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Preparation of long alumina fibers by sol-gel method using tartaric acid

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Abstract: Long alumina fibers were prepared by sol-gel method. The spinning sol was obtained by mixing aluminum nitrate, tartaric acid, and polyvinylpyrrolidone with a mass ratio of 10:3:1.5. Thermogravimetry-differential scanning calorimetry (TG-DSC), Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used to characterize the properties of the gel and ceramic fibers. A little of α-Al_2O_3 phase is observed in the alumina precursor gel fibers sintered at 1273 K. The fibers with a uniform diameter can be obtained when sintered at 1473 K, and its main phase is also indentified as α-Al_2O_3.

Keywords: alumina; fibers; sol-gel process; polyvinylpyrrolidone

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1. 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 1273 K, and good electrical insulation [1-2]. It also has high melting point (T_m>2313 K) and low thermal conductivity (10^{-18} $W \cdot m^{-1} \cdot K^{-1}$) [3]. An important potential application of alumina is as fiber reinforcement of metals, ceramics, and resins.

Main processes for the manufacture of ceramic fibers can be classified as melt-spinning process and sol-gel spinning process [4]. Usually, the melt-spinning method is adopted for the synthesis of ceramic fibers with low melting point. Thus, this method is not suitable for the preparation of alumina fibers.

The preparation of short alumina fibers has been widely reported [5-8]. Chandradass *et al*. [5] prepared alumina short fibers by sol-gel process using aluminum-tri-isopropoxide as starting materials, and Shojaie-Bahaabad *et al*. [6] 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 long fibers have not been observed in the relevant reports.

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

2. Experimental procedure

2.1. Samples preparation

Starting materials used were AN (chemical grade, Xi'an Reagent Factory, Xi'an, China), TA (chemical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and PVP (chemical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China).

Alumina fibers are prepared in the processing steps as shown in Fig. 1. The alumina sol was prepared by mixing H_2O, AN, and TA, followed by being heated in a water bath at 353 K. The proper amount of water and spinning additive (PVP) were added in the alumina sol, and then the precursor

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sol was concentrated to obtain a spinning sol in the water bath (333 K). 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 1473 K for 1 h, respectively, with a heating rate of 1 K/min.

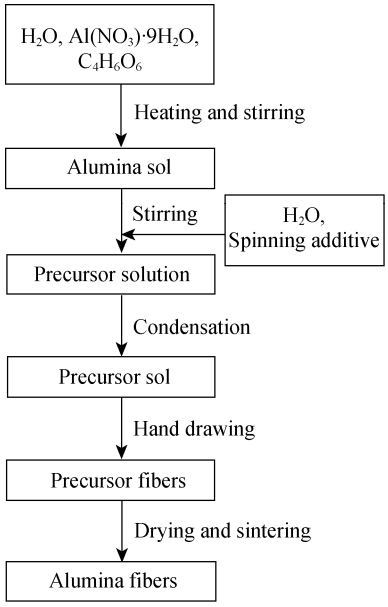


Fig. 1. Schematic view of the production route for alumina fibers.

2.2. Characterization

The thermal behaviors of the gel fibers were measured by TG/DSC instruments (SDT Q600, TA Instrument, American) with a heating rate of 10 K/min in the flowing N_2, and Fourier transform infrared (FT-IR) spectra were recorded on an infrared spectrometer (6700, Nicolet Magna, American) with the samples as KBr pellets. X-ray diffraction (XRD) analysis was carried out on an X-ray diffractometer (D/max2400, Rigaku, Japan) using Cu K_α radiation with a step of 0.05°/s. The morphologies of fibers were characterized by scanning electron microscopy (SEM, S-2700, Hitachi, Japan). All tests were done at room temperature.

3. Results and discussion

Alumina sol was prepared by the synthesis and hydrolysis reactions between aluminum nitrate and tartaric acid in aqueous solution during the stirring and heating. The main chemical reactions may be simplified as the following equations, although the actual reactions were complex [7-8].

Synthesis reactions:

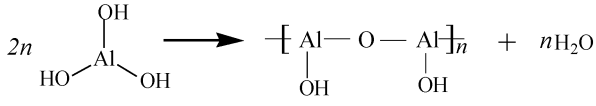
$$3C_4H_6O_6+2Al(NO_3)_3 \rightarrow Al_2(C_4H_4O_6)_3+6HNO_3 \quad (1)$$

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

Hydrolysis reaction:

$$Al_2(C_4H_4O_6)_3+6H_2O \rightarrow 2Al(OH)_3+3C_4H_6O_6 \quad (3)$$

The spinnability of different precursor sols estimated from the length of the gel fibers drawn from the spinnable condensed sols, is shown in Table 1 using different amounts of tartaric acid or polyvinylpyrrolidone. The mass ratio of AN and distilled water was 1:5. The spinnability of the sol is determined by the content of tartaric acid or polyvinylpyrrolidone. For example, when the tartaric acid amounts to 6 g in sol 2, the sol is spinnable because most of aluminum nitrate is involved in the reaction to generate aluminum tartrate. The hydrolysis and condensation polycondensation can occur when the aluminum tartrate solution is condensed, and a spinnable sol with the linear molecular chains is obtained after a concentrating process in a water bath at 333 K. The main condensation polycondensation reaction can be simplified as the following [6].

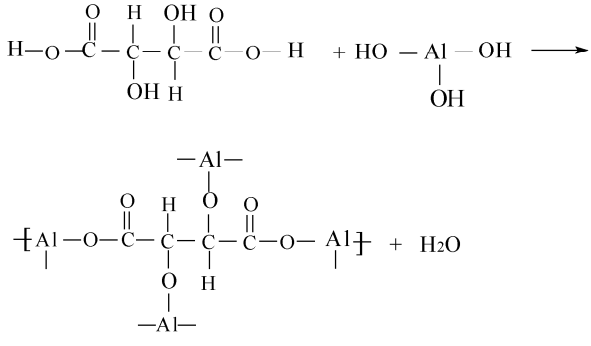


(4)

Table 1. Effect of TA or PVP on the spinnability of precursor sols with constant AN of 10 g

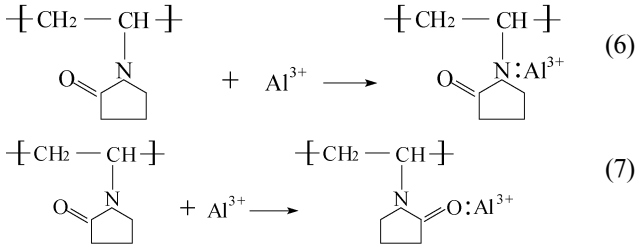
Sol number	TA / g	PVP / g	Spinnability / cm
1	3	0	0
2	6	0	40
3	3	0.5	10
4	3	1.0	60
5	3	1.5	>90

Moreover, the hydroxyl groups and carboxyl groups of tartaric acid can react with the alumina sol and form an organic-inorganic hybrid structure [4].



(5)

Long alumina fibers can be obtained, only by adding the spinning additive (*e.g.* PVP), because Al ions or particles will coordinate with N or O ions in PVP. The reactions can be written as Eqs. (6)-(7) [9].



(6)

(7)

Otherwise, if too much organic acid remains, the densification of alumina ceramic fibers will be delayed during calcinations [10]. Therefore, PVP is added to decrease the content of tartaric acid. When the content of PVP increases, the spinnability also increases in sols 3-5. Sol 5 is suitable for fiber preparation because long fibers can be obtained.

The TG/DSC curves of the precursor gel fibers are shown in Fig. 2 with a heating rate of 10 K/min. The DSC curve of the gel fibers exhibits two endothermic peaks at about 363 and 629 K, and two exothermic peaks at about 701 and 1251 K. The endothermic peaks are assigned to evaporation of the adsorbed water and decomposition of hydroxides in the gel fibers, whereas the two exothermic peaks are assigned to the decomposition of organics and α-Al_2O_3 phase crystallization, respectively [11]. The TG curve of the gel fibers shows a weight loss around 76wt% at 1073 K, while no further weight loss is observed above 1073 K.

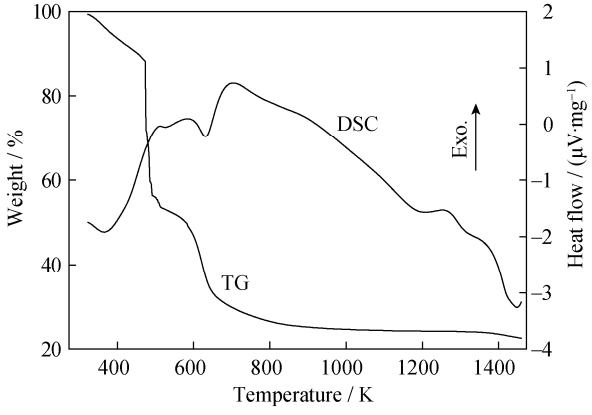


Fig. 2. TG and DSC curves of alumina precursor gel fibers.

The FT-IR spectrum of precursor gel fibers is shown in Fig. 3. As can be seen, the bands at 3440 and 1640 cm^{-1} are assigned to the O–H stretching and bending modes, respectively, of adhesive and constitution water as well as tartaric acid and polyvinylpyrrolidone. The band at 2550 cm^{-1} is assigned to the O–N stretching mode of nitric acid. The bands at 1700 and 476 cm^{-1} are assigned to the C=O stretching and bending modes, respectively. The band at 914cm^{-1} is assigned to the C–C stretching mode. The bands at 1380 and 820 cm^{-1} may be assigned to the C–O stretching and bending modes, respectively. As can be seen, a little of nitric acid is present in the samples.

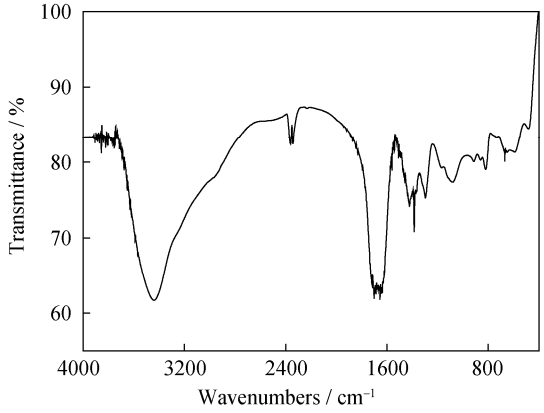


Fig. 3. FT-IR spectrum of the precursor gel fibers.

As shown in Fig. 3, the band observed at 1430 cm^{-1} corresponds to the Al–OH bonding mode [5]. The stretching modes of Al–O–Al linkages are observed at 600 and 820 cm^{-1} [12]. When the precursor solution is condensed, hydrolysis and condensation polycondensation can occur. So, the stretching modes of Al–O–Al linkages are observed.

The X-ray diffraction patterns of gel fibers sintered at 1073, 1273, and 1473 K are shown in Fig. 4. Only amorphous and γ-Al_2O_3 phase are present when fibers are sintered at 1073 K. α-Al_2O_3 phase is observed in the samples sintered at 1273 K, while main α-Al_2O_3 phase at 1473 K. From the DSC and XRD results, it can be concluded that α-Al_2O_3 phase crystallization of the fibers occurs at about 1251 K shown in the DSC curves in Fig. 2.

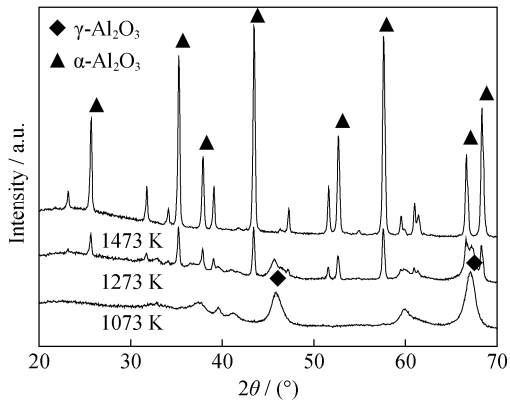


Fig. 4. XRD patterns of alumina precursor gel fibers heated at different temperatures for 1 h.

It has been shown that the phase development during crystallization of amorphous alumina takes place through the following route [2]: Amorphous→Eta(η)→Gamma (γ)→Delta(δ)→Theta(θ)→Alpha(α)

During 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 [13]. During the reconstructive transformation from θ-Al_2O_3 to α-Al_2O_3, 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^3 Al_2O_3) [13]. A low intrinsic nucleation density results in large spacing between nucleation events and the formation of micrometer-scale and single crystal α-Al_2O_3 grains with dendritic protrusions surrounded by continuous pore channels [14]. The resulting vermicular microstructure requires the sintering temperature higher than 1873 K to obtain high densities [15]. The sintering temperature can be decreased by adding the sintering aids with low melting point (*e.g.* SiO_2, B_2O_3, and TiO_2).

The SEM micrographs of alumina fibers sintered at 1473 K are shown in Fig. 5. The diameter of fibers is uniform and about 9-10 μm, which is influenced by the viscosity and surface tension of the spinning sol, speed of hand drawing, and so on. Further researches need to be performed to define well these correlations.

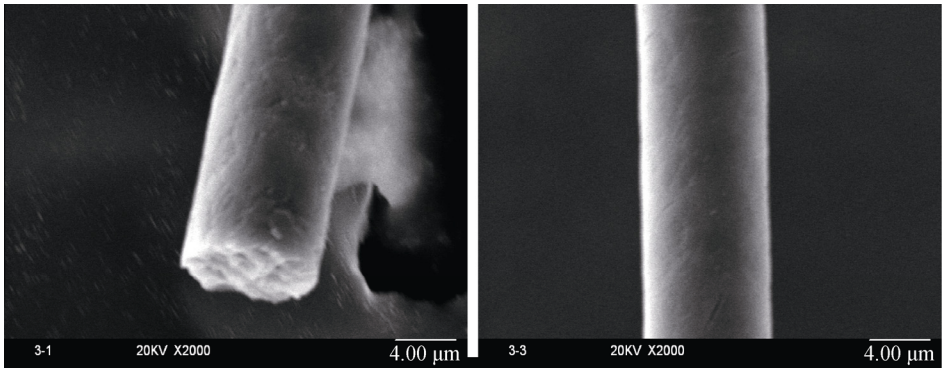


Fig. 5. SEM microstructures of alumina precursor gel fibers heated at 1473 K for 1 h: (a) cross-section; (b) surface of fibers.

4. Conclusion

Long fibers of alumina were prepared by sol-gel method when the spinning sol was prepared by mixing aluminum nitrate, tartaric acid, and polyvinylpyrrolidone with a mass ratio of 10:3:1.5. The main phases are amorphous and γ-Al_2O_3 in alumina precursor gel fibers sintered at 1073 K. The main phase of fibers is α-Al_2O_3 by sintering at 1473 K, with a uniform diameter of about 9-10 μm.

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