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# Materials Research Express



## PAPER

# Preparation of alumina precursor sols with a high solid content for alumina fibers

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**Keywords:** alumina, sol-gel process, fibers, dissolution

## Abstract

Precursor sol with a high solid content is significant for alumina fiber synthesis. In the present work, alumina precursor sols used for preparing alumina fibers were synthesized by dissolving aluminum powder (AP) into a mixture of formic acid, acetic acid and deionized water. The effects of preparation temperatures on solubility of AP, structure of the synthesized sols and gels were investigated. The reaction mechanism of hydrolysis and polymerization was also studied. Based on the reaction mechanism, alumina precursor sol with a high solid content was acquired through the adjustment of temperature. The results revealed that all the sols synthesized at the temperature from 85 °C to 115 °C consisted of polymers, linear oligomers and monomeric species. Colloidal particles presented spherical shape with a uniform size. However, AP cannot dissolve entirely at 85 °C and white precipitates (HO)Al(CH<sub>3</sub>COO)<sub>2</sub> was produced at 105 °C and 115 °C. AP had the highest dissolution degree at 95 °C. A colorless and transparent alumina sol with the highest solid content was acquired at this temperature. The structure of concentrated gels was also discussed. It was revealed that network polymers increased when using sols synthesized at temperature above 105 °C, which were negative for spinning. Continuous green fibers were obtained successfully using the alumina sol prepared at 95 °C.

## 1. Introduction

Alumina fiber is a kind of excellent ceramic material, which exhibits excellent high temperature strength, high chemical and thermal stability, low thermal expansion coefficient and good dielectric properties [1]. The alumina fiber has been widely used in many fields. A significant application is used as reinforced material in metals, ceramics, and resins [2]. The alumina fiber can be prepared by melt-spinning method [3], slurry and solution process [4, 5] and sol-gel method [6, 7]. Among them, sol-gel route is the best one [8]. It has the advantage to attain fibers with high alumina content at a low temperature [9].

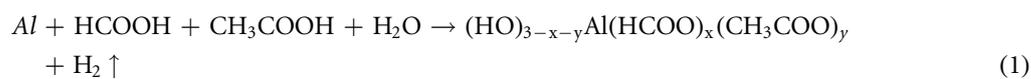
During the sol-gel process, molecular structure of gel is determined by composition of precursor sol, especially the structure of aluminum cations [10]. Aluminum cation speciation depends strongly on the preparation condition [10], such as starting materials and preparation temperature. Generally, aluminum isopropoxide (AIP) and some kinds of inorganic salts of aluminum are selected as Al source. Appropriate viscosities can be easily obtained through the polymerization of AIP [11]. Moreover, inorganic salts of aluminum have a good solubility in water. Okada *et al* [12] employed AIP and aluminum nitrate to prepare alumina fibers. They found that the decomposition of aluminum nitrate resulted in cracks [2]. Zhang *et al* [2] selected AIP and aluminum chloride as the starting materials. They revealed that the removal of chlorine resulted in a rough surface. In addition, although fibers with smooth surface and dense microstructure can be obtained by using AIP [11], the toxicity and expensive price of AIP limits the widespread applications of AIP [13]. Farias *et al* [14, 15] used inorganic salts of aluminum or aluminum powder (AP) and inorganic salts of aluminum as starting materials. They found that it was difficult to obtain appropriate spinning viscosity without spinning additives.

Tan *et al* [16] employed AP, formic acid and oxalic acid to synthesize aluminum carboxylates for fibers. However, insoluble oxalates led to precipitate. AP, formic acid, and acetic acid were chosen as the starting materials by some researchers [17–19], and fibers with uniform diameter and smooth surface were obtained. But the dissolution speed of AP is slow in solution. The use of catalysis can accelerate dissolution but also contribute to the reduction of purity. Chen *et al* [17] added toxic mercury chloride as a catalyst to assist aluminum dissolution, introducing chloride in alumina sol. Ma *et al* [18] obtained fibers with cracks by using aluminum chloride as an additive. They adopted a high molar ratio of carboxy acid and aluminum, such as 2:1, or even 7:1, resulting in a low alumina content. The low alumina content causes low ceramic yield. However, the sol with high solid content tends to precipitate. Through the adjustment of preparing temperature, solid content can increase without introduction of impurities. Wood *et al* [20] adopted a lower ratio of carboxy acid and aluminum 1.3:1. A high temperature was used to boil solution to improve the dissolution of aluminum. The solid content of precursor sol increased to 7.16%. But precipitates were generated due to the high preparing temperature, which results in a waste of starting materials. Meanwhile, there are many chemical reactions in the process to form alumina precursor sol [21], which has a significant influence on the following processing steps for alumina fibers. The effect mechanism of temperature is still not deeply studied.

In this research, AP, formic acid and acetic acid with a molar ratio of 1:0.68:0.6 were chose as starting materials to obtain precursor sols with high aluminum content. No additive or catalyst was used. The effects of preparation temperatures on solubility of AP were investigated. The structures of precursor sols and gels prepared at different temperature were studied. The relation between spinnability and structure of precursor gels was discussed.

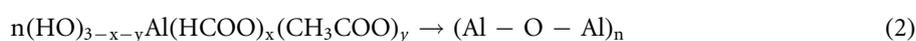
## 2. Theory

When AP is dissolved in the mixture of formic acid, acetic acid and deionized water, many complicated chemical reactions occur, including solvation reaction, hydrolysis reaction etc. These reactions can be simplified in the following equation.



where  $x$  and  $y$  are ranging from 0 to 3, and the sum of  $x$  and  $y$  is not larger than 3. Aluminum triformate ( $x = 3, y = 0$ ) is partially soluble in cool water. The solubility of aluminum triformate increases rapidly with the temperature increasing. It remains in a supersaturated state in solution instead of precipitates or crystallizes when cooled down. Aluminum diformate ( $x = 2, y = 0$ ) can hydrolyze to form aluminum monoformate ( $x = 1, y = 0$ ) or aluminum hydroxide and aluminum monoformate can hydrolyze to form aluminum hydroxide in water. Normal aluminum acetate ( $x = 0, y = 3$ ) hydrolyzes in water because it is also not stable in the absence of stabilizers such as boric acid [17]. Aluminum diacetate ( $x = 0, y = 2$ ) is soluble in water and insoluble in most organic solvents [22]. Basic aluminum formoactate,  $(\text{HO})\text{Al}(\text{HCOO})(\text{CH}_3\text{COO})$ , is soluble in water and stable in acidic aqueous solution.

At the initial stage, aluminum dissolves and hydrolyzes rapidly. Then, polynuclear cations form and grow through oxolation and other condensation reactions [10]. In the concentration process, oxolation and other condensation reactions occur to form higher molecule polynuclear aluminum cations with the decrease of solvent. These reactions can be simplified in equation (2).



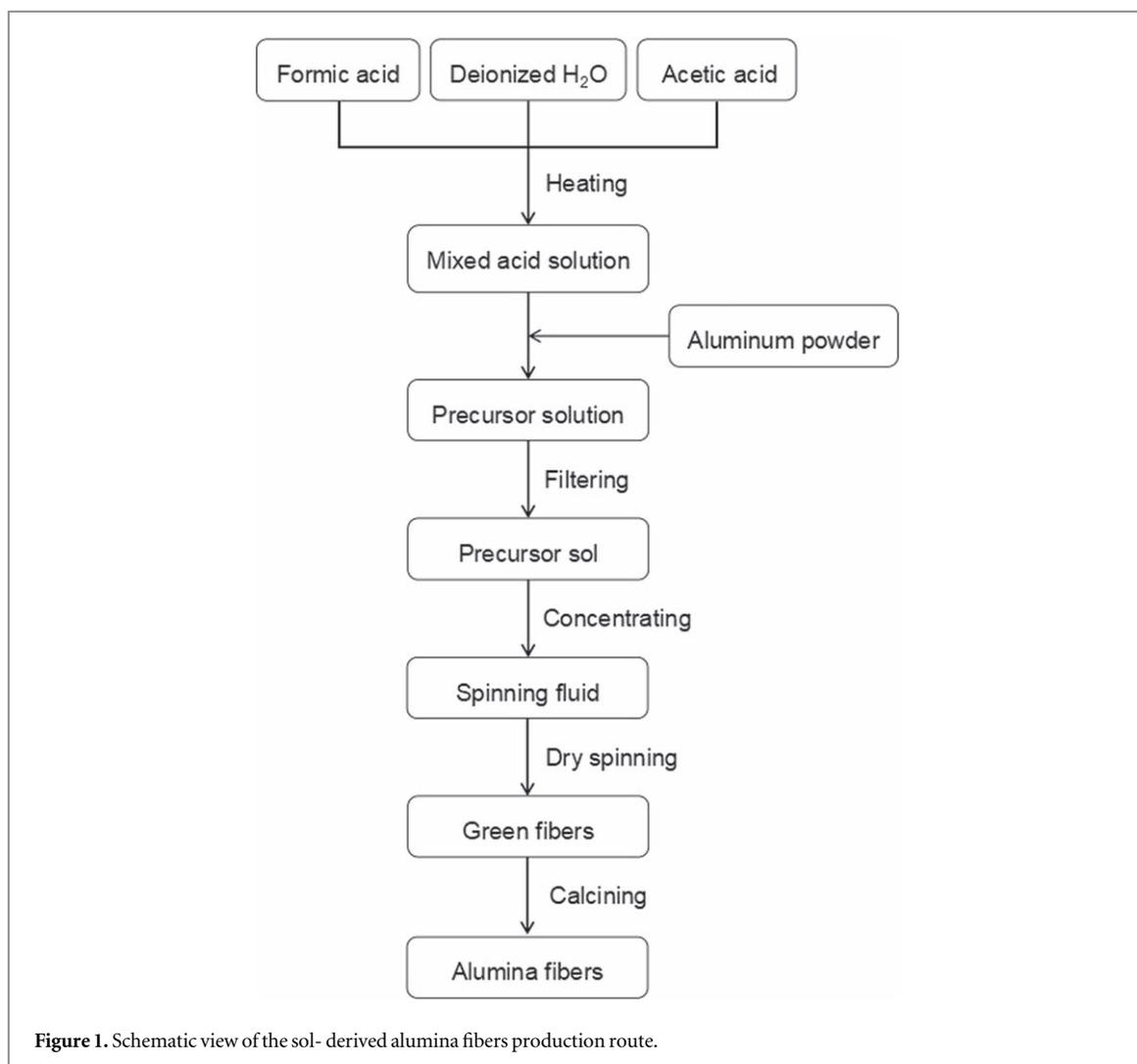
## 3. Experimental

### 3.1. Materials

Aluminum powder (>99.5%, Aladdin Industrial Corporation, Shanghai, China) was used as alumina source. Formic acid (99%, Aladdin Industrial Corporation, Shanghai, China), acetic acid (99.5%, glacier, Aladdin Industrial Corporation, Shanghai, China) and deionized water were employed to dissolve and react with aluminum.

### 3.2. Sample preparation

The processing steps of sol-derived alumina fibers are shown in figure 1. Acetic acid, formic acid, and deionized water were mixed with a molar ratio of 1:1.1:37 in an oil bath device. The temperature of oil bath was set as 85 °C, 95 °C, 105 °C and 115 °C respectively. Then AP was added to the mixed acid solution. The ratio of AP and total carboxylate was 1:1.3. The heat lasted for 12 h to obtain precursor sols. After cooled, precursor sols were filtered



from a  $1\ \mu\text{m}$  filter and a  $0.45\ \mu\text{m}$  filter membrane. Then filtered precursor sols were concentrated in vacuum to obtain gels with a suitable viscosity around  $6 \times 10^4\ \text{mPa} \cdot \text{s}$  for spinning. Green fibers were spun with a collecting speed of  $8\ \text{m min}^{-1}$  in a laboratory dry-spinning apparatus.

### 3.3. Characterization

The particles of sols were characterized by field emission transmission electron microscopy (FETEM, JEM-2100F, JEOL, Japan). The  $^{27}\text{Al}$  nuclear magnetic resonance (NMR) spectra were obtained by using the spectrometer (Ascend-400, Bruker, Switzerland). The solid content refers to the content of  $\text{Al}_2\text{O}_3$  in precursor sol. It was obtained by drying the liquid samples and calcining at  $1000\ ^\circ\text{C}$  for 1 h. Precipitates produced in precursor sols were analyzed by X-ray diffraction (XRD, Bruker Advance D8, Switzerland) using  $\text{Cu K}\alpha$  radiation. The IR spectra of gel fibers were measured in a wave number range from  $500$  to  $4000\ \text{cm}^{-1}$ , using FT-IR spectroscopy (Nicolet iS50, Thermo, USA). The fibers were characterized by scanning electron microscopy (SEM, Nano SEM 230, FEI, USA).

## 4. Results and discussion

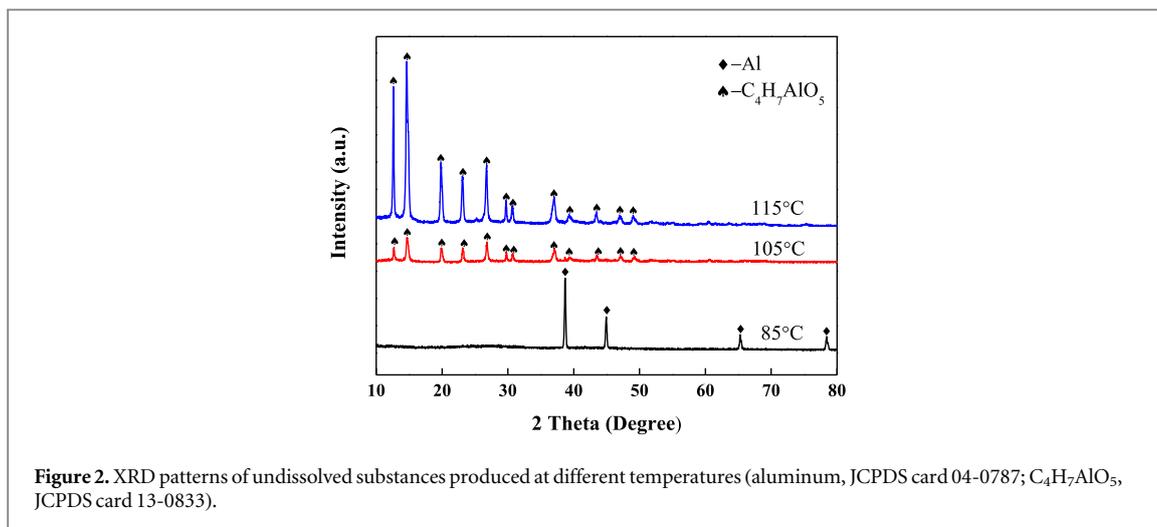
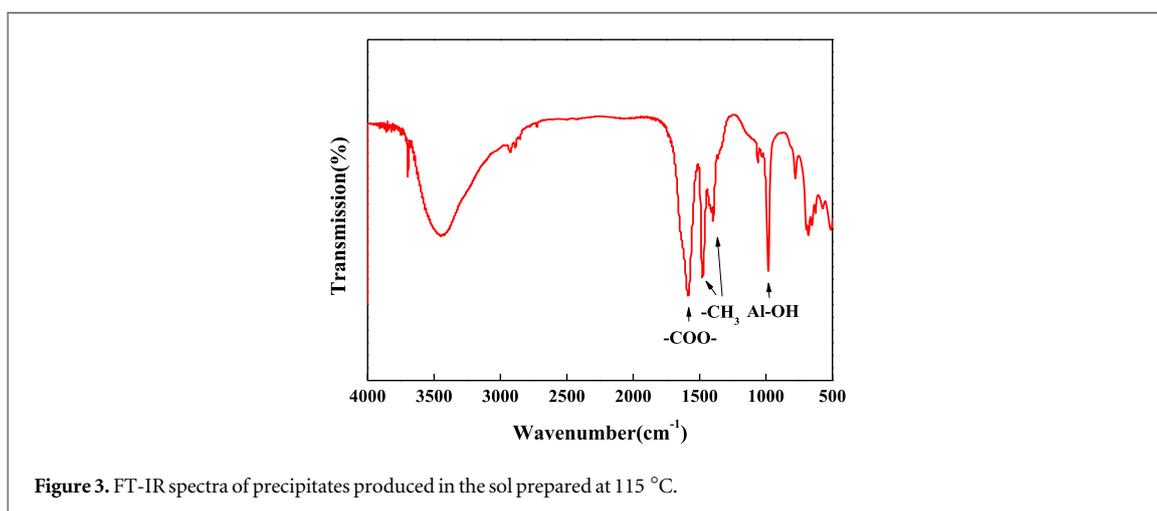
### 4.1. Alumina precursor sols

The characterization of as-prepared solutions and filtered alumina sols prepared at different temperatures are summarized and listed in table 1. The solution prepared at  $85\ ^\circ\text{C}$  was grey and opaque. The undissolved substances in solution were filtered, dried and then examined by XRD measurement. As revealed in figure 2, the undissolved substance was aluminum. That is, AP was not dissolved completely at  $85\ ^\circ\text{C}$ . When preparation temperature increases to  $95\ ^\circ\text{C}$ , the solution turns to be light grey and semitransparent, indicating the better solubility of AP. At  $105\ ^\circ\text{C}$ , white precipitates emerge during dissolution process. In this case, light milky and semitransparent solution was obtained. When the preparation temperature reaches up to  $115\ ^\circ\text{C}$ , more

**Table 1.** Characterization of as-prepared solutions and filtered alumina sols prepared at different temperatures.

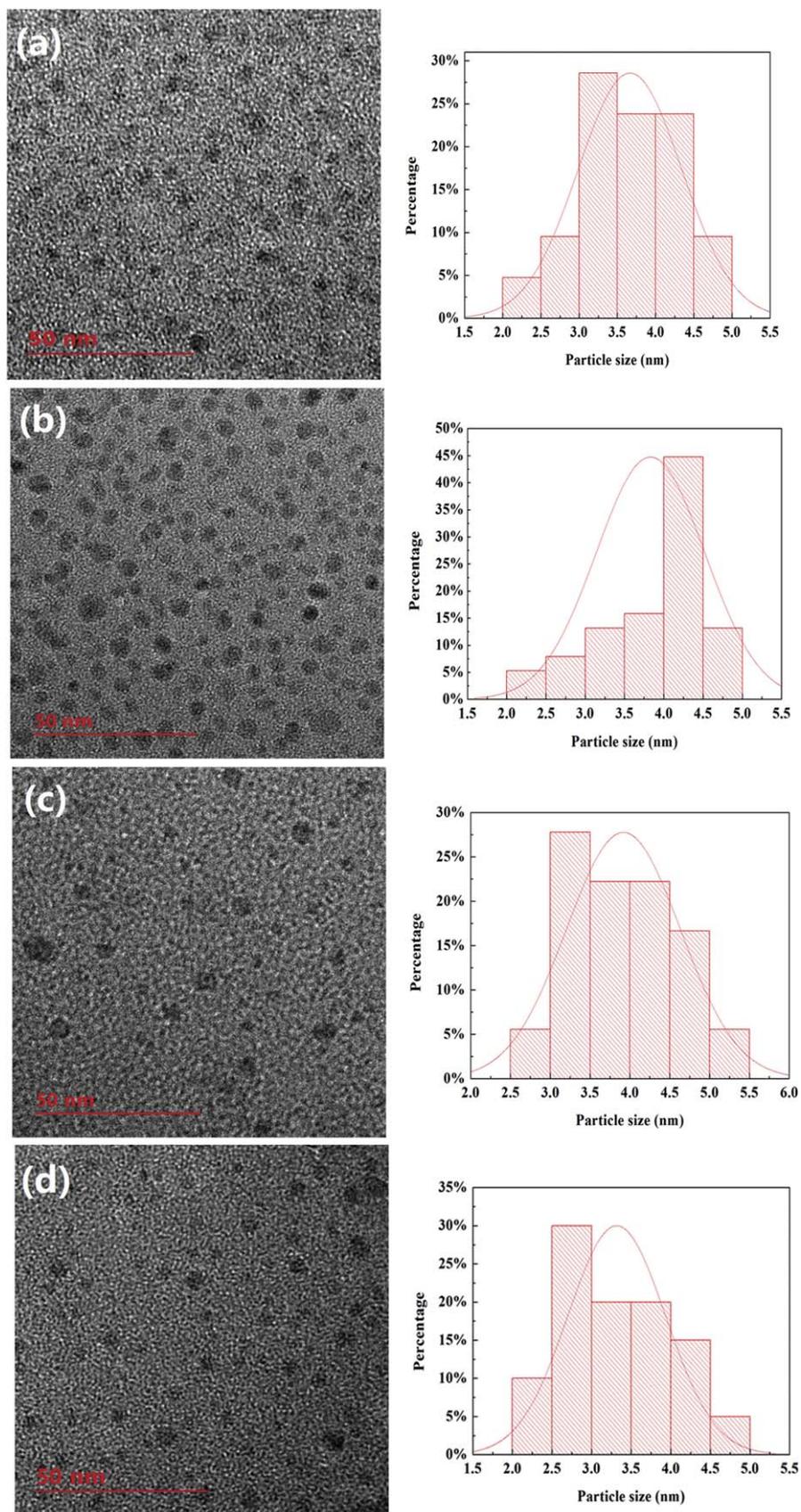
Temperature (°C)	As-prepared solutions		Filtered alumina sols	
	Appearance	Solid content (%)	Appearance	Solid content (%)
85	G; O	10.0	C; T	9.0
95	LG; ST	9.8	C; T	9.4
105	LM; ST	9.7	C; T	8.2
115	M; O	9.8	C; T	7.7

G = Grey, LG = Light grey, M = Milky, LM = Light milky, T = Transparent, ST = Semitransparent, O = Opaque, C = Colorless.

**Figure 2.** XRD patterns of undissolved substances produced at different temperatures (aluminum, JCPDS card 04-0787;  $C_4H_7AlO_5$ , JCPDS card 13-0833).**Figure 3.** FT-IR spectra of precipitates produced in the sol prepared at 115 °C.

precipitates generate, and the solution becomes milky and opaque. As shown in figure 2, the white precipitates generated at 105 and 115 °C were identified as aluminum acetate hydroxide  $C_4H_7AlO_5$ . Figure 3 shows the FT-IR spectra of precipitates. In this figure, the peaks corresponding to the asymmetrical stretching mode of  $-COO-$ , the bending mode of  $-CH_3$  and the bending mode of  $Al-OH$  were observed [23–25]. Thus, the precipitates were further confirmed to be  $(HO)Al(CH_3COO)_2$ . According to equation (1), when the temperature reaches up to 105 °C or higher, aluminum tends to react with acetic acid and  $H_2O$  to form  $(HO)Al(CH_3COO)_2$ .

Both incomplete dissolution of AP and production of precipitate can decrease the solid content of alumina precursor sol. As shown in table 1, when the temperature increases from 85 °C to 95 °C, the solid content increases by about 4%. However, when the temperature increases from 95 °C to 105 °C, the solid content decreases by about 13%. Therefore, in order to obtain alumina precursor sol with high solid content, the proper dissolution temperature for AP in the mixture of formic acid and acetic acid is 95 °C.



**Figure 4.** TEM images and size distribution histograms of colloidal particles of alumina sols. (a) sol prepared at 85 °C (b) sol prepared at 95 °C (c) sol prepared at 105 °C (d) sol prepared at 115 °C.

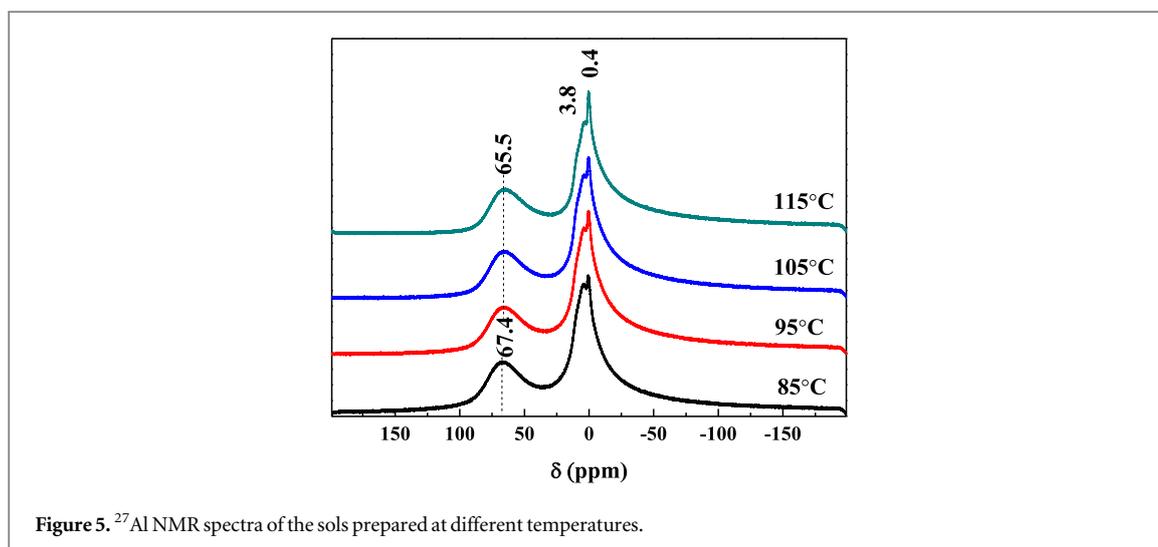


Figure 5.  $^{27}\text{Al}$  NMR spectra of the sols prepared at different temperatures.

After filtering, all the obtained alumina sols were colorless and transparent. The microstructures of alumina sols prepared at different temperatures were characterized by TEM. The colloidal particles size of precursor sols were measured and their distribution histograms were drawn. As shown in figure 4(a), the colloidal particles in the sol prepared at 85 °C exhibit approximate spherical shapes. Distribution histogram reveals that colloidal particles of the filtered sol prepared at 85 °C have a uniform size about 2 ~ 5.5 nm. With the temperature increasing, the morphologies of sols have no obvious difference and the colloidal particle size distributions are approximately similar.

Figure 5 displays the  $^{27}\text{Al}$  NMR spectroscopies of the alumina sols prepared at different temperatures. The local structure of Al in the samples was ascertained. The chemical shifts and linewidths are dependent on ligand type, coordination number, ligand field symmetry [10]. The different organic-Al species cannot be distinguished, resulting in the broader line width in NMR spectrum [26]. As shown in figure 5, the corresponding  $^{27}\text{Al}$  spectra showed two close sharp peaks emerged at around 0.4 ppm and 3.8 ppm and a broad peak at around 65.5 ppm. The two low-frequency resonances arise from Al in octahedral coordination. Actually, when AP was dissolved, aluminum existed in the form of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in solution. When pH value is beyond 3, the water ligands are deprotonated to form the ions  $[\text{Al}(\text{OH})_n(\text{H}_2\text{O})_{6-n}]^{(3+Z)+}$ , where  $n$  is defined as coordination number and  $Z$  as charge [27]. In detail, resonance near 0.4 ppm corresponds to the aluminum ions in monomeric species ( $\text{Al}_1$ ) such as  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$  and  $\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4^+$  [8]. The band at around 3.8 ppm accords with 2–4 nuclear oligomers ( $\text{Al}_{2-4}$ ) like  $\text{Al}_2(\text{Al}_2(\text{OH})_5^+)$ ,  $\text{Al}_3(\text{Al}_3(\text{OH})_8^+)$  and  $\text{Al}_4(\text{Al}_4(\text{OH})_8^{4+})$  [28]. The band around 65.5 ppm is broad and it corresponds to some polymer like  $\text{Al}_{13}$ ,  $\text{Al}_{30}$  or polymers with other complicated structure [29].

The structure of oligomers is linear and oligomers transform into complex polymers with network structure in the process of polymerization [30]. Figure 5 reveals that the intensity of peak assigned to oligomers is highest at 85 °C and lowest at 115 °C. The chemical shift of peak assigned to polymers is relatively higher at 85 °C. According to these results, it was found that the proportions of oligomers and polymers decreased with the increase of temperature. It was likely because that the polymerization of organic-Al species was an exothermic reaction [31]. With the temperature increase, polymers and oligomers decompose into aluminum ions.

#### 4.2. Alumina precursor gels

Figure 6 displays the  $^{27}\text{Al}$  NMR spectroscopies of alumina gels produced by sols prepared at different temperatures. The corresponding  $^{27}\text{Al}$  spectra show that two close sharp peaks emerge at around -0.6 ppm and 8.4 ppm and a broad peak at around 68.2 ppm. Compared with  $^{27}\text{Al}$  NMR spectroscopies of alumina sols, the chemical shifts of oligomers and polymers heighten in a small range. That suggests the proportions of oligomers and polymers increase since polymerization reactions predominate during concentration process. As shown in figure 6, the intensity of oligomers peak is the lowest at 85 °C and the highest at 115 °C. In addition, the dash line at around 68.2 ppm indicates the chemical shift of polymers at 85 °C. The chemical shift of the broad polymer peak is also the lowest at 85 °C and the highest at 115 °C. And the intensity of polymer peak at 85 °C is weaker. These results suggest that even though the proportions of oligomers and polymers are the highest in the sol prepared at 85 °C, they are the lowest after concentrating compared with other samples.

It has been well known that the structures of gels are determined by precursor sols. The ratio of acid and aluminum determined the degree of compactness of network structure in sol [21]. The polymer with high degree of compactness has more difficulty in decomposing. Since AP cannot dissolve entirely at 85 °C, the ratio of

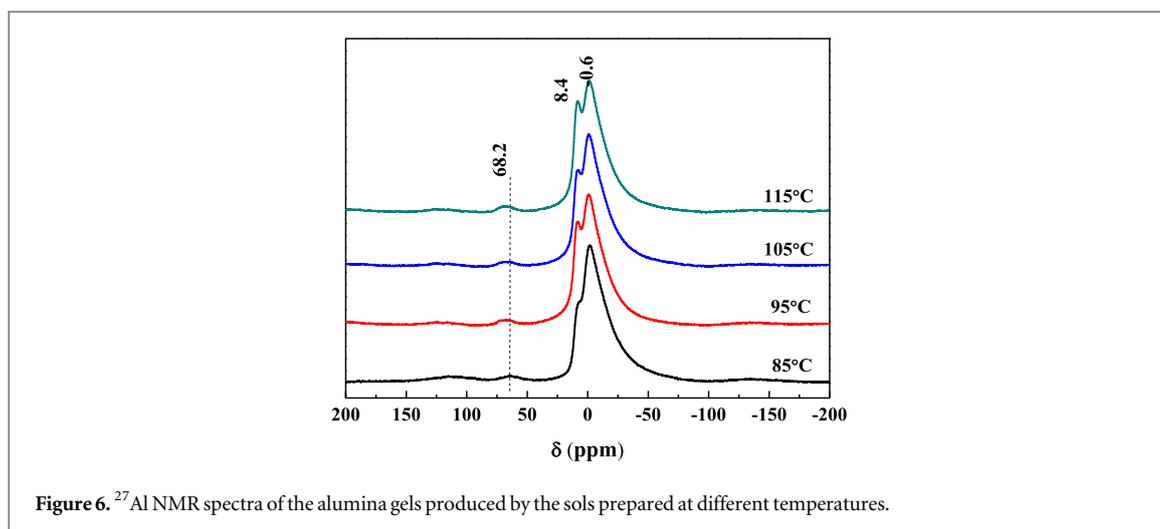


Figure 6.  $^{27}\text{Al}$  NMR spectra of the alumina gels produced by the sols prepared at different temperatures.

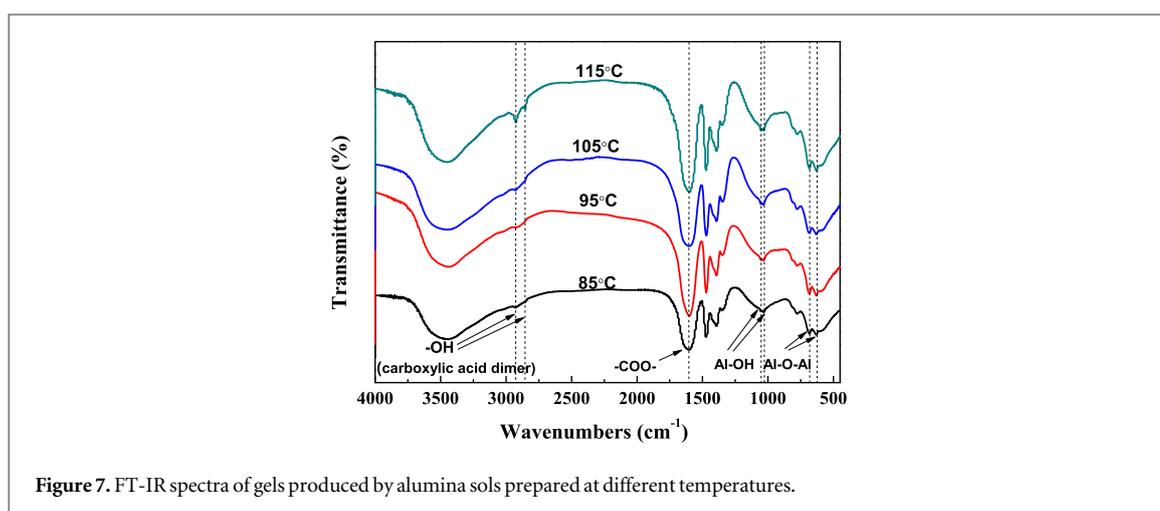


Figure 7. FT-IR spectra of gels produced by alumina sols prepared at different temperatures.

aluminum and carboxylic acid was the lowest in the sol prepared at 85 °C. According to the precipitate structural formula  $(\text{HO})\text{Al}(\text{CH}_3\text{COO})_2$ , aluminum reacted with acetic acid at the ratio of 1:2 at 105 °C and 115 °C. Therefore, when this precipitate generated, the relative content of carboxylic acid reduced. Since more precipitates were produced at 115 °C, the ratio of aluminum and carboxylic acid was the highest in the sol prepared at 115 °C. With the decrease of solvent during concentration process, oligomers and polymers partly decomposed in sol prepared at 85 °C due to the high acid content. Therefore, the polymerization degree of sol prepared at 85 °C was the lowest in concentration process. Conversely, the polymerization degree of sol prepared at 115 °C was the highest in concentration process.

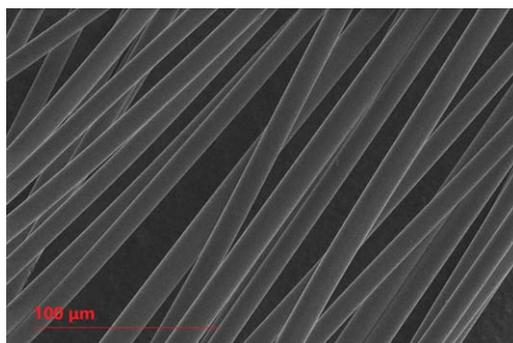
FT-IR spectra of alumina gels are shown in figure 7. Assignments of the IR absorption frequencies are shown in table 2. It can be seen in figure 7, the peaks assigned to  $-\text{COO}-$  are weaker at 85 °C. It suggests that the amount of acid decreased in the process of vacuum concentration. The intensities of  $\text{Al}-\text{O}-\text{Al}$  peaks are the lowest at 85 °C and the highest at 115 °C. It also suggests that a high ratio of acid and aluminum inhibited polymerization reaction. The intensities of peaks assigned to the  $\text{O}-\text{H}$  stretching modes of carboxylic acid dimers [32] and  $-\text{COO}-$  stretching modes are the highest at 115 °C and the lowest at 85 °C. It shows that besides Al species, carboxylate species created at high temperature in sols were also easier to polymerize. Therefore, there were more polymers with network structure at 115 °C.

#### 4.3. Alumina fibers

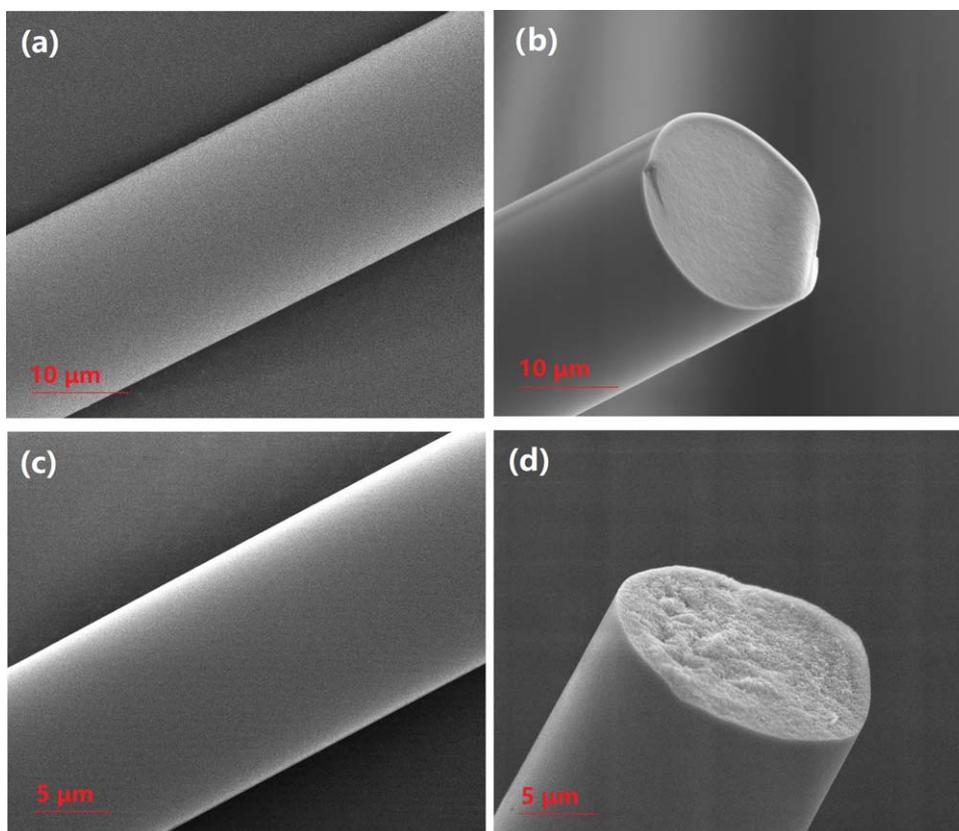
The dry spinning method is adopted to produce green fibers. In this study, viscosity of spinning fluid and spinning parameters were adjusted to be the same. Thus, the effect of viscosity and spinning parameters on the spinnability can be ignored. The spinnability of spinning fluid all depends on the inter-molecular twining degree. The structure of oligomers is linear and both polymers and carboxylic acid dimer have complex network structure [30]. 95 °C is the most appropriate among the four preparing temperature under the preparing condition in this research. The linear structure is necessary for spinning process. The precursor gel prepared at

**Table 2.** Assignments of the IR absorption frequencies of the gels produced by alumina sols prepared at different temperatures [13, 16, 23–25, 33, 34].

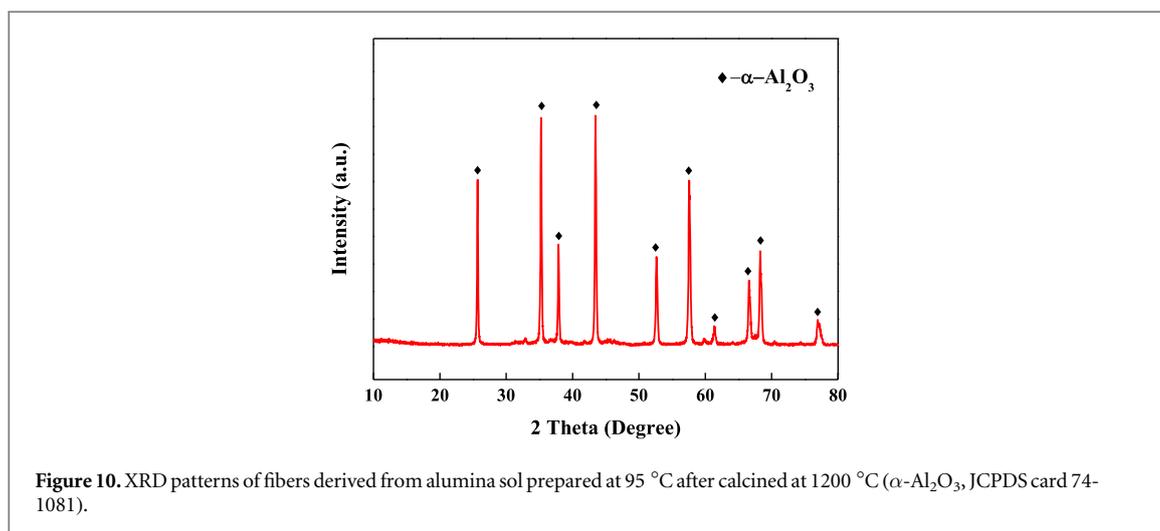
Absorption wavenumber ( $\text{cm}^{-1}$ )	Band assignment
3440	O–H
2920, 2890	O–H of carboxylic acid dimers
1600	–COO–
1470, 1390	–CH <sub>3</sub>
1345	–CH–
1060, 1035	Al–OH
820, 780	Al–O–Al in tetrahedron
680, 630	Al–O–Al in octahedron



**Figure 8.** SEM image of the green fibers prepared by the spinning fluid derived from alumina sol produced at 95 °C.



**Figure 9.** SEM images of green fibers and calcined fibers derived from alumina sol prepared at 95 °C. (a) surface of green fibers (b) cross-section of green fibers (c) surface of fibers calcined at 1200 °C (d) cross-section of fibers calcined at 1200 °C.



**Figure 10.** XRD patterns of fibers derived from alumina sol prepared at 95 °C after calcined at 1200 °C ( $\alpha$ - $\text{Al}_2\text{O}_3$ , JCPDS card 74-1081).

85 °C contained the least linear oligomers and the precursor gel prepared at 105 °C and 115 °C contained more polymers with network structure. As shown in figure 8, green fibers derived from the alumina sol produced at 95 °C were obtained. The fibers are continuous and uniform.

Figure 9 shows the SEM images of green fibers and calcined fibers derived from alumina sols prepared at 95 °C. As is observed in figure 9, the green fibers are smooth, indicating that the spinning fluid derived from prepared alumina sols were suitable for fiber synthesis. As shown in figures 9(a), (c), both green fiber and calcined fiber are smooth with no voids or cracks on the surface. The cross-sections of green fiber and calcined fiber are shown in figures 9(b), (d). It can be seen that the fibers have dense microstructures. Moreover, the XRD pattern of calcined fibers at 1200 °C is shown in figure 10. According to the XRD pattern, the calcined fibers exhibit  $\alpha$ - $\text{Al}_2\text{O}_3$  phase.

## 5. Conclusions

In this study, alumina fibers with smooth surface and uniform diameter were obtained by the spinning fluid derived from alumina precursor sol prepared at 95 °C. The sols prepared at temperature from 85 °C to 115 °C all consist of monomeric species, oligomers and polymers. The colloidal particles are approximate spherical with a uniform size. It was found that temperature has an important effect on the dissolution of AP. AP cannot dissolve entirely at 85 °C and the white precipitate  $(\text{HO})\text{Al}(\text{CH}_3\text{COO})_2$  was produced at 105 °C and 115 °C, resulting in the low solid content in sols. The solid content of precursor sol can increase to 9.4% at 95 °C. The spinning fluid derived from the sol prepared at 85 °C consisted little linear oligomers. With the temperature elevating, the polymerization degree increased and more network polymers were produced, which were negative for spinning. Continuous gel fibers obtained from the sol prepared at 95 °C were transformed into  $\alpha$ - $\text{Al}_2\text{O}_3$  phase after calcining at 1200 °C.

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