CONTINUOUS ALUMINA GEL FIBERS BY SOL-GEL METHOD USING GLYCOLIC ACID, ALUMINUM NITRATE AND POLYVINYLPYRROLIDONE

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Continuous alumina fibers were prepared by sol-gel method. The spinning sol was obtained by mixing aluminum nitrate, glycolic acid and polyvinylpyrrolidone with a weight ratio of 10:3:1.5. Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used to characterize the properties of the gel and ceramic fibers. The fibers with a uniform diameter and smooth surface were obtained by sintering at 1473K, and its main phase was indentified as α-Al_2O_3.

INTRODUCTION

Alumina is one of the most important materials because of its high strength and modulus, resistance to attack from molten metals and non-oxide materials, chemical inertness in both oxidizing and reducing atmospheres up to 1273K, and good electrical insulation [1, 2]. It also has high melting point (T_m > 2313 K) and low thermal conductivity (10^{-18} W/m·K) [3]. An important potential application of alumina is as fibers reinforcement of metals, ceramics and resins matrix composites, which composites capable of maintaining excellent mechanical properties continue to attract attention as candidate materials for aerospace applications [4-6]. Such as, alumina fibers reinforced aluminium or magnesium matrix composites have shown promising modulus, fatigue, high temperature strength and wear resistance, and reduced the creep rate of the alloy at high temperature [7-10].

Main processes for the manufacture of ceramic fibers can be classified as melt-spinning processes and sol-gel spinning processes [11]. Usually, the melt-spinning method was adopted for the synthesis of ceramic fibers with low melting point. Thus, this method was not suitable for the preparation of the alumina fibers. The preparation of short alumina fibers has been widely reported [12-13], such as Chandradass et al. [5] prepared alumina short fibers by the sol-gel process using aluminum-tri-isopropoxide as starting materials, and Shojaie-Bahaabad et al [13] synthesized composite fibers (YAG/Al_2O_3) from an aqueous solution of aluminum powder, aluminum chloride hexahydrate and yttrium oxide by the sol-gel method. But, the preparation processes of continuous fibers have not observed in the relevant reports.

In the present work, continuous alumina fibers were prepared by the sol-gel method using aluminum nitrate (AN) and glycolic acid (GA) as raw materials, polyvinylpyrrolidone (PVP) as a spinning additive. The process, phase crystallization and surface morphology were investigated in detail..

EXPERIMENTAL

Preparation of samples

Starting materials used were AN (Chemically grade, Xi'an reagent factory, Xi'an, China), GA (Chemically grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and PVP (Chemically grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China).

The alumina fibers were prepared in the processing steps as shown in Figure 1. The alumina sol was prepared by mixing H_2O, aluminum nitrate and glycolic acid, followed by being heated in water bath (353 K). The proper amount of water and spinning additive (PVP) were added in the alumina sol, and then the precursor sol was concentrated to obtain spinning sol in water bath

(333 K). The gel fibers were prepared by pulling a thin glass rod slowly from the sol after immersing, and dried at 333 K for 24 h in an oven. The gel fibers were then sintered at 1073, 1273 and 1473K for 1 h, respectively, with a heating rate of 1 K/min.

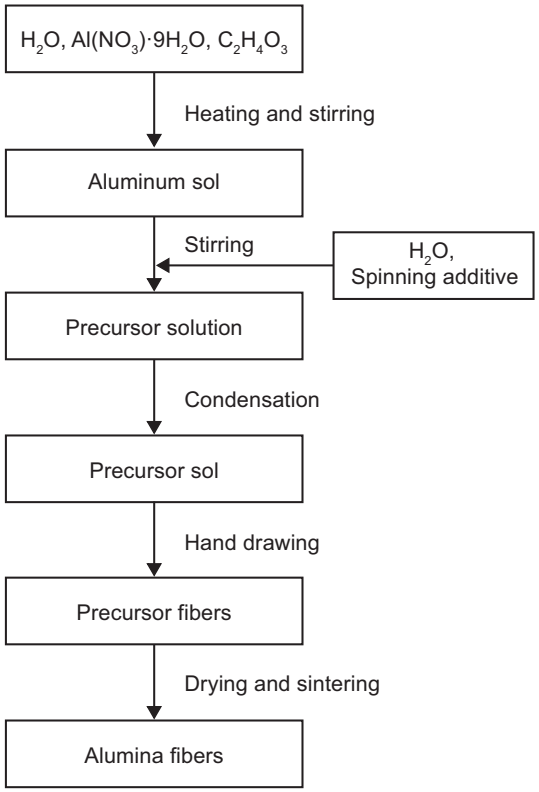


Figure 1. Schematic view of the production route for alumina fibers.

Characterization techniques

Fourier transform infrared (FTIR) spectra was recorded on an infrared spectrometer (6700, Nicolet Magna, American) with the samples as KBr pellets. X-ray diffraction analysis was carried out on an X-ray diffractometer (DX-2500, Dandong Fangyuan, 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

Alumina sol was prepared by the synthesis and hydrolysis reactions between aluminum nitrate and glycolic acid in aqueous solution during the stirring and heating. The main chemical reactions may be simplified as the following equation (1), (2) and (3), although the actual reactions were complex:

Synthesis reactions:

$$3C_2H_4O_3 + Al(NO_3)_3 \rightarrow Al(C_2H_3O_3)_3 + 3HNO_3 \quad (1)$$

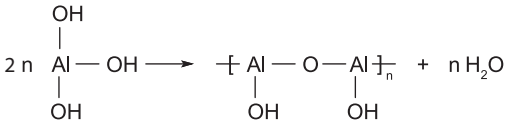
$$HNO_3 \rightarrow 1/2H_2O + 1/4O_2\uparrow + NO_2\uparrow \quad (2)$$

Hydrolysis reaction:

$$Al(C_2H_3O_3)_3 + 3H_2O \rightarrow Al(OH)_3 + 3\ C_2H_4O_3 \quad (3)$$

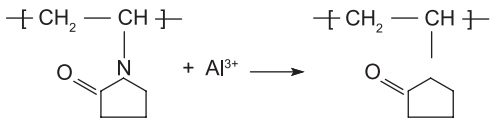
The spinnability of different precursor sols, which was prepared using the different amounts of glycolic acid or polyvinylpyrrolidone, is shown in Table 1. The spinnability of sol was determined by the content of glycolic acid or polyvinylpyrrolidone. For example, when the glycolic acid amounted to 6g in the sol (1), the sol was spinnable because most of aluminum nitrate was involved in the reaction to generate aluminum glycolate. The hydrolysis and condensation polycondensation could occur when the aluminum glycolate solution was condensed, and obtained a spinnable sol with the linear molecular chains after a concentrating process in water bath at 333K. The main condensation polycondensation reaction can be simplified as the following equation (4) [13]:

Condensation polymerization:

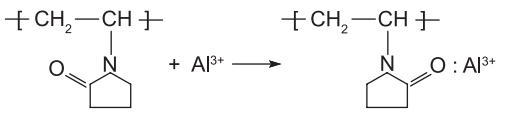


(4)

Continuous alumina fibers can be obtained, only by adding the spinning additive (e.g. PVP), because Al ions or particles would coordinate with N or O ions in PVP. The reactions can be written as (5) and (6) [14].



(5)



(6)

Table 1. Effect of the GA or PVP on spinnability of the precursor sols.

NO.	AN (g)	GA (g)	PVP (g)	Spinnability (cm)
1	10	3	0	0
2	10	6	0	20
3	10	3	0.5	10
4	10	3	1.0	70
5	10	3	1.5	>80

AN - aluminum nitrate, GA - glycolic acid, PVP - polyvinylpyrrolidone. A weight ratio of AN and distilled water was 1:5. The spinnability of the alumina sol was estimated from the length of the gel fibers drawn from the spinnable condensed sols.

Otherwise, if too much organic acids remained, the densification of alumina ceramic fibers would be delayed during calcinations [15]. Therefore, PVP was added to decrease the content of glycolic acid. When the content of PVP increased, the spinnability also increased in the sol (3) to (5). The sol (5) was suitable for fibers preparation because continuous fibers could be obtained.

The FTIR spectra of precursor gel fibers are shown in Figure 2. As can be seen, the bands at 3430cm^{-1} and 1640 cm^{-1} are assigned to the O–H stretching and bending modes of adhesive and constitution water as well as glycolic acid, respectively. The band at 2570cm^{-1} is assigned to the O-N stretching mode of nitric acid. The bands at 1700cm^{-1} and 480cm^{-1} are assigned to the C=O stretching and bending modes, respectively. The band at 920cm^{-1} is assigned to the C-C stretching mode. The bands at 1380cm^{-1} and 820cm^{-1} may be assigned to the C-O stretching and bending modes, respectively. As can be seen, a little of nitric acid was present in the samples. As shown in Figure 2, the band observed at 1420 cm^{-1} corresponds to Al–OH bonding mode [12]. The stretching modes of Al–O–Al linkages are observed at 590 cm^{-1} and 820 cm^{-1} [16]. When the precursor solution was condensed, hydrolysis and condensation polycondensation could occur. So, the stretching modes of Al–O–Al linkages are observed.

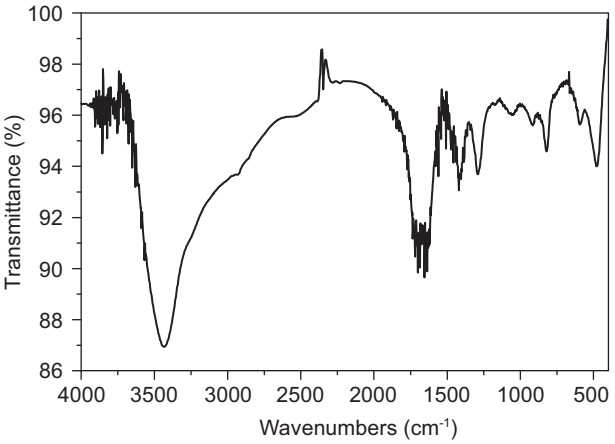


Figure 2. FT-IR spectra of the precursor gel fibers.

The X-ray diffraction patterns of gel fibers sintered at 1073, 1273, and 1473K are shown in Figure 3. Only amorphous and γ-Al_2O_3 phase were present when fibers were sintered at 1073K. α-Al_2O_3 phase was observed in the samples sintered at 1273K, while main α-Al_2O_3 phase at 1473K.

It has been shown that the phase development during crystallisation of amorphous alumina takes place through the following route [2].

Amorphous → Etae (η) → Gammae (γ) →Deltae (δ) → → Thetae (θ) → Alphae (α)

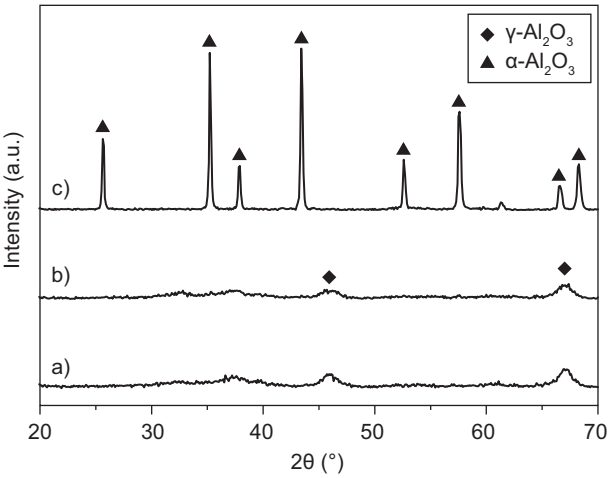


Figure 3. XRD patterns of the alumina precursor gel fibers heated at a)1073, b)1273, and c) 1473 K for 1 h.

Upon heating, the θ-Al_2O_3 undergoes a reconstructive transformation by nucleation and growth, where the oxygen atoms rearrange into a hexagonal close packed structure to form the thermodynamically stable α-Al_2O_3 [17]. During the reconstructive transformation from θ- to α-alumina, there is a specific volume reduction (28.6-25.6 cm^3/mol Al_2O_3), due to the difference of theoretical density (3.6-3.986 g/cm^3Al_2O_3) [10]. A low intrinsic nucleation density results in large spacing between nucleation events and the formation of micrometer scale, single crystal α-Al_2O_3 grains with dendritic protrusions surrounded by continuous pore channels [18]. The resulting vermicular microstructure requires the sintering temperature higher than 1873 K to obtain high densities[19]. The sintering temperature can be decreased by adding the sintering aids with low melting point (e.g. SiO_2, B_2O_3, TiO_2).

SEM micrograph of alumina fibers sintered at 1473K is shown in Figure 4. The fibers were obtained, with smooth surface and dense structure. The diameter of fibers is uniform, and about 4 ~8μm, 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

Continuous fibers of alumina were prepared by sol-gel method when the spinning sol was prepared by mixing aluminum nitrate, glycolic acid and polyvinylpyrrolidone with a weight ratio of 10:3:1.5. The main phases were amorphous and γ-Al_2O_3 by sintering at 1073 K. The main phase of fibers was α-Al_2O_3 by sintering at 1473K, with a uniform diameter and smooth surface.

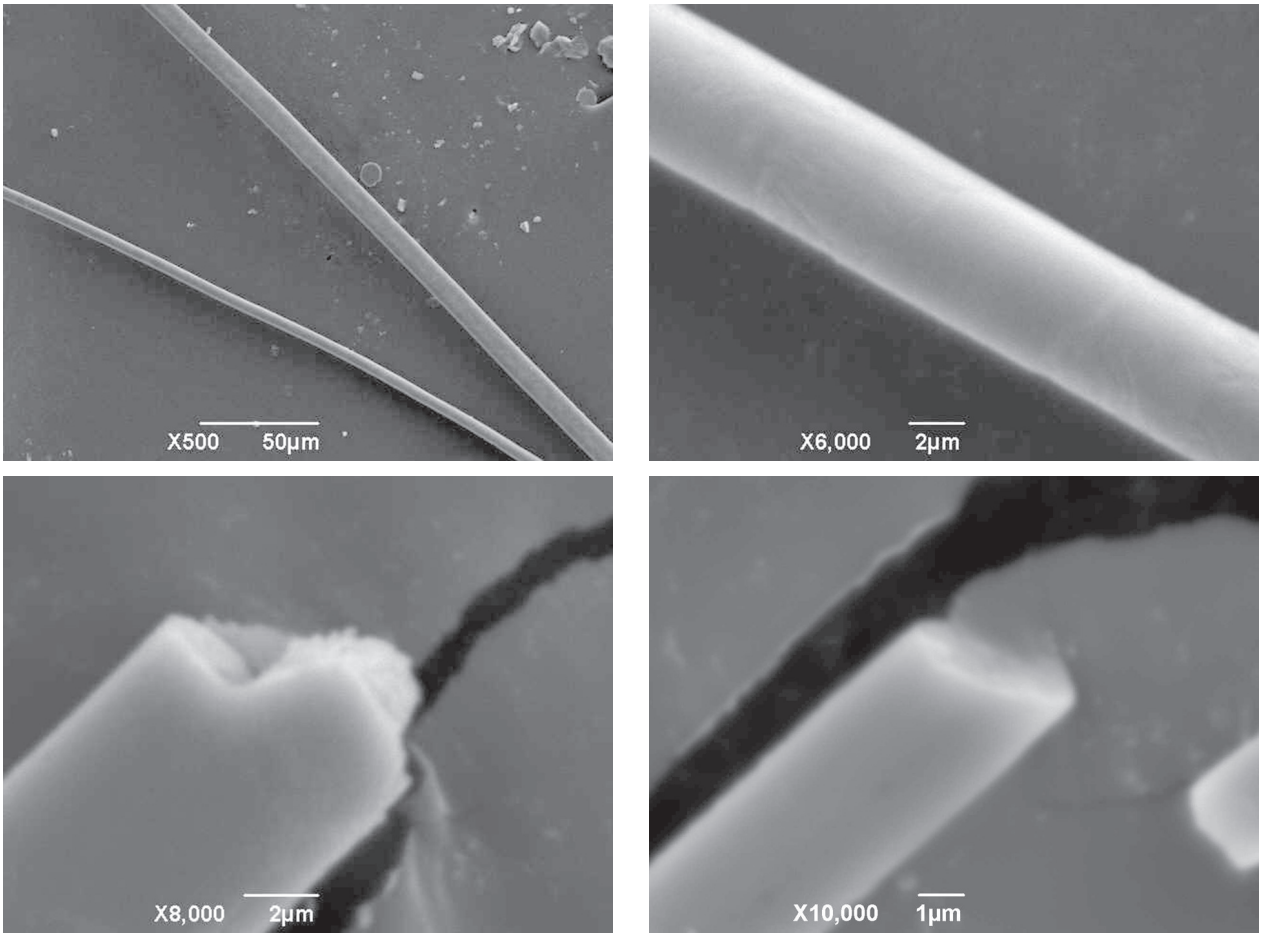


Figure 4. SEM microstructures of alumina precursor gel fibers heated at 1473 K for 1 h

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References

1. Zhu L.H., Huang Q.W., Liu W.: Ceram. Inter. 34, 1729 (2008).
2. Venkatesh R., Ramanan S.R.: Mater. Lett. *55*, 189 (2002).
3. Sedaghat A., Taheri-Nassaj E., Naghizadeh R.: J. Non-Cryst. Solids *352*, 2818 (2006).
4. Rossoll A., Otto C., Moser B., Weber L., Wanner A., Mortense A.: Scr. Mater. *59*, 842 (2008).
5. Licciulli A., Contaldi V., l Padmanabhan S. K., Balakrishnan A., Siligardi C., Dis D.: J. Eur. Ceram. Soc. *31*, 385 (2011).
6. Johnson A.C., Zhao F.M., Hayes S.A., Jones F.R.: *Comp. Sci. Technol.*, 66, 2023 (2006).
7. Güden M., Akil O., Tasdemirci A., Çiftçioglu M., Hal I.W.: *Mater. Sci. Eng. A*, *425*, 145 (2006).
8. Requena G., Degische H.P.: Mater. Sci. Eng.: *A*, *420*, 265 (2006).
9. Ochi Y., . Masaki, Matsumura M.T., Wadasak M.: *Mater. Sci. Eng. A 468-470*, 230 (2007).
10. Riehemann W., Trojanová Z., Mielczarek A.: *Pro. Eng.* 2, 2151 (2010).
11. Zhang Y.B., Ding Y.P., Gao J.Q., Yang J.F.: *J. Eur. Ceram. Soc.* 29, 1101 (2009).
12. Chandradass J., Balasubramanian M.: J. Mater. Proc. Technol. *173*, 275 (2006).
13. Shojaie-Bahaabad M., Taheri-Nassaj E., Naghizadeh R.: Ceram. Inter. *34*, 1893 (2008).
14. Wang H.S., Qiao X.L., Chen J.G., Wang X.J., Ding S.Y.: Mater. Chem. Phys. *94*, 449 (2005).
15. Leivo J., Linden M., Ritola M., Vippola M., Levanen E., Mantyla T.A.: Mater. Chem. Phys., *115*, 56 (2009).
16. Padmaj P., Anilkumar G.M., Mukundan P., Aruldhas G., Warrier K.G.K,: Int. J. Inorg. Mater. *3*, 693 (2001).
17. Nordahl C.S., Messing G.L.: Therm. Acta. *318*, 187 (1998).
18. Nordahl C.S., Messing G.L.: J. Eur. Ceram. Soc. *22*, 415 (2002).
19. Li J.G., Sun X.D.: Acta Mater. *48*, 3103 (2000).