

# KINETICS OF GRAIN-GROWTH OF YTTRIUM ALUMINUM GARNET FIBERS PREPARED BY SOL-GEL METHOD

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*The yttrium aluminum garnet (YAG) long fibers were prepared by the sol-gel method using aluminum chloride, aluminum powder, yttrium oxide and acetic acid as raw materials. The grain growth law is given by  $D^n - D_0^n = Kt$  ( $D_0$  = initial grain size,  $D$  = average grain size at time  $t$ ,  $n$  = grain growth exponent and  $K$  = reaction constant). The grain growth exponent and activation energy of YAG fibers are  $\approx 3$  and 200 kJ/mol, respectively. The grain-growth behaviors of YAG were influenced by experimental conditions such as raw materials, initial particle size, initial particle distribution, etc.*

## INTRODUCTION

Yttrium aluminum garnet ( $\text{Al}_5\text{Y}_3\text{O}_{12}$  or YAG) possesses a cubic structure and constitutes a complex oxide of  $\text{Y}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . YAG, with low creep rate, high elastic modulus, high tensile strength, thermal shock resistance, excellent thermal stability, oxidation and reduction atmosphere resistance at high temperatures, is widely used as high temperature structural materials [1]. YAG fiber is a suitable candidate material which is used as reinforcement in the ceramic matrix, particularly in high temperature applications over 1400°C [2].

Of all the ceramic materials currently investigated, single crystal YAG also demonstrates the best all-round resistance to creep, exhibiting a creep resistance 10 times higher than single crystal alumina [2]. In polycrystalline YAG lattice and boundary diffusion will reduce the creep resistance of the material, but nevertheless, at 1400°C polycrystalline YAG with a grain size of 3  $\mu\text{m}$  is three times better than polycrystalline alumina of the same grain size [2]. Although the exact mechanism of creep in single crystal YAG is still uncertain, it is suggested that it is largely a diffusion-controlled process, as the large size of the cubic unit cell and large lattice parameters of the garnet dramatically reduce the number of dislocations, especially dislocations climb which are a key creep mechanism [3].

As is known, even small grain coarsening has a strong negative influence on the mechanical properties, especially in case of ceramic fibers [4]. Hou et al. [5] prepared YAG ceramic with citric acid, glycine or a mixture of citric acid-glycine as chelating agents, respectively. The grain size increased with different chelating agents from citric acid to glycine and citric acid-glycine. Kochawattana et al [6] prepared YAG and  $\text{SiO}_2$  doped YAG ceramic using  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , tetraethoxysilane as raw materials. The pure YAG samples fit an  $n = 2$  (grain growth exponent) dependence and the  $\text{SiO}_2$  doped samples fit an  $n = 3$  dependence. They considered a grain growth exponent of 2 indicates that solid state mass transport is the dominant mechanism for coarsening, while  $n = 3$  indicate that liquid phase mass transport occurs in the sample (for the case of boundary controlled migration). The grain-growth of YAG was generally strongly influenced by experimental conditions such as raw materials, initial particle size, initial particle distribution, etc. Although YAG fibers is one of the most widely studied ceramics, no comprehensive quantitative research work has been reported on its grain-growth behaviors.

The grain growth exponent of mullite fibers was remarkably low ( $n=1/12$ ) by sintering between 1500 and 1600°C, and it was  $\approx 1/3$  by sintering above 1600°C [4]. YAG demonstrates perfect high temperature properties.

The properties of fibers will be affected by grain growth. In order to compare the mullite with YAG, the sintering temperature 1500°C was selected.

In the present study, YAG fibers were prepared by the sol-gel method. The YAG grain growth behaviors were analyzed using the grain-size data.

## 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 (PVP, chemical grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China).

The preparation of YAG fibers has been fully discussed in the reference [7]. 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, a 1 wt. % polyvinylpyrrolidone was added in the solution. Then, the precursor solution was concentrated to obtain spinning sol in water bath (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 different time and temperature with heating rate of 2°C/min, respectively.

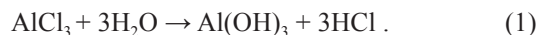
### Characterization techniques

For the gel fibers, thermal behaviors was measured by TG/DSC instruments (SDT Q600, TA Instrument, American) at a heating rate of 15°C/min in flowing air. X-ray diffraction analysis was carried out on an X-ray diffractometer (X'Pert PRO X-ray diffraction, PANalytical, Holland) using CuK $\alpha$  radiation with a step of 0.1 °/s. The morphologies of fibers were characterized by scanning electron microscopy (JSM-6700F, JEOL, Japan) and average grain size obtained by images analysis. Grain sizes of the fibers were obtained by the linear intercept method on the surface of fibers and along the axis of fibers or on the cross-section of fibers (at least 50 counts) where the average intercept length was multiplied by 1.5 to calculate the average grain size [5, 8].

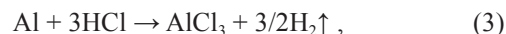
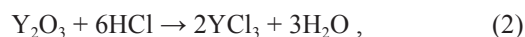
## RESULTS AND DISCUSSION

When aluminum chloride hexahydrate was added in water, it was firstly hydrolyzed with water and formed

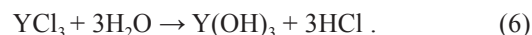
aluminum hydroxide in acid solution, according to the following chemical reaction:



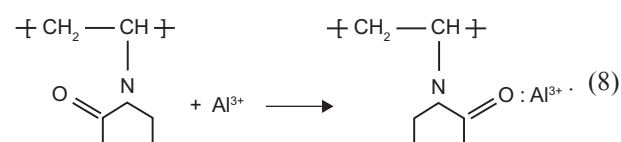
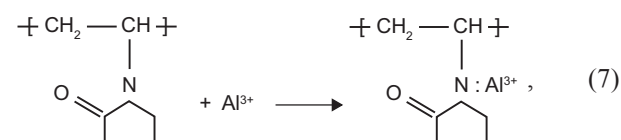
Hydrolysis reaction occurred because water molecules coordinated to metal ions were more acidic than in the noncoordinated state due to charge transfer from the oxygen to the metal atom [3]. Yttria and aluminum powder were dissolved during the stirring and heating in the mixed solution of aluminum chloride and acetic acid, and their main chemical reactions can be simplified in the following set of equations, though the actual reactions are more complex:



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



The viscous sol was obtained by condensation 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]. Long fibers can be obtained by adding a 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 (7) and (8), Al<sup>3+</sup> as an example [10].



The TG/DSC curves of the precursor gel fibers are shown in Figure 1 with a heating rate of 15°C/min. The DSC curve of the gel fibers exhibited four endothermic peaks at about 132, 252, 293 and 369°C, and two exothermic peaks at about 619°C and 943°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 [1]. But the exothermic peak at about 943°C is weak, because it coincides with the grain growth. The TG curve of the

gel fibers showed the weight loss around 65 wt. % at 900°C, while almost no further weight loss appeared with increasing the temperatures.

The X-ray diffraction patterns of YAG gel fibers sintered at 1000°C and 1500°C for 2 h are shown in Figure 2. YAG phase is observed when fibers are sintered at 1000°C and 1500°C in the YAG fiber samples, respectively. The YAG crystallizes directly from the amorphous precursor without the formation of any intermediate phase [1].

The grain-growth behaviors of YAG by sintering at 1200, 1400 and 1500°C for 6 h are shown in Figure 3. The grain size increased significantly while the sintering temperature increased.

The grain-growth behaviors of YAG by sintering at 1500°C for 2, 4, 6 and 8 h are shown in Figure 4. The grain size increased significantly when the fibers were sintered from 2 to 4 h, but the grain size increased slowly when the fibers were sintered from 4 to 8 h. With the heat treatment processing, the grain size increased because the surface area and surface energy of grain decreased. As a result, lattice stability of grain increases, structural defects and diffusion and growth driving force of grain reduce and the grain size growth rate became slowly.

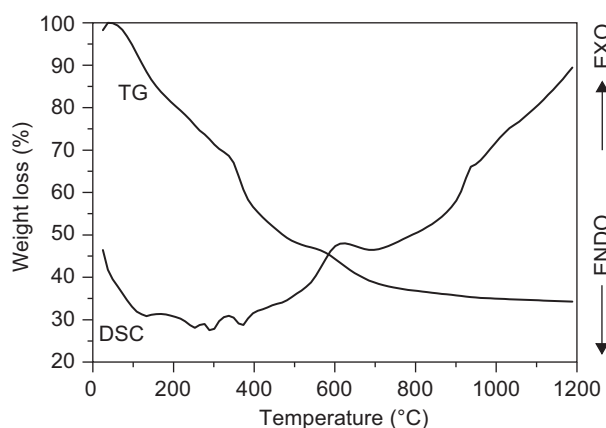


Figure 1. TG and DSC curves of YAG precursor gel fibers.

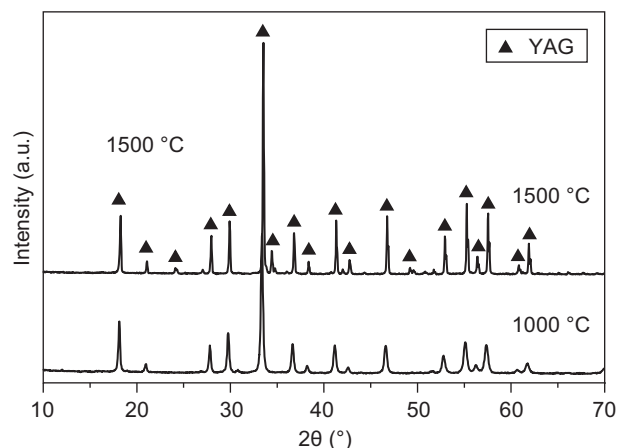


Figure 2. X-ray diffraction patterns of YAG gel fibers sintered at 1000°C and 1500°C for 2 h.

SEM micrographs of YAG gel fibers sintered at 1500°C for 2 and 8 h are shown in Figure 5. The coarsening of the fibers microstructure with increasing sintering time is observed. The grain size of the fibers sintered for 2 h varies from 0.2 to 1.2 μm, whereas it sintered for 8 h varies from 0.3 to 2 μm.

It is well known that the micro-structural evolution of a material can usually be described using grain size and size distribution. The grain growth depends on sintering temperatures and time, which can be analyzed by well-known grain growth kinetics equation [11],

$$D^n - D_0^n = Kt \quad (9)$$

and

$$K = K_0 \exp(-Q/RT) \quad (10)$$

where  $D_0$  = initial grain size,  $D$  = average grain size at time  $t$ ,  $n$  = grain growth exponent,  $K$  = reaction constant,  $K_0$  = a pre-exponential constant,  $Q$  = the activation energy of grain growth,  $R$  = gas constant and  $T$  = the temperature. When  $D_0$  is significantly smaller than  $D$ ,  $D_0$  can be neglected to  $D^n$ . Equation 9 can be simplified as follows:

$$D^n = K_0 \exp(-Q/RT)t \quad (11)$$

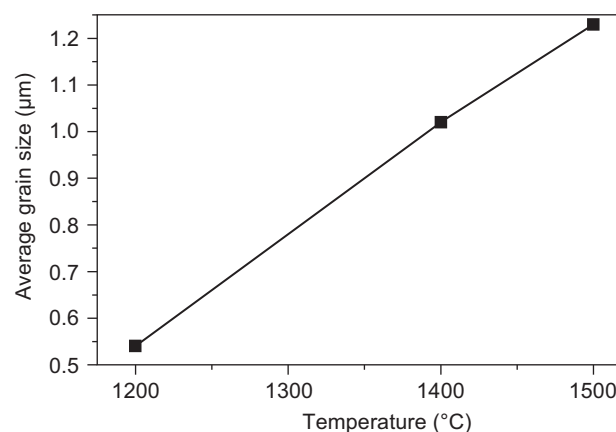


Figure 3. Average grain size in YAG fibers as a function of holding temperature at sintering time of 6 h.

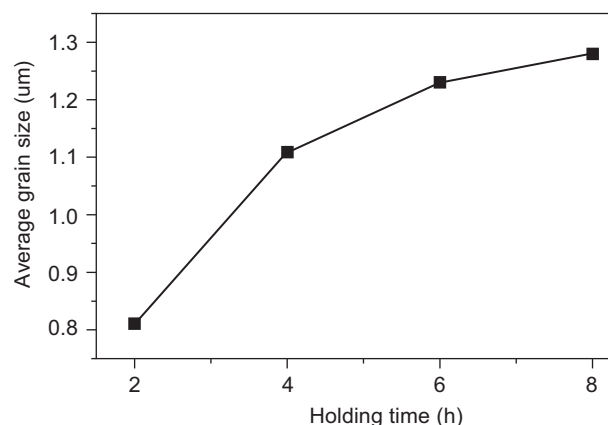
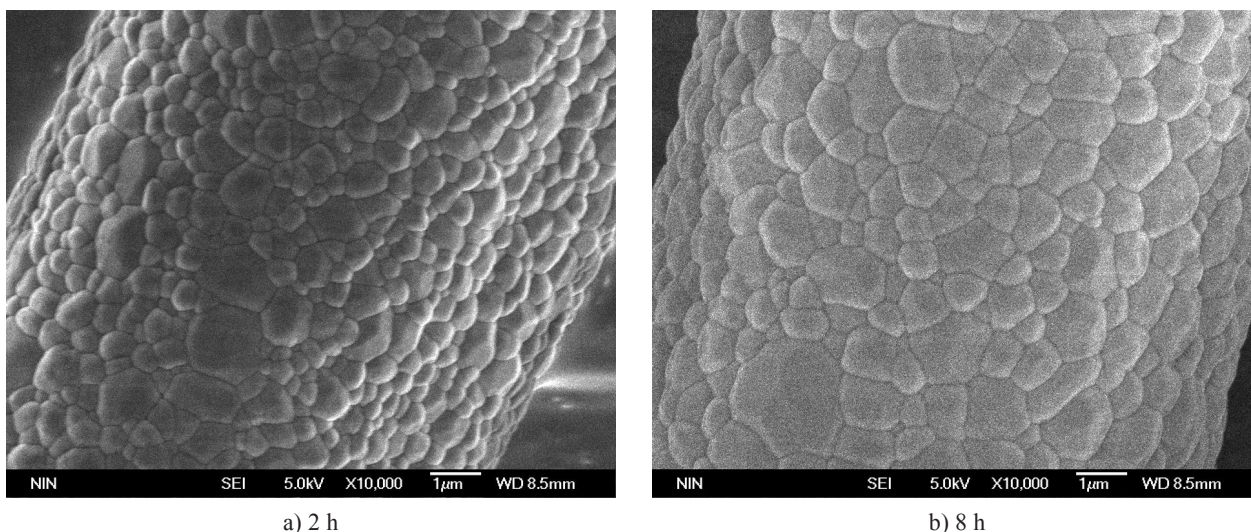


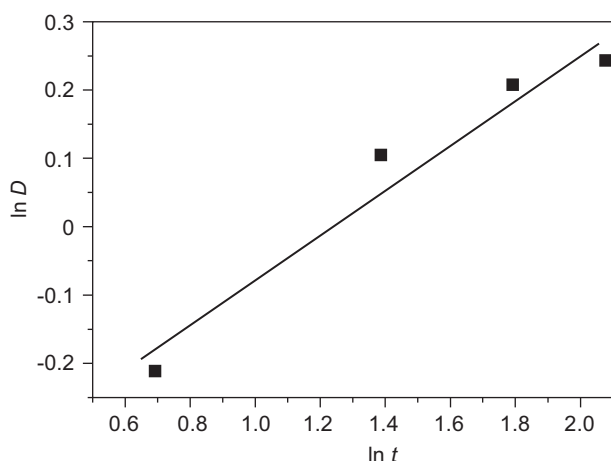
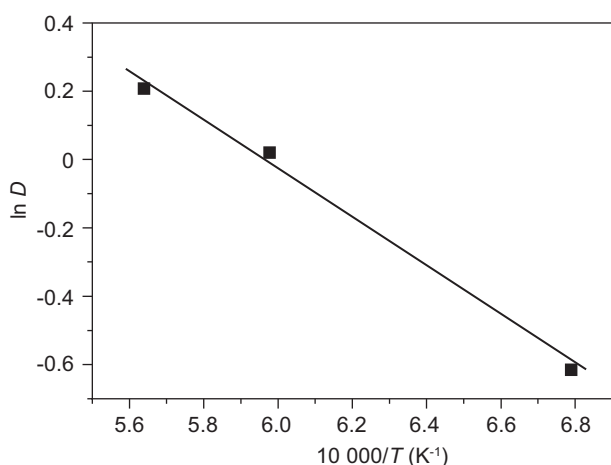
Figure 4. Average grain size in YAG fibers as a function of holding time at sintering temperatures of 1500°C.



a) 2 h

b) 8 h

Figure 5. SEM microstructures of precursor gel fibers heated at 1500°C for a) 2 h and b) 8 h.

Figure 6. The plots of  $\ln(D)$  vs.  $\ln(t)$  for YAG fibers.Figure 7. The plots of  $\ln(D)$  vs.  $1/T$  for YAG fibers.

The natural logarithmic form of Equation (11):

$$n \ln D = \ln t - (Q/RT) + \ln K_0 \quad (12)$$

In a proper temperature range, the activation energy,  $Q$ , is a constant. So the exponent,  $n$ , can be determined from the slope of the plot of  $\ln D$  versus  $\ln t$ . Subsequently the activation energy,  $Q$ , can be obtained from the slope of an Arrhenius plot of  $\ln(D)$  versus  $1/T$ , based on Equation 9.

According to Equation 9, by plotting of  $\ln D$  versus  $\ln t$ , the grain growth exponent can be determined from the slope. As can be shown in Figure 6, the grain growth exponent of YAG fibers is  $\approx 3$ .

According to Equation 12, by plotting of the plot of  $\ln(D)$  versus  $1/T$ , the grain growth exponent can be determined from the slope. As can be shown in Figure 7, the activation energy is  $\approx 200$  kJ/mol.

Stevenson et al. [8] considered that in boundary-controlled systems, grain growth exponents equal to 3 are explained by solute drag mechanisms in solid-state systems. Boulesteix et al. [12] prepared Nd:YAG substrates using  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  powder as raw materials. They considered the grain growth should be limited by the reaction at interfaces at a temperature lower than 1500°C, with an activation energy of about 880 kJ/mol. This result is different with other authors' because of rare earth ion impeding grain growth. On the other hand, the activation energy will be influenced by raw materials.

## CONCLUSION

YAG fibers were prepared by the sol-gel method. The phase of YAG is YAG after sintering at 1000 and 1500°C for 2 h. The average grain size of the YAG fibers is about 1.28  $\mu\text{m}$  by sintering at 1500°C for 8 h. The grain growth exponent and activation energy of YAG are  $\approx 3$  and 200 kJ/mol, respectively.

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#### REFERENCES

1. Li C.H., Zhang Y.J., Gong H.Y., Zhang J.D., Nie L.F.: Materials Chemistry and Physics 113, 31 (2009).
2. Pullar R.C., Taylor M.D., Bhattacharya A.K.: Journal of the European Ceramic Society 26, 1577 (2006).
3. Pullar R. C., Taylor M. D., Bhattacharya A. K.: Journal of the European Ceramic Society 19, 1747 (1999).
4. Schmucker M., Schneider H., Mauer T., Clauß B.: Journal of the European Ceramic Society 25, 3249 (2005).
5. Hou J.G., Kumar R.V., Qu Y.F., Krsmanovic D.: Materials Research Bulletin 44, 1786 (2009).
6. Kochawattana S., Stevenson A., Lee S.-H., Ramirez M., Gopalan V., Dumm J., Castillo V. K., Quarles G. J., Messing G. L.: Journal of the European Ceramic Society 28, 1527 (2008).
7. Tan H., Ma X., Lu J., Li K.: Ceramics–Silikáty 56, 187 (2012).
8. Stevenson Adam J., Li Xin, Martinez Miguel A. Anderson Julie M., Suchy Daniel L., Kupp Elizabeth R., Dickey Elizabeth C., Mueller Karl T., Messing Gary L.: Journal of the American Ceramic Society 94, 1380 (2011).
9. Tan H., Ma X., Fu M.: Bulletin of Materials Science 36, 153 (2013).
10. Liu C., Sun W., Zhuo Y., et al.: Journal of Alloys and Compounds 581, 115 (2013).
11. Zhang T.S., Ma J., Leng Y.J., He Z.M.: Journal of Crystal Growth 274, 603 (2005).
12. Boulesteix R., Maître A., Baumarda J.-F., Rabinovitch Y., SalléC., Weber S., Kilo M.: Journal of the European Ceramic Society 29, 2517 (2009).