PREPARATION OF YTTRIUM ALUMINUM GARNET FIBERS BY THE SOL-GEL METHOD

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Submitted September 14, 2011; accepted June 26, 2012

Keywords: YAG, Fibers, Sol-Gel Method, PVP

The yttrium aluminum garnet (YAG) fibers were prepared by the sol-gel method using aluminum chloride, aluminum powder, yttrium oxide and acetic acid as raw materials. The effect of the spinning additive on gel fibers length was studied. Long gel fibers were obtained by added polyvinylpyrrolidone (PVP) as an additive, with 23 cm in length. YAG fibers were obtained by sintering at 1000°C for 1 h, with about 16 μm in diameter and smooth surface.

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 atmosphere resistance at high temperatures, are widely used as high temperature structural materials and as a reinforcing phase to reinforce composites [1].

Two main processes for the manufacturing of ceramic fibers exist, melt-spinning processes and sol-gel spinning processes [2]. 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. [1] prepared YAG fibers by sol-gel method using Al powder, $Y(CH_3COOH)_3{\cdot}4H_2O$ 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 isopropoxide and yttrium isopropoxide as raw materials and isopropanol solutions as solvent.

However, the preparation of long YAG fibers has not been reported so far. It is desirable to use raw materials with low cost leading to high fiber quality. In the present work, long YAG fibers were prepared by the sol-gel method using aluminum powder, aluminium chloride and yttria as raw materials. The process, phase crystallization and surface morphology of fibers were investigated in detail.

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), and polyvinylpyrrolidone (chemical grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China).

The YAG precursor sols with different compositions were prepared according to Table 1. The YAG fibers were prepared in the processing steps as shown in Figure 1. The yttria powder, aluminum powder, 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. Then the gel fibers were dried at 60°C for 24 h in an oven. The dried gel fibers were then sintered at 800 and 1000°C for 1 h with heating rate of 1°C/min.

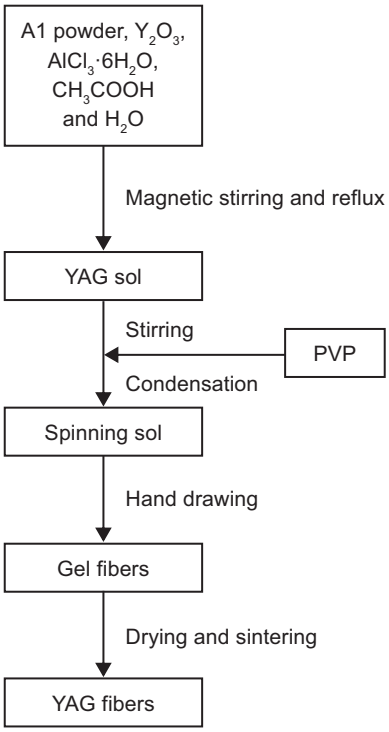


Figure 1. Schematic view of the production route for YAG fibers.

Characterization techniques

The pH of the sol was measured using PHS-25 pH-meter (Shanghai Precision Instruments Co. Ltd., Shanghai, China). Fourier transform infrared (FTIR) spectra of gel fibers was recorded on a infrared spectrometer (6700, Nicolet Magna, USA) with the samples as KBr pellets. 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.

Table 1. Effect of a molar ratio of Al powder and aluminum chloride on the solubility of Al powder*.

No.	$AlCl_3 \cdot 6H_2O$: Al (mol : mol)	pH value	Reaction time (h)	Appearance of sol
1	5:1	2.6	2	Transparent
2	3:1	3.2	2	Transparent
3	2:1	3.8	2	Transparent
4	1:1	3.9	4	Translucent

**A molar ratio of Al and Y, CH_3COOH and Y, and H_2O and Al was 5:3, 3:1, 20:1 in precursor sol, respectively.*

RESULTS AND DISCUSSION

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

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

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 [7]. Yttria and aluminum powder were dissolved during the stirring and heating in the mixed solution of aluminum chloride and acetic acid, and its main chemical reactions can be simplified in the following set of equations, though the actual reactions are more complex:

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

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

$$3CH_3COOH + Al \rightarrow Al(CH_3COO)_3 + 3/2H_2\uparrow \quad (4)$$

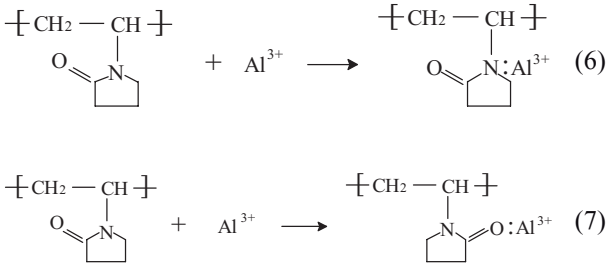
In addition, yttrium chloride was also hydrolyzed with water and formed yttrium hydroxide in the acid sol, according to the chemical reaction:

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

Macroscopic properties of the precursor sols prepared with different amounts of aluminum powder and aluminum chloride are shown in Table 1. When the composition ranged between an $AlCl_3 \cdot 6H_2O$/Al molar ratio of 5 to 1, pH varied from 2.6 to 3.9, and the transparency decreased because the content of aluminum hydroxide increased in the sol. A 2:1 molar ratio of $AlCl_3 \cdot 6H_2O$ and Al was optimal to obtain a sol appropriate for spinning. The mechanical properties of fibers could decrease if precursors contained Cl^- ions, since the Cl^- ions in the dried fibers evaporated at

relatively high temperature [8]. On the other hand, if the content of acetic acid was too high, insoluble acetates could be produced.

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 [7]. But, long fibers can be obtained, with 23 cm in length, only by adding 1 wt. % PVP as spinning additive. Al and Y ions or particles would coordinate with N or O ions in PVP, resulting in the formation of the coordinative complex in aqueous solution. The reactions can be written as (6) and (7), Al^{3+} as an example [9, 10].



The FTIR spectra of precursor gel fibers are shown in Figure 2. As can be seen, the bands at 3420 cm^{-1} and 1640 cm^{-1} are assigned to the O–H stretching and bending modes of adhesive and constitution water, respectively. The bands at 1580 and 1460 cm^{-1} correspond to asymmetrical and symmetrical stretching vibrations of carboxylate (O–C=O), respectively [1]. The stretching modes of Al–OH–Al linkages are observed at 1040 cm^{-1} and 870 cm^{-1} [11]. Stretching modes of Al–O–Y linkages are observed at 560 cm^{-1} and 510 cm^{-1}, the band at 670 cm^{-1} is assigned to the O–Al stretching mode, and the band at 770 cm^{-1} is assigned to the O–Y stretching mode [12, 13, 14, 15]. When precursor solution was condensed, hydrolysis and condensation/polycondensation could occur. Thus, the stretching modes of Al–O–Al and Al–O–Y linkages are observed.

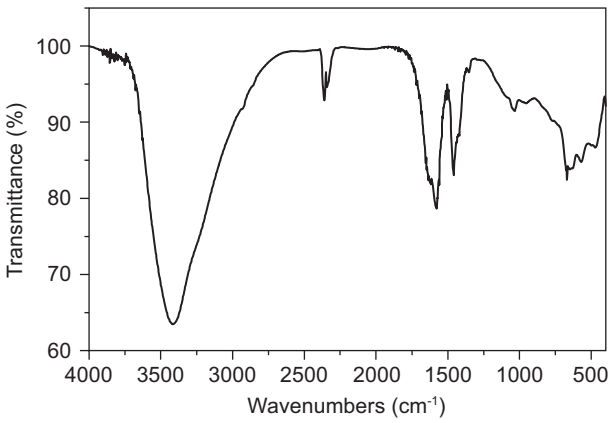


Figure 2. FT-IR spectra of the precursor gel fibers.

The X-ray diffraction patterns of gel fibers sintered at 800°C and 1000°C are shown in Figure 3. Amorphous and a small amount of YAG phases were present when fibers were sintered at 800°C YAG phase was only observed in the samples sintered at 1000°C.

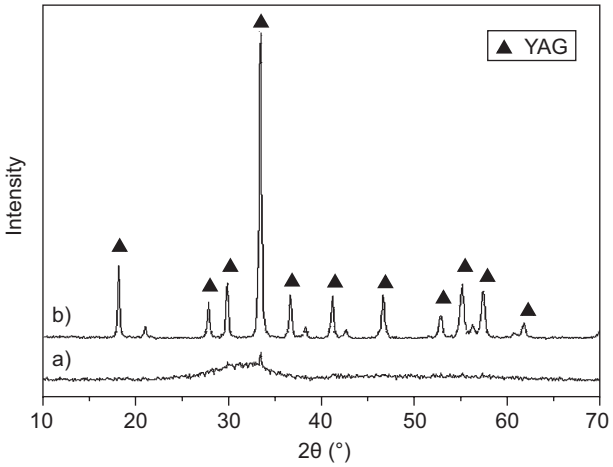
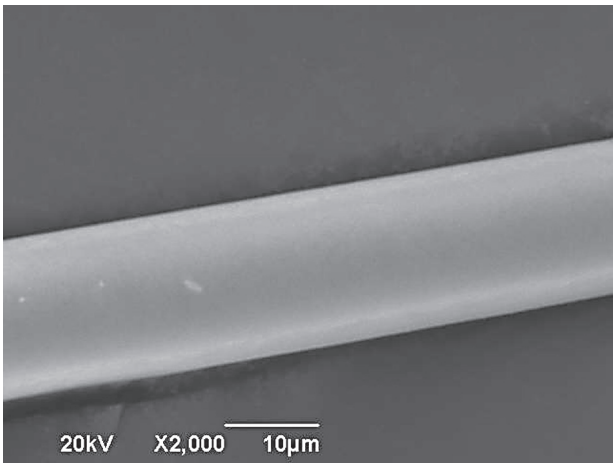
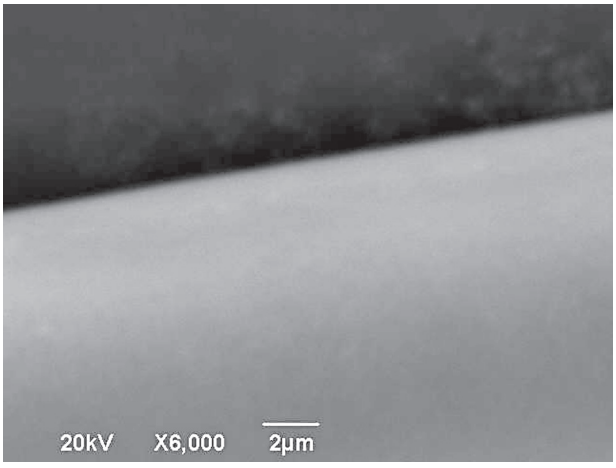


Figure 3. XRD patterns of the YAG precursor gel fibers heated at: a) 800 and b) 1000°C for 1 h.



a)



b)

Figure 4. SEM microstructures of YAG precursor gel fibers heated at 1000°C for 1 h.

SEM micrographs of alumina fibers sintered at 1000°C are shown in Figure 4. The fibers obtained have a smooth surface and dense structure. The diameter of fibers is uniform, and about 16 μm, which was influenced by the viscosity and surface tension of spinning sol, speed of hand drawing and so on. Further researches need to be performed to define well these correlations.

CONCLUSION

A spinning YAG sol appropriate for spinning was obtained, with a 2:1 molar ratio of $AlCl_3 \cdot 6H_2O$ and Al. Long gel fibers can be obtained, with 23 cm in length, by adding 1 wt. % PVP as a spinning additive. The main phase of the fibers was amorphous after sintering at 800°C. The main phase of fibers after sintering at 1000°C for 1 h was YAG, and the fibers had a uniform diameter and smooth surface.

Acknowledgments

This work was supported by the Education Department Foundation of Shaanxi in China (No. 12JK0437).

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