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Sol–gel synthesis of YAG/Al_2O_3 long fibres from water solvent systems

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Abstract

$Y_3Al_5O_{12}$(YAG)/Al_2O_3 long fibres were prepared by a sol–gel method using water as the solvent. They were synthesized from aluminium nitrate and chloride solutions, aluminium salt, aluminium metal and Y_2O_3. The starting materials were dissolved by refluxing at 100°C for 2–18 h and were then condensed. The fibre spinnability was examined by a hand drawing method using a glass rod. In the nitrate solution system, the composition range available for fibre preparation was very limited because nitrate ions decomposed during the refluxing, raising the solution pH and precipitating the Y component. On the other hand, the composition range of the fibres prepared from the chloride system was $0/10 \leqslant \text{YAG}/Al_2O_3 \leqslant 6/4$ (volume ratio) and was wider than that from the nitrate system. The YAG/Al_2O_3 fibres prepared by firing at 1300°C became denser with faster heating rates. The grain size in the fired fibres was small, below the firing temperature at 1400°C, but increased greatly above that temperature. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fibre processing; Microstructure-final; Sol-gel processes; YAG/Al_2O_3 fibres

1. Introduction

Oxide long fibre-reinforced oxide matrix composites are promising materials for applications requiring high temperatures, damage tolerance, oxidation resistance and long term stability, especially in atmospheres containing oxygen. One of the important factors in the development of such composites is the improvement of the mechanical properties of the oxide long fibres as well as the design of the interface between the fibres and matrix. In the case of non-oxide fibres, materials such as Si–C–O[1] and Si–Ti–C–O[2] have excellent mechanical properties not only at room temperature but also at high temperature. However, these superior properties are restricted to use in inert atmospheres and are not available for long term use under ambient atmospheres. It is, therefore, essential to develop oxide fibres for oxidizing applications. Although some oxide fibres such as Al_2O_3,[3,4] mullite[5,6] and ZrO_2[7] have been reported, fibres with enhanced mechanical properties are required, especially for use at high temperatures.

Comparing the mechanical properties of oxide fibres, Al_2O_3 fibres[3,4] exhibit superior mechanical strength at room temperature. However, these excellent mechanical properties degrade considerably at high temperatures because of poor creep resistance. On the other hand, mullite ceramics[8] have been reported to retain good mechanical properties at room temperature up to high temperature with only slight degradation. This is considered to result from the good creep resistance of mullite. We,[9] therefore, prepared mullite long fibres by a sol–gel method using water as a solvent because of the potential of this material as a candidate for oxide fibre applications in oxide/oxide fibre composites. In addition to mullite, yttrium aluminium garnet (YAG; $Y_3Al_5O_{12}$) is also well known to exhibit high creep resistance and is, thus, also a candidate fibre material for use in composites.

YAG fibres have previously been prepared by many workers using melt cooling methods and sol–gel methods. Zhu et al.[10] prepared YAG fibres by drawing from a deeply undercooled melt. Yang et al.[11] prepared YAG/Al_2O_3 fibres by directionally solidifying the eutectic melt in the YAG–Al_2O_3 binary system. YAG fibres have also been prepared by sol–gel methods. King and Halloran[12] prepared the fibres from mixtures of

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Y_2O_3 sol and AlOOH sol using polyethyleneoxide as a viscosity adjusting agent. YAG fibres were also prepared from various precursor solutions, i.e. from tetrahydrofran solutions of $Y(O^iC_4H_9)_3$ and $Al(O^iC_4H_9)_3$, from solutions of yttrium acetate and aluminium formate,[13] and also from solutions of metalloorganic precursors.[14] The reported mechanical strength of these YAG fibres is, however, not as high as expected, the maximum strength at room temperature being 1.7 GPa.[14] In the Al_2O_3 and mullite binary system, composite fibres of Al_2O_3/mullite, which have a microstructure of fine Al_2O_3 grains dispersed in a matrix of mullite grains, showed enhanced creep resistance over that of mullite fibres because of the pinning effect of the fine Al_2O_3 grains segregated in the mullite grain boundaries. It is therefore expected that YAG/Al_2O_3 fibres might exhibit both the high room temperature strength of Al_2O_3 fibres and the good high temperature creep resistance of YAG fibres.

In this paper, we studied the preparation conditions of YAG/Al_2O_3 gel fibres from two precursor solution systems (nitrate and chloride) containing various combinations of reagents in water. We also investigated the effect of the firing conditions on the resulting gel fibres.

2. Experimental

Fibres were drawn from both nitrate and chloride solutions. The starting materials were $Al(NO_3)_3$ $9H_2O$(AN), $Al(O^iC_3H_7)_3$(AIP), Al metal, Y_2O_3 and HNO_3 for the nitrate system, and $AlCl_36H_2O$(AC), Al metal, Y_2O_3 and HCl for the chloride system. All the reagents except Y_2O_3 (Japan Yttrium Co.) were supplied by Wako Pure Chemicals. In the nitrate system, precursor solutions were prepared variously by changing the order in which the starting materials were dissolved in de-ionized water and/or aqueous HNO_3 to prepare good precursor solutions. The ratios of YAG/Al_2O_3 varied from 0:10, 1:9, 2:8 to 10:0 (volume ratio) but the (Al metal):AN ratio was fixed at 1.9:1 in all the precursor solutions. The precursors were refluxed at 100°C for 5–18 h, then condensed at 80°C for a fixed time. They were then further condensed at room temperature and the spinnability of the gel fibres was checked repeatedly at fixed time intervals up to the gellation of the precursor solution. The gel fibres were prepared by immersing a glass rod into the condensed precursor solution and pulling out it slowly. Fig. 1 shows a flow chart for the preparation of gel fibres from the chloride solution. The calculated amount of Y_2O_3 was first dissolved in aqueous HCl (2–6 M) and mixed with deionized water. The required amount of AC followed by Al metal powder was added to the solution. The precursor solution was then refluxed at 100°C for 2–5 h to completely dissolve the starting materials and was condensed at 80°C. After further condensation at room temperature, the spinnability of the gel fibres was examined as for the nitrate system. The ratios of YAG/Al_2O_3 and (Al metal):AC studied in this system were the same as studied in the nitrate system.

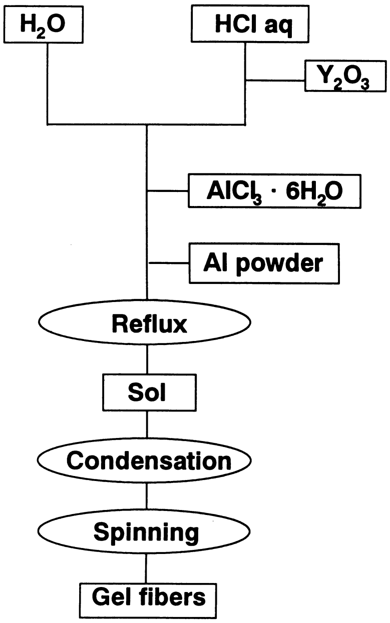


Fig. 1. Flow chart of fibre preparation in the chloride system.

The gel fibres were dried at room temperature for 1 h and further dried and/or fired under various conditions, i.e. stored in a desiccator at room temperature before firing, fired to 300°C at a heating rate of 1°C min^{-1} and held for 1 h at 100 and 200°C before firing, and calcined to 900°C at various heating rates immediately after drying at room temperature. The dried and calcined fibres were further fired at various temperatures at heating rates of 0.33–20°C min^{-1}.

The fibres and gels prepared from the precursor solution after the fibres had been drawn and dried at 110°C, were characterized by thermogravimetric analysis/differential thermal analysis (TG/DTA), powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The TG/DTA of the precursor gels was recorded at a heating rate of 5°C min^{-1} in flowing dry air using a Rigaku Thermoplus 8120 instrument. The phases formed in the fired samples were identified by XRD using a Rigaku Geigerflex diffractometer with monochromated Cu K_α radiation. The microstructure of the fibres was observed using Hitachi S-2050 and JEOL JSM-T200 instruments at accelerating voltage of 15 kV.

3. Results and discussion

3.1. Preparation of gel fibres

In the nitrate system, the precursor solutions were always a little opaque after refluxing irrespective of the preparation methods or the order in which the starting materials were dissolved. This opacity suggests that very fine particles are formed in these precursor solutions. Since the pH of the precursor solutions was about 4 after refluxing, having increased from the very strongly acidic conditions of the starting solution, the Y component is considered to precipitate fine particles. This pH increase is caused by decomposition of the nitrates, since the refluxing temperature (100°C) is higher than the decomposition temperature of nitrate (86°C). Therefore, the nitrates decomposed to NO_x gas and escaped during refluxing. In order to avoid this, it is necessary to lower the refluxing temperature but this makes it difficult to dissolve Al metal powder completely even with longer refluxing times. Fibres could not be spun from these precursor solutions because their viscosity was too low. Even when the viscosity of the precursor solution was adjusted by adding polyethyleneoxide as a thickener, fibres could not be spun. Fibre drawing experiments from precursor solutions of various composition showed that gel fibres could only be drawn from compositions very close to $A1_2O_3$, i.e. $YAG/Al_2O_3 \leqslant 5{:}95$ (volume ratio) in the nitrate system.

By contrast, gel fibres could be obtained from a much wider composition range in the chloride system than in the nitrate system. This may be related to the pH of the precursor solutions in this system, which remained strongly acidic after refluxing. The spinnable composition range of the YAG/Al_2O_3 gel fibres could thus be examined as a function of the total amount of water in the precursor solution as well as its composition (it has been reported that the water content is an important factor in the preparation of Al_2O_3 fibres by the sol–gel method using water as a solvent[15]). Fig. 2 shows the spinnable conditions of the gel fibres as a function of the YAG content (vol%) and the water content of the precursor solution. Gel fibres could be drawn in the composition range $0{:}10 \leqslant YAG/Al_2O_3 \leqslant 6{:}4$. The spinnable region also correlates with the amount of water necessary for fibre drawing, which increases with increasing YAG content because more water is required to prepare the precursor solution. This may be related to the fact that more water is necessary to dissolve the Y_2O_3 than the Al_2O_3 component.

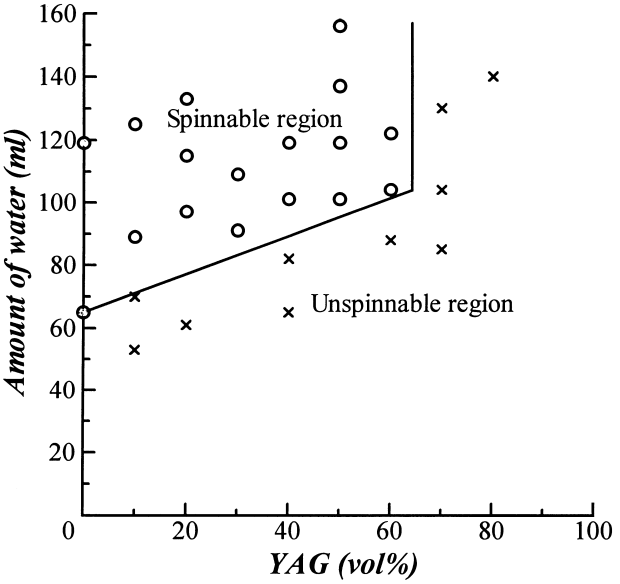


Fig. 2. Spinnable region of gel fibres as a function of the amount of water in the precursor solution and its chemical composition.

3.2. Drying and firing of gel fibres

Since the gel fibres obtained from the nitrate system were restricted to very low YAG contents, the drying and firing conditions were examined only for those obtained from chloride solutions. The DTA and TG curves of the YAG/Al_2O_3 precursor gels are shown in Fig. 3. The DTA curves show a number of overlapping endothermic peaks of varying degrees of broadness, due to dehydration of water at 100 to 300°C. Corresponding weight losses of 35–45 mass% appear in the TG curves, which show either continuous mass losses or slight inflexions below about 300°C. The exothermic peaks occurring at about 650°C become weaker with increasing YAG content. These exothermic peaks are due to the loss of Cl_2 gas by decomposition of residual chloride in the gels. A similar result was found in the preparation of mullite fibres[9] from a chloride system. In that case, the fibres became porous due to decomposition of chloride. Since the exothermic peak became weaker and the weight loss became smaller with increasing YAG content, the effect may be less detrimental to YAG/Al_2O_3 fibres than to mullite fibres.

No exothermic signal due to crystallization is observed in the DTA curves although XRD of the samples after the DTA experiments showed the formation of crystalline phases. The gels were, therefore, fired at various temperatures to determine the crystalline phases formed. Fig. 4 maps the fields of crystalline yttrium aluminate and alumina as a function of firing temperature and chemical composition. Crystallization is found to occur at about 1000°C. The first crystalline alumina phase formed was γ-Al_2O_3, which transformed to α-Al_2O_3 above 1200°C via θ-Al_2O_3. On the other hand, the yttrium aluminates depended on both the firing temperature and chemical composition. In samples of low Y_2O_3 content, the first yttrium aluminate to crystallize was hexagonal $YAlO_3$, which changed to YAG and orthorhombic $YAlO_3$ (yttrium aluminate perovskite or YAP) at higher temperatures. The amount of YAP decreased at higher temperatures but was still present up to 1400°C in the $YAG/Al_2O_3 = 1{:}9$ and 2:8 samples. In the high Y_2O_3 content samples, the first yttrium aluminates to crystallize were YAG and $Y_4Al_2O_9$ (monoclinic yttrium aluminate or YAM). The

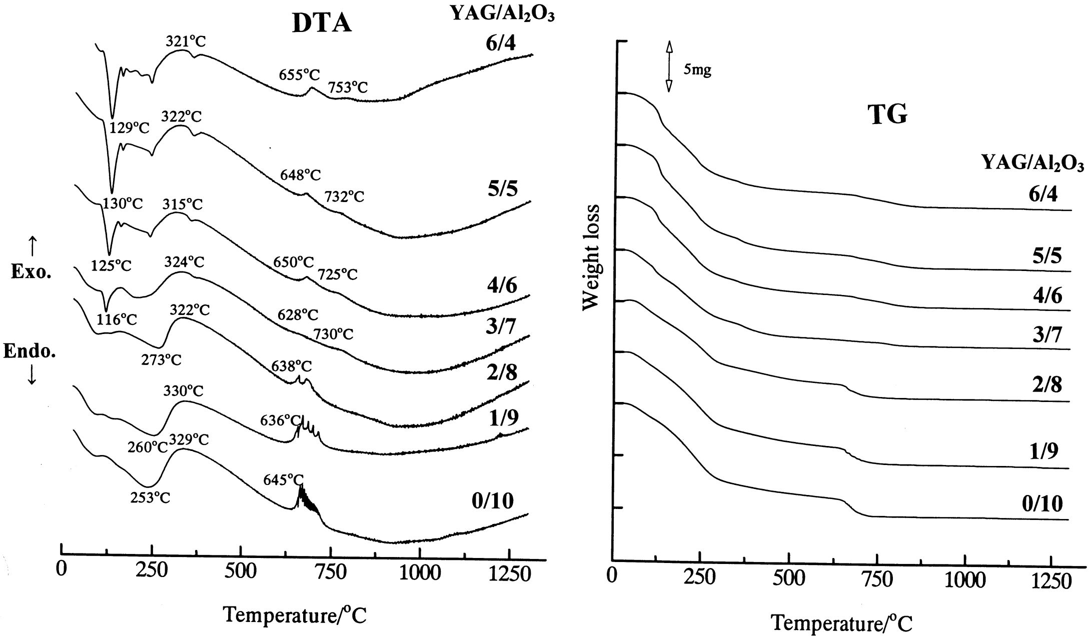


Fig. 3. DTA and TG curves of YAG/Al_2O_3 precursor gels of various compositions.

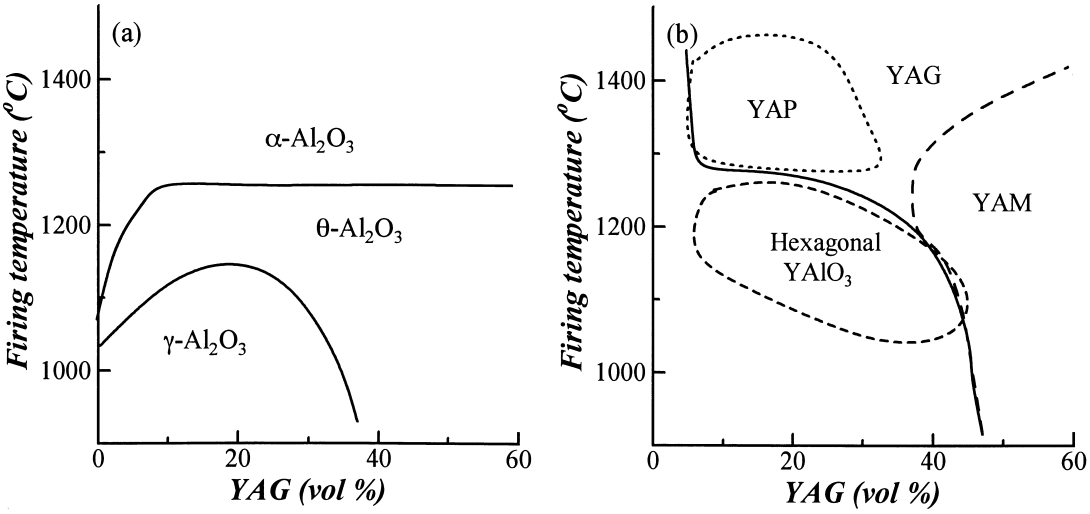
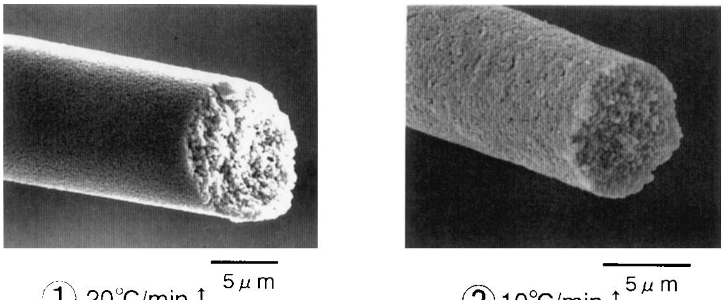


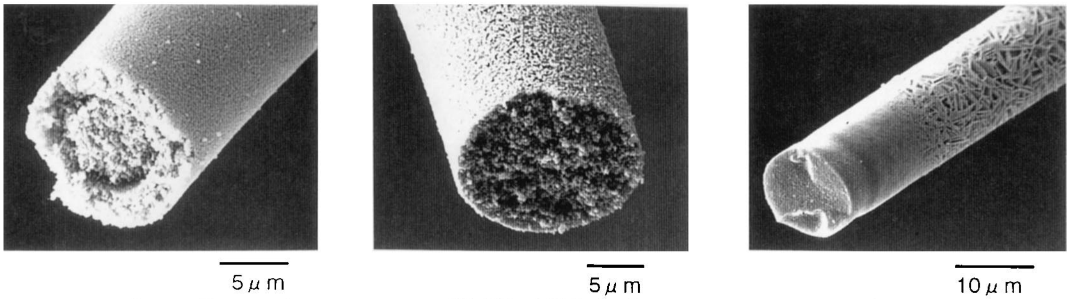
Fig. 4. Field of crystalline phases formed in the gels as a function of firing temperature and chemical composition; (a) for alumina phases and (b) for yttrium aluminate phases.

amount of YAM decreased at higher temperatures but continued to be present up to 1400°C in the YAG/$Al_2O_3 = 6{:}4$ sample. In the samples of intermediate Y_2O_3 content, i.e. YAG/$Al_2O_3 = 3{:}7$ and 4:6, YAG formed at lower firing temperature than in the other samples.

Considering the composite effect, it is well known that the introduction of up to 10–20 vol% of a second phase is generally most effective in enhancing the various properties. Therefore, the fibres with YAG/$Al_2O_3 = 2{:}8$ were used to study the effect of the firing conditions. Three factors were considered to be major causes of cracking in the fired fibres, i.e. (1) dehydration of large amounts of water from the precursor fibres in the drying step, (2) evaporation of Cl_2 gas from decomposition of the residual chloride in the calcining step, and (3) extensive shrinkage of the fibres during crystallization. In the drying step, crack free fibres were more readily obtained in the YAG/$Al_2O_3 = 2{:}8$ system than for Al_2O_3. The reason why the presence of Y produces crack free fibres after drying is not clear, even from a composition of the TG and DTA curves. The fibres were calcined up to 900°C, which is just below their crystallization temperature, using various heating rates, holding temperatures and times. All the calcined fibres were dense, with smooth surfaces, irrespective of the calcining conditions. This result is very different from



① 20°C/min ↑ ② 10°C/min ↑



③ ~900°C 10°C/min ↑
~1300°C 1°C/min ↑

④ ~900°C 1°C/min ↑
~1300°C 10°C/min ↑

⑤ ~1250°C 1°C/min ↑
~1300°C 0.33°C/min ↑

Fig. 5. Microstructure of fibres of YAG/Al_2O_3 = 2:8 composition fired at 1300°C for 1 h under various firing conditions.

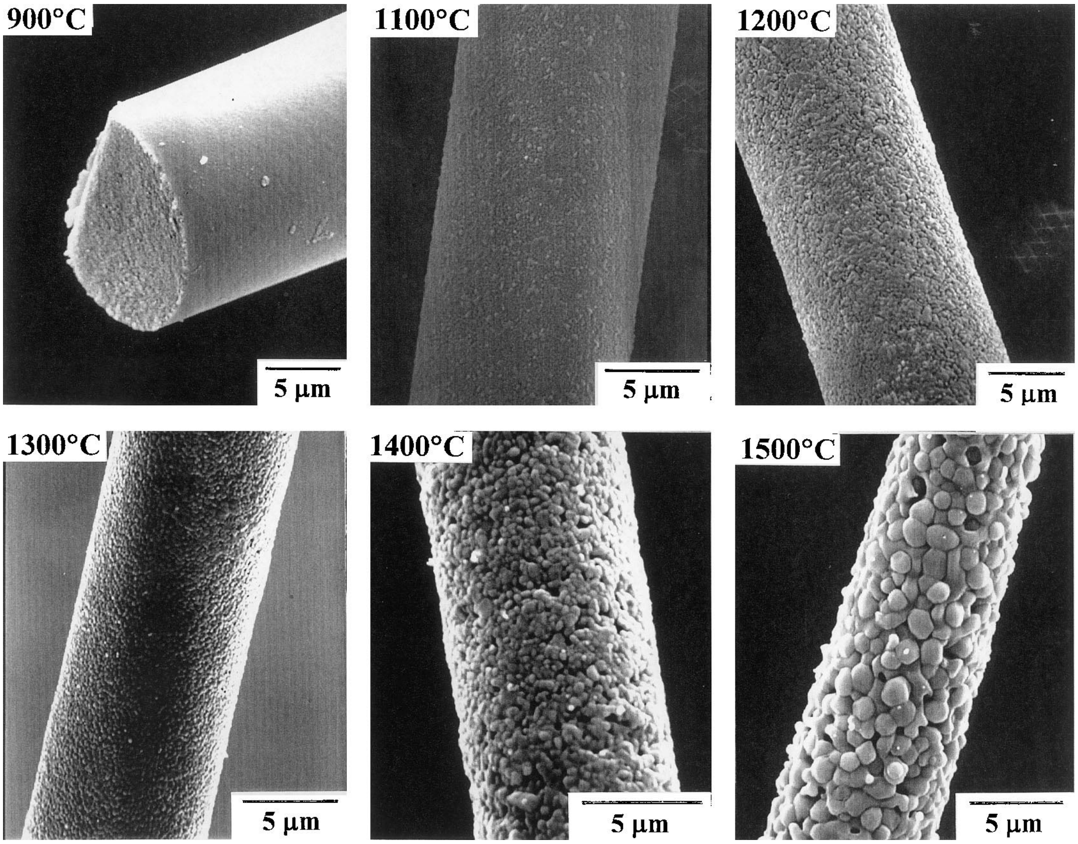


Fig. 6. Microstructure of fibres of YAG/Al_2O_3 = 2:8 composition fired at various temperatures at a heating rate of 20°C min^{-1}.

that for mullite fibres[9] which became porous by evaporation of Cl_2 gas. As previously suggested, the introduction of Y into the gel fibres may change the pore structure and/or the decomposition reaction of the residual chlorides. On the other hand, fibres fired at 1300°C crystallized, showing an apparent difference in the microstructure which depended on the heating rate (Fig. 5). The microstructure of slowly fired fibres, especially No. 5, became inhomogeneous and porous and consisted of both dense and porous regions, the latter formed by large aggregated platy grains. However, the microstructure became homogeneous and dense with faster heating rates. The microstructures of these fibres consisted of fine equiaxed grains.

The microstructural change of $YAG/Al_2O_3 = 2{:}8$ fibres has examined as a function of firing temperature at a heating rate of 20°C/min, the fastest rate possible with our equipment. Fig. 6 shows the microstructures of fibres fired at 900, 1100, 1200, 1300, 1400 and 1500°C, respectively. Since the fibres fired at 900°C are amorphous, their surfaces are smooth, with very small internal grains. On crystallization, the surface of the fibres became a little rough due to the development of grain boundaries. The grains remained small up to at 1300°C, but between 1300 and 1400°C, the grain growth changed, and the surface became rougher, with some open pore like dimples appearing in the microstructure at 1400°C due to the coalescence of the grains. A further drastic microstructure change was observed between 1400 and 1500°C. The microstructure of the 1500°C fired fibres showed not only apparent grain growth but also a change in grain shape, the YAG grains acquiring a faceted granular shape and the alumina grains becoming irregular and rounded in shape and filling the spaces between the YAG grains. On the basis of the volume ratio of YAG to Al_2O_3 in these fibres, the proportion of YAG grains on the surface is higher than expected, suggesting that the Y component diffused from the inside to the surface during YAG crystallization. Alternatively, the YAG grains have moved to the surface during the firing treatment. The characteristics of the microstructure suggest that liquid phase sintering has occurred in this sample even though it is not expected from the stable phase diagram.[16] There is, however, some possibility that it may occur during metastable supercooling of Al_2O_3 as suggested from the reported metastable diagram.[17]

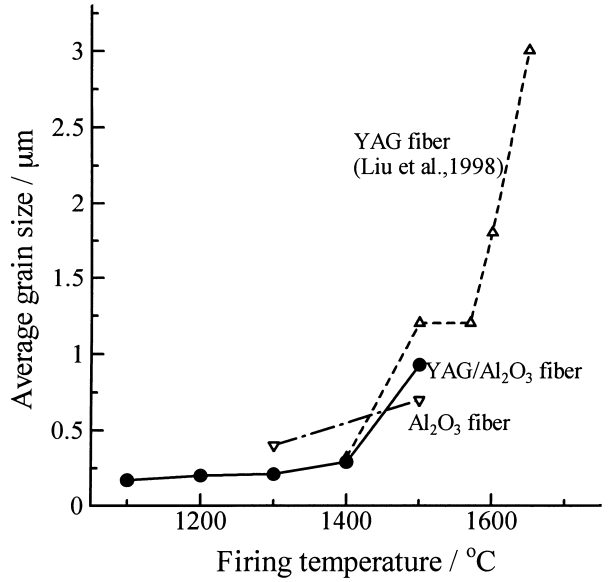


Fig. 7. Change of average grain size in the fibres as a function of firing temperature.

Fig. 7 shows the change in grain size of the YAG/Al_2O_3 fibres as a function of firing temperature and also includes data for Al_2O_3 fibres and YAG fibres.[14] The grain size of the present YAG/Al_2O_3 fibres remained small up to 1400°C but increased steeply at 1500°C. This steep grain growth above 1400°C was in good agreement with the previously reported grain size change in YAG fibres.[14] Below 1400°C, the grain size in our YAG/Al_2O_3 fibres was even smaller than that in Al_2O_3 fibres below 1400°C, but above that temperature it becomes larger than in Al_2O_3 due to the steep grain growth of the YAG in this temperature range.

4. Conclusions

YAG/Al_2O_3 long fibres were prepared by the sol–gel method using nitrate and chloride solutions and water as the solvent.

1. The spinnable composition range of YAG/Al_2O_3 fibres from nitrate solutions was very limited owing to the decomposition of the nitrate during refluxing.
2. The spinnable composition range of YAG/Al_2O_3 fibres from chloride solutions was $0{:}10 \leqslant YAG/Al_2O_3$ (volume ratio)$\leqslant 6{:}4$ and was wider than from nitrate solutions.
3. The microstructure of YAG/Al_2O_3 fibres depended strongly on the heating rate; dense fibres were obtained by firing at 20°C/min.
4. Below 1400°C, the grain sizes of the fibres remained small but increased steeply above that temperature. Liquid phase sintering is suggested by the microstructure of these fibres.

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