EFFECT OF ZIRCONIA ON CRYSTALLIZATION OF YTTRIUM ALUMINUM GARNET PRECURSOR GEL FIBERS

#HONGBIN TAN*, **, XIAOLING MA**, JINHUA LU*, KEZHI LI*

*State Key Laboratory of Solidification Processing, Northwestern Polytechnical University,
Xi;an Shaanxi 723003, People's Republic of China
**School of Materials Science and Engineering; Shaanxi University of Technology,
Hanzhong Shaanxi 710072, People's Republic of China

#E-mail: hb-t@163.com

The zirconia-yttrium aluminum garnet (Zr–YAG) long fibers were successfully prepared through sol-gel method following by sintering at 1000°C, with aluminum powder, yttria, zirconium oxychloride and aluminum chloride as raw materials and polyvinylpyrrolidone as spinning additive. YAG phase was only observed in the fibers with smooth surface after sintering at 1000°C for 2 hours. However, a rough surface with an average grain size of 2 μm could appear when gel fibers were sintered at 1400°C for 6 hours. Calculated from Kissinger equation, the crystallization activation energy value (Ea) of Zr–YAG fibers was 59.69 kJ/mol. The Ea value is lower than YAG crystallization values by other authors.

INTRODUCTION

Yttrium aluminum garnet (YAG or $Al_5Y_3O_{12}$) possesses a cubic structure and constitutes a complex oxide of Al_2O_3 and Y_2O_3. YAG fibers, with low creep rates, high tensile strength, high elastic modulus, excellent thermal stability, thermal shock resistance, oxidation and reduction atomsphere resistance at high temperatures, are widely used as high temperature structural materials and as a reinforcing phase to reinforce composites [1, 2].

Two main processes for the manufacturing of ceramic fibers exist, melt-spinning processes and sol-gel spinning processes. López et al. [3] prepared YAG fibers by the melt extraction technique. The calcined YAG powders were mixed with a plasticizer to extrude 3-mm diameter rods that were dried in air for 24 h at room temperature. The rods were then sintered at 1500°C for 1 h to give them enough resistance for handling. The sintered rods were melted using an oxy-acetylene torch to form a small molten drop beneath a rotating Cu–Be wheel. The shallow contact of the wheel tip with the molten drop resulted in rapid solidification and formation of the fibers. Mileiko et al. [4] produced single crystalline YAG fibers by an internal crystallization method. The method was crystallization of the oxide melt infiltrated into continuous channels made in an auxiliary matrix, normally molybdenum, and then extracting the fibers from the auxiliary matrix by chemical dissolution of it.

Conventionally, melt-spinning methods are adopted for the synthesis of ceramic fibers with low-melting point, so it is difficult to prepare YAG fibers due to the high melting points (1970°C).

Many successful processes have been reported in the preparation of YAG fibers by the sol-gel method. Li et al. [2] prepared YAG fibers by sol-gel method using Al powder, $Y(CH_3COOH)_3 \cdot 4 H_2O$ and HCl were used as raw materials, polyethylene oxide as viscosity adjusting agent and water as the solvent. YAG fibers were obtained by sintering at 900°C, with 25 nm in grain size and 970 MPa in tensile strength. Pullar et al. [5] obtained YAG fibers using alumina sol and yttria sol as precursors. The alumina sol was made from aluminium sulphate, and the yttria sol was made from yttrium chloride. Towata et al. [6] synthesized YAG fibers by sol-gel method, using aluminum iso-propoxide and yttrium isopropoxide as raw materials and isopropanol solutions as solvent.

One of the directions of modification of ceramics in order to attain desirable properties is creating a secondary crystalline phase [7]. Ceramic material containing ZrO_2 is extensively studied because martensitic phase transformation of zirconia under applied stress that contributes considerably to the mechanical properties of ceramics [8]. The Zr–YAG (zirconia-yttrium aluminum garnet) composites fibers were prepared by adding zirconium oxychloride in YAG precursor solution.

According to the crystallization kinetics, the optimal sintered process can be obtained. In the work, Zr–YAG fibers were prepared by the sol-gel method. The crystallization behaviour of the Zr–YAG precursor gel fibers was investigated by non-isothermal experiments, by the analysis of DSC data for samples heated at different heating rates.

EXPERIMENTAL

Preparation of samples

The starting materials used were aluminum powder (chemical grade, Shanghai Chemistry Co. Ltd., Shanghai, China), aluminum chloride hexahydrate (chemical grade, Xi'an reagent factory, Xi'an, China), yttria (99.99 wt. %, Wanbao Rare-Earth Co. Ltd, Ganzhou, China), glacial acetic acid (chemical grade, Tianjin Yaohua Chemistry Co. Ltd., Tianjin, China), zirconium oxychloride (chemical grade, Guangtong Chemical Co. Ltd., Zibo, China) and polyvinylpyrrolidone (chemical grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China).

The Zr–YAG fibers were prepared in the processing steps as shown in Figure 1. The yttria powder, aluminum powder, zirconium oxychloride and aluminum chloride were dissolved in acetic acid solution when the mixtures were heated and stirred using magnetic stirring under reflux at 80°C. Then, spinning sols were obtained by condensing at 60°C. The gel fibers were prepared by pulling a thin glass rod slowly from the sol after immersing.
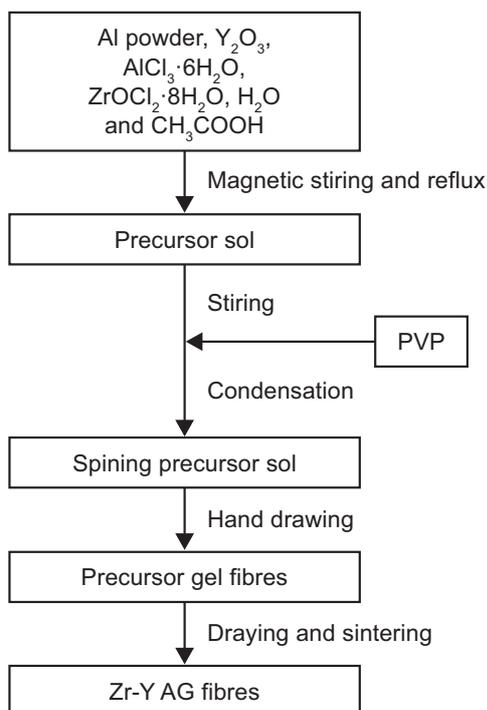
Figure 1. Schematic view of the production route for Zr–YAG fibers.

Then the gel fibers were dried at 60°C for 24 h in an oven. The dried gel fibres were then sintered at 1000°C for 2 h with heating rate of 1°C/min.

Characterization techniques

For the gel fibers, thermal behaviors was measured by TG/DSC instruments (SDT Q600, TA Instrument, American) at a heating rate of 5, 10 and 20°C/min in flowing air. X-ray diffraction analysis was carried out on an X-ray diffractometer (DX-2500, Dandong Fangyuan Instruments Co. Ltd., Dandong, China) using CuKα radiation with a step of 0.1°/s. The morphologies of fibers were characterized by scanning electron microscopy (JSM-6390LV, JEOL, Japan). All tests were done at room temperature.

RESULTS AND DISCUSSION

Characterization of the precursors

Aluminum chloride hexahydrate was firstly hydrolyzed with water and formed aluminum hydroxide in acid solution, according to the chemical reaction:

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl \qquad (1)$$

Hydrolysis reaction occurred because water molecules coordinated to metal ions were more acidic than in the noncoordinated state due to charge transfer from the oxygen to the metal atom [9]. Yttria and aluminum powder were dissolved during the stirring and heating in the mixed solution of aluminum chloride, zirconium oxychloride and acetic acid, and its main chemical reactions can be simplified in the following set of equations, though the actual reactions are more complex:

$$Y_2O_3 + 6HCl \rightarrow 2YCl_3 + 3H_2O\uparrow \qquad (2)$$

$$Al + 3HCl \rightarrow AlCl_3 + 3/2H_2\uparrow \qquad (3)$$

$$3CH_3COOH + Al \rightarrow Al(CH_3COO)_3 + 3/2H_2\uparrow \qquad (4)$$
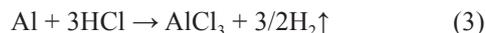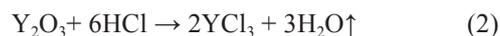
In addition, yttrium chloride and zirconium oxychloride were also hydrolyzed with water and formed yttrium and zirconium hydroxide in the acid sol, according to the chemical reaction:

$$YCl_3 + 3H_2O \rightarrow Y_2(OH)_3 + 3HCl \qquad (5)$$

$$ZrOCl_2 + 2H_2O \rightarrow Zr(OH)_4 + 2HCl \qquad (6)$$
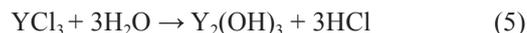
The viscous sol was obtained by condensating because poly-nuclear species are formed by condensation reactions (olation and oxolation) and formation of M–OH–M and M–O–M with linear or non-linear links [9]. But, long fibers can be obtained, only by adding 1 wt. % PVP as spinning additive. Al, Y and Zr ions or particles would coordinate with N or O ions in PVP, resulting in the formation of the coordinative complex in aqueous solution [10].

The TG/DSC curves of the precursor gel fibers are shown in Figure 2 with a heating rate of 10°C/min. The DSC curve of the gel fibers exhibited four endothermic peaks at about 150, 268 and 376, and two exothermic peaks at about 600°C and 936°C. The endothermic peaks are assigned to dehydration of the residual water and decomposition of different hydroxides in the gel fibers, whereas the two exothermic peaks are assigned to decomposition of organic component and crystallization of YAG, respectively [2]. But the exothermic peak at about 936°C is weak, because of the exothermic peak coincides with the grain growth. The TG curve of the gel fibers showed the weight loss around 63 wt. % at 900°C, while almost no further weight loss appeared with increasing the temperatures.
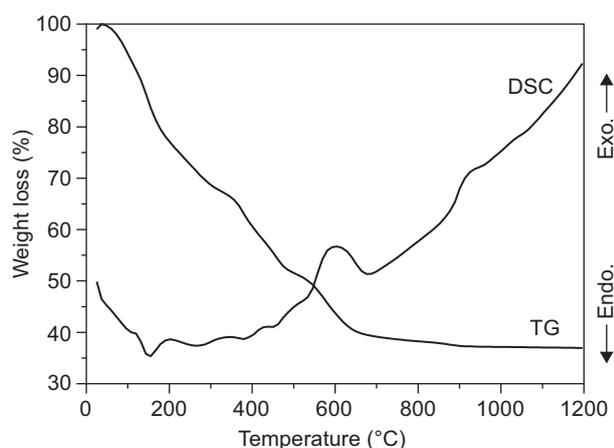
Figure 2. TG and DSC curves of Zr–YAG precursor gel fibers.

The X-ray diffraction pattern of gel fibers sintered at 1000°C is shown in Figure 3. YAG phase was observed in the samples sintered at 1000°C, but zirconia phase was not observed because the amount of zirconia was less and it was not detected by XRD.
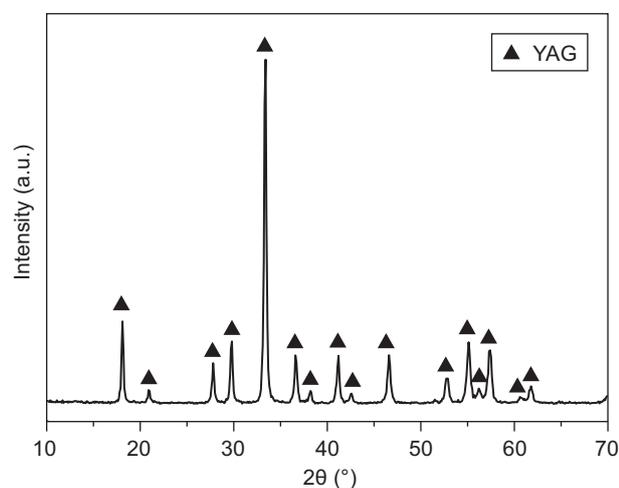
Figure 3. XRD pattern of the Zr–YAG precursor gel fibers heated at 1000°C for 2 h.

SEM micrographs of Zr–YAG fibers sintered at 1000°C for 2 h are shown in Figure 4. The Zr–YAG fibers were obtained with smooth surface, uniform and 40 µm in diameter.
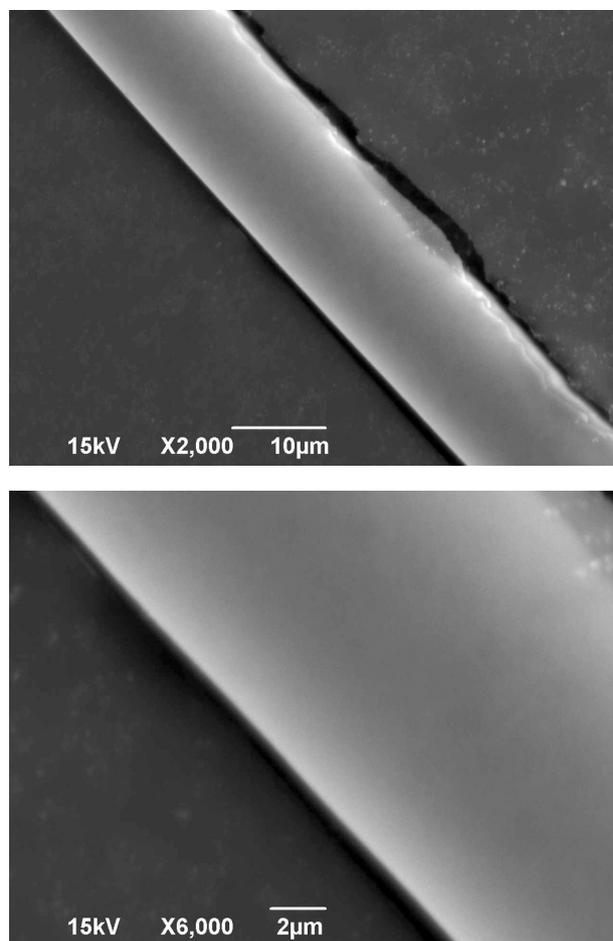
Figure 4. SEM microstructures of Zr–YAG precursor gel fibers heated at 1000°C for 2 h.

SEM micrograph of YAG and zirconia-YAG fibers sintered at 1400°C for 6 h are shown in Figure 5. The YAG fiber was obtained with smooth surface, fine grains and 40 µm in diameter (Figure 5a). But the zirconia-YAG fibers were observed with rough surface, some pores on fiber surface and 30 µm in diameter (Figure 5b). And coarse columnar grains were observed with an aspect ratio of > 2 (about 0.5 - 1 µm in diameter). So, zirconia promoted YAG grain growth and limited the YAG application in high temperature condition.

The activation energy (E_a) of YAG crystallization can be determined by isothermal or non-isothermal methods. Under non-isothermal conditions, DSC or DTA curves were used to obtain E_a values from peak temperature measurements at different heating rates. A non-isothermal method was experimentally easier than an isothermal method, but the accuracy of the resulting E_a value was generally strongly influenced by experimental

conditions such as particle size, particle distribution, packing state, etc [9]. In general, using larger sample sizes and faster heating rates may result in a reduction of the activation energy.

Figure 6 show the thermo-grams obtained for the DSC runs with heating rates of 5, 10 and 20°C/min for precursors. The exothermic peak, in the range of 906 - 937°C, corresponds to YAG crystallization.
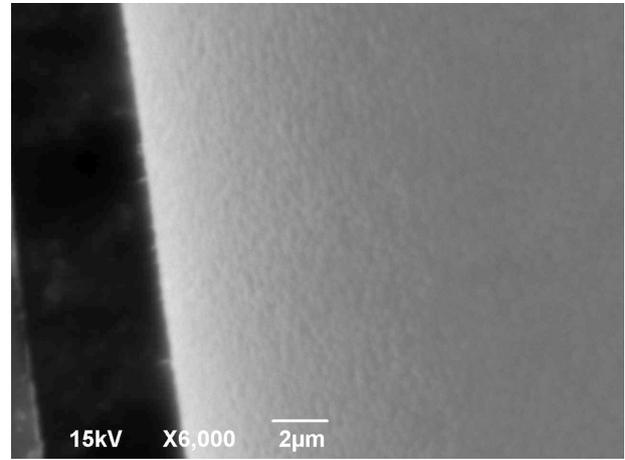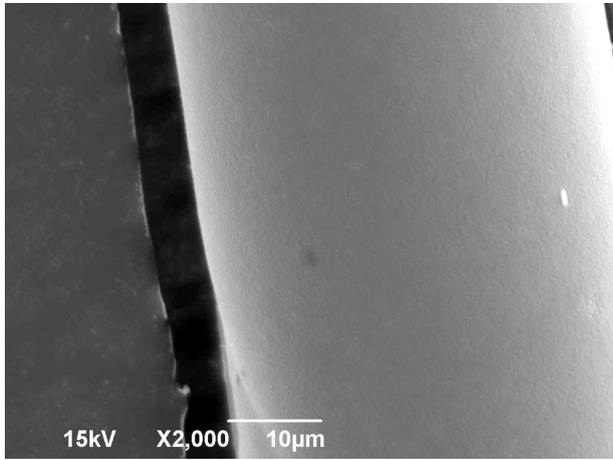
a) YAG fiber
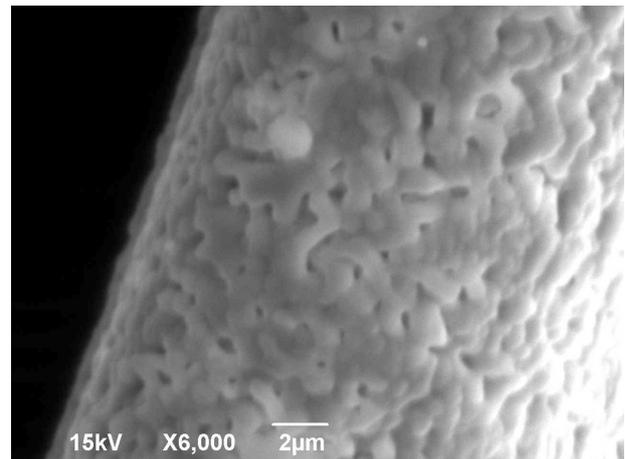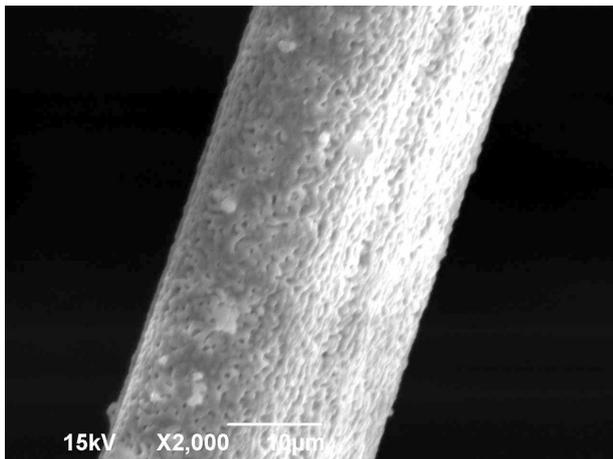
b) Zirconia-YAG fiber

Figure 5. SEM microstructures of the a) YAG and b) zirconia-YAG precursor gel fibers heated at 1400°C for 6 h.
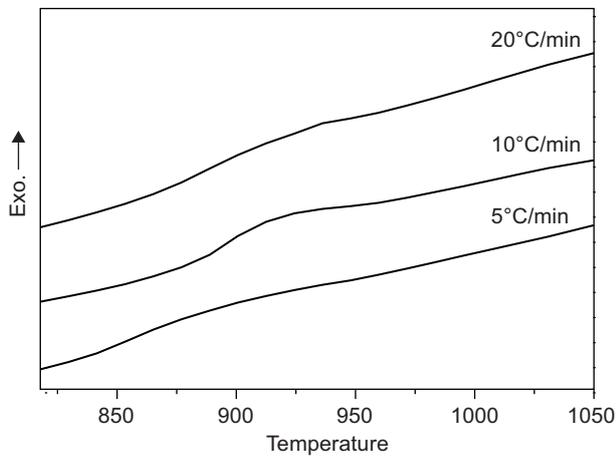
Figure 6. DSC Curves of the Zr–YAG precursor gel fibers at different heating rate.
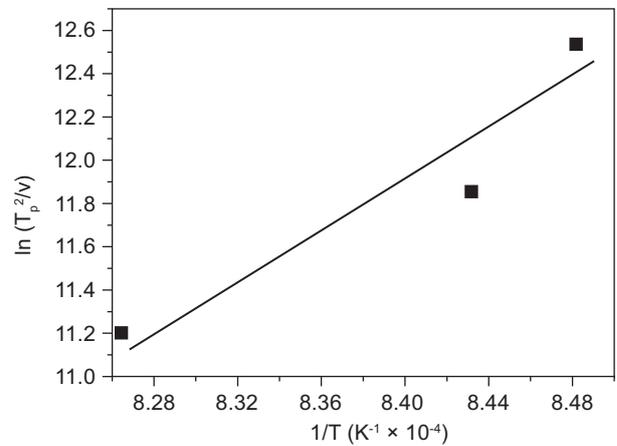
Figure 7. Activation energy plot for Zr–YAG crystallization, according to Equation 7.

Table 1. Activation energy of YAG reported by different authors.

Authors	Solvent	Chelating agents	Activation energy (kJ/mol)
Hou et al. [11]		Citric acid	160.5
	Distilled water	Glycine	142.2
		Citric acid–glycine	140.4
Gong et al. [12]	Ethanol-deionized water	Citric acid	361.7
	Deionized water		480.6

*Aluminium nitrate and yttrium nitrate were used as raw materials by the authors.

Although many mathematical equations had been proposed for the calculations, the Kissinger equation (Equation 7) was most commonly used [11].

$$\ln(T_p^2/v) = \ln(E_a/R) - \ln \phi + E_a/RT_p \qquad (7)$$

where T_p is the temperature of the exothermic peak top (crystallization temperature), v the heating rate, E_a activation energy, R universal gas constant and ϕ the frequency factor (it is a constant dependent of the sample).

According to Equation 7, by plotting of $\ln(T_p^2/v)$ versus $1/T_p$, the activation energy can be determined from the slope. As can be shown in Figure 7, the value $E_a = 59.69$ kJ/mol was determined.

The E_a values of YAG crystallization were reported by other authors listing in Table 1. The E_a value is lower than YAG' values because ZrO_2 accelerated YAG crystallization.

CONCLUSION

A Zr–YAG sol appropriate for spinning was obtained using aluminum chloride, zirconium oxychloride, aluminum powder, yttrium oxide and acetic acid as raw materials. The main phase of the fibers was YAG after sintering at 1000°C, with smooth surface. But the zirconia-YAG fibers were observed with coarse grain.

The activation energy for Zr–YAG formation in precursor gel fibers was determined by non-isothermal methods. The E_a value was 59.69 kJ/mol by Kissinger equation.

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