceramic fibres produced from both routes were too fragile to withstand any diameter of wire indentation in the strain estimation experiments, indicating a very low percentage strain to break ($<0{\cdot}2\%$). The friability test also demonstrated their weakness with no fibre retained at all from the chloride containing fibre and a negligible amount from the nitrate containing fibre, both fired to 1200°C. While the weakness of the nitrate containing fibres may be due in part to their high porosity, it was suspected that the weakness was largely due to the hemispherical faults caused by the retention of chlorine until the formation of the ceramic.

Steaming at an early stage of heat treatment improves the strength of alumina fibres derived from aluminium chlorohydrate. Aluminium chloride is readily decomposed by steam, the reaction to hydroxide proceeding to thermodynamic completion at ambient temperature. Yttrium chloride is more stable, with 50% thermodynamic conversion being achieved around 400°C.[24] It was therefore decided to run a series of experiments where the fibres were heated in steam, before and up-to the temperatures at which YAG forms, in an attempt to remove the damaging chlorine before this crystallisation step.

3.3 Steaming of fibres

Both types of gel fibre were steamed in various regimes including those described in the experimental, and compared to one another. All of the steamed fibres showed an improvement regarding the number of faults to differing degrees. There was no observed difference between the two kinds of fibre once they had been steamed, and after the YAG phase had been formed they behaved as before, except for the improved morphology and strength. From here on the discussion shall refer only to the chloride containing fibres, due to their better sintering behaviour.

Firstly it was noted that if the fibres were in the form of tight bundles of random staple fibre, or if the aligned blankets were folded up or compressed together, the fibres away from the surface of these masses would retain the surface faults and make the whole bundle brittle and powdery, presumably through the chlorine being unable to diffuse out of the fibre properly. The steamed fibres were also sometimes black in colour, again if in tight bundles, due to the presence of trace amounts of incompletely-combusted carbon from the organic compounds becoming trapped in the fibre. This black colour had also occasionally been noted in tight masses of air fired fibre, and in both cases would disappear by 800°C leaving the fibres colourless and apparently unharmed. This effect has been reported by other observers,[13] both as a feature of the decomposition of aluminosilicates and metalloorganic YAG precursors. The blankets of aligned fibre underwent no such colour change and were successfully steamed, and thus displayed an advantage over random fibre.

The fibres steamed from 200 to 500°C were much stronger and more handleable, and there were no surface faults apparent on the fibre. However, the XRD pattern showed that no YAG had been formed, only an amorphous hump at this temperature [Fig. 7(a)], and the faults had never been seen in the non-steamed fibre until the onset of YAG crystallisation. The fibres were fired to 800°C in air and proved to be YAG by XRD, but they still showed no sign of the hemispherical faults and maintained their strength. The calculated crystallite size of the YAG (20 nm) was the same as the air fired nitrate containing fibres at an equivalent temperature.

The fibres steamed at 500°C turned black, but again this discolouration disappeared at higher temperatures. The XRD pattern showed them to consist of poorly crystalline YAG [Fig. 7(b)], and this is a remarkably low temperature for the formation of the ceramic YAG even if it is still mixed with some amorphous material. Unfortunately the fibres were still quite fragile, and on examination they were found to still contain some faults, the YAG crystallisation apparently having occurred before the removal of all of the chlorine, and these persisted upon firing to higher temperatures in air. These faults persisted when the fibers were fired to 800°C to form fully crystalline YAG.

Steaming from 200 to 800°C at 200 K h^{-1} was a wholly unsuccessful procedure. The XRD pattern of the fibres showed only the amorphous YAG precursor [Fig. 7(c)], and the fibre was of a very poor quality, powdering to the touch. Closer examination revealed that many of the fibres had fused together into tightly bound masses which had retained most of their faults, and crumbled to the touch. The few intact fibres were coated with this powdery residue as well. It was thought that the fusing might have been caused by the rapid heating rate at low temperatures, and so a second steaming was carried out between 200 and 800°C at a rate of 100 K h^{-1} and with the fibres held at the end temperature for 1 h. This resulted in a less fused fibre, but it was still powdery and mechanically very weak, rendering it totally unhandleable. It also had still not resulted in a crystalline form of YAG.

The fibres which were steamed at 800°C were of a much better quality, second only to those steamed from 200 to 500°C for strength. There were still a few fibres with the circular surface faults apparent, but a greatly reduced number compared to those fired at 500°C. The fibre had also formed single phase crystalline YAG at this. point [Fig. 7(d)], exhibiting both more sharply defined peaks in the XRD than that formed by the nitrate containing fibres fired in air to this temperature and a larger crystallite size of 25 nm. This indicates that there may well be a small amount of chloride retained in the nitrate containing fibre from the aluminium chlorohydrate, and its removal via steaming may have resulted in a more crystalline product due to a yet lower formation temperature.

Despite this last steaming regime having produced a more crystalline YAG fibre at 800°C, the fibre steamed at this temperature still contained some faults, whereas the fibre steamed from 200 to 500°C and then fired in air to 800°C appeared to be entirely fault free. Therefore the heat treatment chosen to produce the YAG fibres for strength and creep assessment was steaming from 200 to 500°C at 100 K h^{-1}, then firing in air up to 800°C at 300 K h^{-1} and holding at this temperature for three hours. These fibres had no apparent grain structure within the resolution of the SEM ($<0{\cdot}1$ μm, Fig. 8), and none was observed up to 1400°C. However, upon firing to 1550°C grain growth had occurred resulting in a surface featuring uniformly sized, equiaxed grains 1 μm in diameter (Fig. 9), and although this had weakened the fibre to some extent it was still very much handleable.

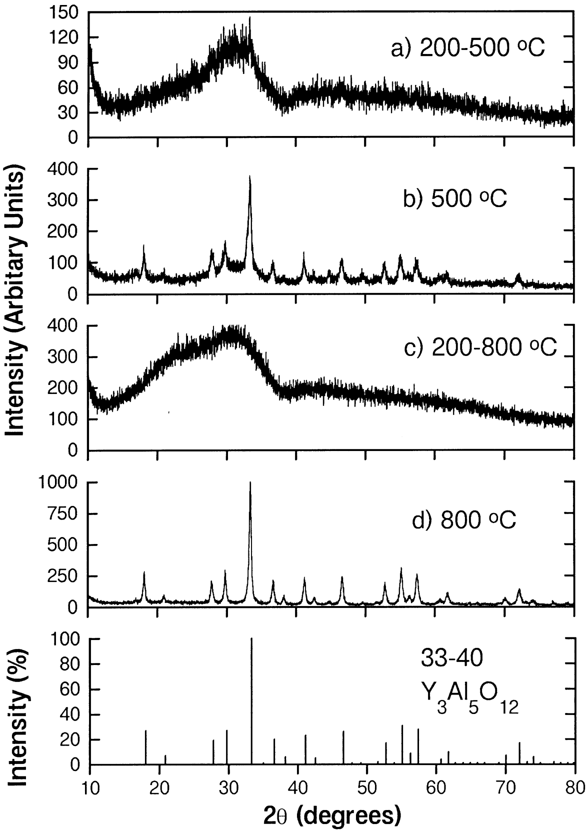

Fig. 7. XRD pattern of YAG fibres steamed at (a) 200–500°C, (b) 500°C, and (c) 200–800°C and (d) 800°C.

3.4 Mechanical properties of steamed YAG fibres

The steamed fibres were considerably stronger and more flexible than their unsteamed counterparts, demonstrated most clearly by the friability test. Whereas the unsteamed fibres had totally disintegrated leaving nothing in the sieve, 63% of the steamed fibres fired to 800°C were retained after tumbling. This had reduced slightly to 61% at 1400°C, but then increased again to 65% at 1550°C. While this could be due to experimental error involved in the technique, it is also quite

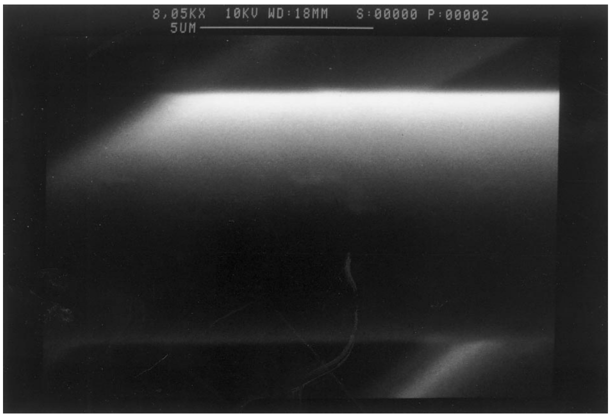

Fig. 8. SEM micrograph of YAG fibres fired steamed from 200 to 500°C at 100°C h^{-1}, then fired in air at 800°C for 3 h.

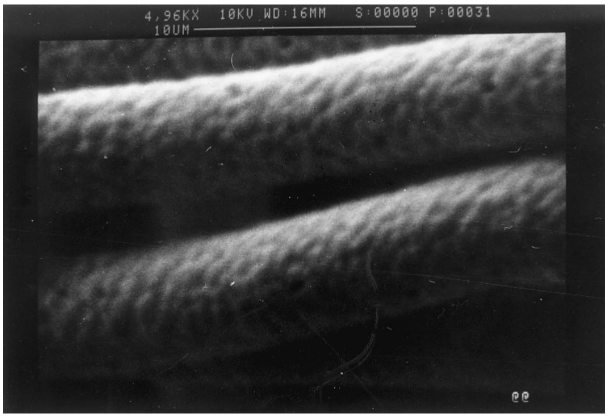

Fig. 9. SEM micrograph of the steamed YAG fibres from Fig. 8 fired in air to 1550°C for 3 h

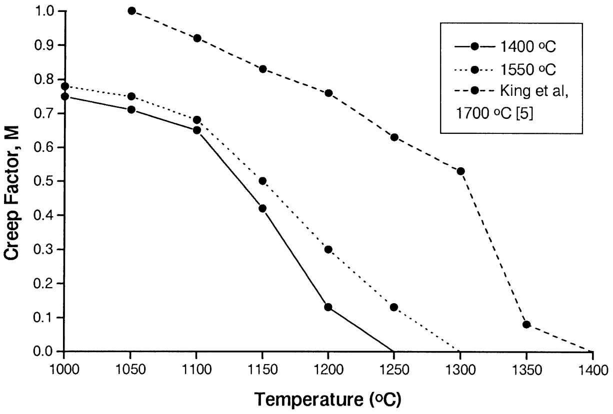

Fig. 10. Comparison of the creep of steamed YAG fibres, prefired to 1400 and 1550°C for 3 h, over the temperature range 1000–1300°C, and previously reported polycrystalline YAG fibres prefired to 1700°C.[5]

possible that the fibres are less friable at the higher temperature due to their higher degree of sintering, despite the relatively large increase in grain size.

This growth would not necessarily effect the friability of the fibres, but it would make them weaker when placed under a strain or a compression. It should also be noted that friability involves factors other than strain to break. Studies on carbon and glass fibres have shown that resistance to abrasion decreases as the diameter falls below 6–8 μm, (D. Williams, Courtaulds Ltd., Spondon, UK, pers. comm.), so that an artificially low index would be expected from fibres of 5·5 μm such as these.

Strain to break measured by wire indentation appeared to deteriorate as firing temperatures were raised. The fibres fired to 1200°C were intact at a strain of 0·73% and had broken under a strain of 0·92%, so their strain to break lay somewhere between those two figures. At 1400 and 1550°C the fracture ranges were 0·51% to 0·64%, and 0·43% to 0·51% respectively. Friability tests indicate that the fibre mechanical properties are maintained on firing to 1550°C, and it is thought that the apparent reduction in strain to break is due to the closer entanglement and binding of individual fibres in the blanket which was observed at higher temperatures. This last point would be resolved by improving the spinner to make a parallel tow of fibres rather than an aligned blanket. In terms of mechanical properties the fibres compare well with those of Liu *et al.*[13] who stated that organic precursors are needed to make a high strength product of textile dimensions.

The creep was measured of YAG fibres prefired to 1400 and 1550°C using the BSR technique, firing for 1 h at 50 K increments between 1000 and 1300°C. As can be seen from the results in Fig. 10, the 1400°C fired material creeps at temperatures up to 50°C lower than the 1550°C fibre, but both have crept totally by 1250 and 1300°C, respectively. The 1550°C fibre creeps to a similar extent, but 100–150°C before the polycrystalline YAG fibres reported by King *et al.*[5]

The creep rates of the present fibres and those of King can be compared between 1100 and 1200°C, where in either work M is between zero and 1. The measurements in Ref.5 are likely to be more accurate as they are made on 120 rather than 5·5 μm fibres. Also in the present work we were obliged to use radius templates to make undistorted measurements of curvature on tape samples from fibre blankets, so that the measurements carry an uncertainty of ±0·4 nm, due to the steps between template sizes. This uncertainty amounts to ±9% as the fibre becomes fully strained. Quantitative comparisons become unrealistic as M approaches 0 as the error in the relative creep strain $(1/M-1)$ is greatly magnified. A reasonable comparison can be made down to $M=0{\cdot}3$ in this work where the uncertainty in M would be ±0·05, and in creep strain ±25%. Over this middle range, $M=0{\cdot}7$ to 0·3, the 1550°C fibre creeps 4·8 to 7·5 times faster than King's fibre, which had been sintered to 1700°C.

If the creep process in YAG is considered to be mostly a diffusion driven process, we can assume the grain size to be the deciding factor in the difference between the creep resistance of the polycrystalline fibres. The King fibre had a grain size of 3 μm, compared to 1 μm for the 1550°C YAG and less than 0·1 μm for the 1400°C YAG fibre. Whilst to maintain the strength and flexibility of the fibre it is preferable to keep the grain size as small as possible, and certainly below the submicron level, for the purposes of good creep properties it is preferable to have the grains as large as possible, to limit the possibility of grain-boundary diffusion. Indeed, with his large diameter fibres King has recommended either an increase in grain size or an axial elongation of the grains to suppress diffusional

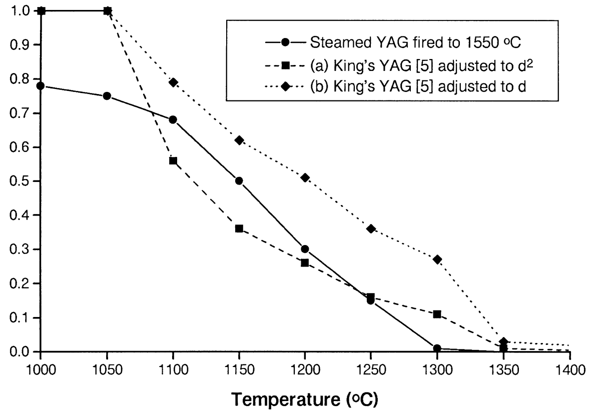

Fig. 11. Comparison of the of creep of steamed YAG fibres prefired to 1550°C against previously reported polycrystalline YAG fibres[5] when adjusted for grain size, d, assuming (a) Nabarro–Herring diffusion (strain $\propto d^2$) or (b) grain boundary effects (strain $\propto d$). As both processes will play a part, the true plot will lie somewhere between these two lines.

creep.[25] However, to balance the requirements of creep resistance against mechanical strength a grain size of 0·5–2 μm is claimed to be ideal,[13] and these fibres clearly satisfy this requirement. The effects of grain size on creep rate are well reported in the literature with rates proportional to $1/d^2$ in a system controlled by Nabarro–Herring lattice diffusion, and proportional to $1/d$ where grain boundary sliding is a predominant mechanism. Figure 11 illustrates that the differences in M between King's fibres with 3 μm grains and our 1550°C fibre are broadly attributable to differences in grain size, whatever detailed mechanism applies.

In this work a further reduction in grain size to 0·1 μm, when the fibre was sintered at 1400°C, increased the creep rate by only 50%. At this stage we cannot explain the difference between the creep rates reported in this work and those of King *et al.*[25] Firing temperatures need to be extended to 1700°C in future work to match Kings and allow a more consistent comparison. It is possible that both studies have been affected by impurities in the precursor materials. King does not declare any impurity levels, but in our case the source of aluminium, 'Locron-L', was found to contain a significant amount of sodium. In future work we shall replace 'Locron-L' with an identified commercial source of sodium free aluminium chlorohydrate.

4 Conclusions

YAG fibres had previously been produced from an aqueous sol–gel route, using a commercially available alumina sol combined with a yttria sol containing nitrate counterions. Gel fibres were successfully blow spun from this precursor and collected as an aligned blanket, which had a degree of alignment comparable to commercially developed fibres and other aligned ceramic fibres manufactured previously by this group. Although upon firing in air to 800°C these produced fully crystalline YAG fibres with an average diameter of 5·5 μm, the resulting fibres remained poorly sintered and mechanically weak even when heated to higher temperatures.

It was demonstrated that if a yttria sol containing chloride counterions was used instead, the precursor was stable at higher concentrations, and this resulted in a denser gel fibre. The chloride containing fibres showed improved sintering characteristics, and they had become 95% sintered at 1400°C and 98·5% at 1550°C, whereas the nitrate containing fibres had given no indication of nearing maximum density. However, when fired in air the amorphous fibres did not become fully crystalline until 900°C, a temperature 100°C higher than in the fibres made from the yttria–nitrate sol. There was evidence that chlorine retained in the fibre up to this temperature delayed the formation of the YAG phase. The chlorine was also responsible for causing many hemispherical faults to form in the fibre, thus drastically reducing its mechanical strength. These faults had to be removed to render the fibres useful, and so a series of firings were carried out in a steam atmosphere to attempt to remove the chlorine.

Fibre heated to 800°C in air and then steamed at this temperature for 3 h produced pure crystalline YAG, but it retained some of the faults, implying that the YAG formation had occurred prior to the complete removal of the chlorine. Fibre steamed from 200 to 500°C over 3 h formed crystalline YAG upon subsequent firing in air to 800°C, with no hemispherical surface faults present, improving the mechanical properties of the fibre. Once YAG had formed the sintering and grain growth of the steamed fibre proceeded just as before, with any grains remaining below 0·1 μm up to 1400°C, and then only increasing to a diameter of 1 μm at 1550°C. The steamed fibres were strong, when tested by wire strain and empirical friability measurements, and of a quality comparable to recently reported fibres hand drawn from organometallic precursors.

Creep properties were improved by post firing, and the creep behaviour of the 1550°C fired fibres was similar to that of coarser polycrystalline YAG fibres when allowance was made for grain size. Therefore, in the tradeoff between creep resistance and mechanical strength these textile-dimension fibres are approaching the optimum with a diameter of 5·5 μm and a grain size of 1 μm. Further work needs to be carried out to extend firing temperatures to 1700°C, and to investigate the effect of trace impurities in the precursor materials on creep.

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