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PREPARATION OF ALUMINA FIBERS FROM ALUMINUM SALTS BY THE SOL-GEL METHOD

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Abstract – Alumina fibers were synthesized from two different systems, $AlCl_3$-Al powder-H_2O and $Al(NO_3)_3$-Al powder-H_2O, by the sol-gel method. For the former system, gel fibers were obtained from solutions in a composition range of Al powder/$AlCl_3$ molar ratios of 2 to 5. For the latter system, the spinnable range was narrower compared to the aluminum chloride system. The thermogravimetry analysis (TGA) curve of the aluminum chloride system showed a weight loss up to 700 °C, while the TGA curve of the aluminum nitrate system showed no weight loss above 400 °C, which indicates that thermal decomposition of Cl^- is more difficult than that of NO_3^-.

Key words: Alumina Fibers, Sol-Gel Method, Aluminum Salts, Spinnability

INTRODUCTION

Ceramic fibers, in particular alumina fibers, are of growing interest and importance for a variety of applications, from high-temperature insulation to metal and polymer reinforcement [Dhingra, 1980; Bitchall, 1983; Maki and Sakka, 1986].

Ceramic fibers have been conventionally prepared by drawing or blowing high temperature melts through a spinneret. Since it is difficult to draw alumina fibers from high temperature melts because of the low viscosity of the melts and the exceedingly high melting temperature, they are produced by a low temperature process such as the sol-gel method. In this method, gel fibers are drawn at near room temperature from highly concentrated, viscous solutions of metal salts or metal alkoxides which are spinnable as a result of hydrolysis and polycondensation. The drawn gel fibers can be converted into alumina fibers by thermal treatments. Advantages of the sol-gel method over the conventional melting method are high purity, better homogeneity, lower reaction temperature and the easy control of final product quality [Hench and Ulrich, 1984].

Various aluminum compounds, such as aluminum alkoxides [Yogo and Iwahara, 1992] and aluminum salts [Bitchall, 1983; Maki and Sakka, 1988; Song et al., 1997], are used as starting materials in preparation of alumina fibers by the sol-gel method. The alkoxide method using aluminum alkoxide as a starting material is time-consuming and costly for synthesis of alumina fibers because aluminum alkoxide must be modified with chelating agents such as ethylacetoacetate and acetylacetone to prevent precipitation during the synthesis of spinnable sols. Therefore, the alkoxide method is not suitable for industrial mass production of alumina fibers. On the other hand, aluminum salts such as aluminum chloride and aluminum nitrate are much cheaper than aluminum alkoxide and do not require a long period of time for the synthesis of spinnable sols. Thus the salt method, which uses aluminum salt as a starting material, is encouraging as a potential method for mass production of industrial alumina fibers. In the salt method, previous works [Bitchall, 1983; Maki and Sakka, 1988; Song et al., 1997] used only the aluminum chloride as the starting material.

The purpose of this study is to compare the differences of alumina fibers synthesized from two different aluminum salts (aluminum chloride and aluminum nitrate) by the sol-gel method. Spinnabilities of sols and thermal changes of gel fibers from the two starting materials are investigated and compared. In addition, changes in microstructure during calcination of gel fibers are discussed.

EXPERIMENTAL

Aluminum chloride ($AlCl_3 \cdot 6H_2O$, Shinyo chemicals, 97 %), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Yakuri chemicals, 98 %), aluminum (Al, Samchun chemicals, 100 %) metal powder and deionized water were used as starting materials to synthesize alumina sols. All sols were synthesized by heating a 200 cm^3 suspension at reflux at approximately 100 °C for 5 hours, which were prepared by adding given moles of Al powder to 1 mol/dm^3 aluminum salt (aluminum chloride or aluminum nitrate) solutions. Synthesized sols were aged in a drying oven maintained at 60 °C until the solutions were spinnable. Sol viscosity was measured for the samples withdrawn at various time intervals during aging at 20 °C using a coaxial cylinder viscometer (VT500, Haake). Spinnability of the sols was determined from the capability of fiber formation by immersing a glass rod of approximately 8 mm in diameter into the sols, then pulling it up quickly by hand. Drawn gel fibers were dried at room temperature for 2 days, then heated in air at a heating rate of 5 °C/min in the range from 600° to 1,200 °C.

The thermal behavior of the gel fibers was investigated by DTA/TGA (STD2960, TA instruments) at a heating rate of 10

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°C/min in flowing air conditions. The IR spectra of the fibers were measured using FT-IR spectroscopy (FTS155, Bio-rad) in the wave number range from 400 to 4,000 cm^{-1}. An X-ray diffractometer (D/MAX-IIIC, Rigaku) was used for identification of crystalline species in the heated fibers. Ni-filtered CuKα radiation was used as the X-ray source and the measurement was performed for the diffraction angles between 10° and 70° in 2 θ. Fiber morphology was characterized by scanning electron microscopy (SEM535M, Phillips).

RESULTS AND DISCUSSION

1. Spinnability of Sols

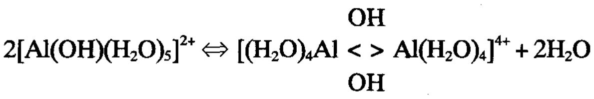
When aluminum salt ($AlCl_3 \cdot 6H_2O$) is dissolved in water, the following reaction occurs [Gimblett, 1963]:

$$AlCl_3 \cdot 6H_2O \Leftrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$$

This solvated ion undergoes a further hydrolysis reaction with water:

$$Al(H_2O)_6]^{3+} + H_2O \Leftrightarrow [Al(OH)(H_2O)_5]^{2+} + H_3O^+$$

The elimination of two molecules of water between two partially hydrolyzed aluminum species leads to the formation of a dinuclear hydroxo-bridged aluminum species:



$$2[Al(OH)(H_2O)_5]^{2+} \Leftrightarrow [(H_2O)_4Al \overset{OH}{\underset{OH}{<\,>}} Al(H_2O)_4]^{4+} + 2H_2O$$

An extension of this polycondensation reaction can lead to an infinite number of polynuclear aluminum cations. The connection between these aluminous cations may lead to the formation of particles with various sizes and shapes, depending on the aluminum ion concentration in the solution. In this study, Al powder was added during refluxing to increase the aluminum ion concentration. The addition of Al powder also hydrolyzes the Al species in solution and causes the formation of a number of polynuclear aluminum cations. Thus, the amount of Al powder added to the solutions during refluxing greatly influences the shapes and sizes of particles formed in the solutions. If no Al powder is added during refluxing, the above hydrolysis and polycondensation reactions do not take place and no particles are formed in the solution.

Tables 1 and 2 show the characteristics of the sols prepared by dissolving various amounts of Al powder in the aluminum chloride and aluminum nitrate solutions, respectively. The spinnability of the sols was remarkably dependent on the amount of Al powder dissolved in the solution. For the aluminum chloride system shown in Table 1, gel fibers could be obtained from viscous solutions in the molar ratios of Al powder/$AlCl_3$ of 2 to 5 (sols 3-6). For the aluminum nitrate system shown in Table 2, the spinnable range was narrower compared to the aluminum chloride system, and gel fibers were obtained from a viscous solution with a molar ratio of Al powder/$Al(NO_3)_3$ of 2 (sol 10). The more Al powder is dissolved, the more opaque and the more viscous the initial state of the solutions becomes just after refluxing.

Table 1. Spinnability of the aluminum chloride system after refluxing

Sol number	Al powder/$AlCl_3$ molar ratio	The state of the sols just after refluxing	Spinnability of solution
1	0	Transparent sol	No
2	1	Silver-gray clear sol	No
3	2	Silver-gray clear sol	Yes
4	3	Silver-gray clear sol	Yes
5	4	Silver-gray clear sol	Yes
6	5	Gray opaque sol	Yes
7	5.4	Gray opaque sol	No

Table 2. Spinnability of the aluminum nitrate system after refluxing

Sol number	Al Powder/ $Al(NO_3)_3$ molar ratio	The state of the sols just after refluxing	Spinnability of solution
8	0	Slight yellow clear sol	No
9	1	Slight yellow clear sol	No
10	2	Slight yellow clear sol	Yes
11	2.3	White opaque sol	No
12	2.5	Gray opaque gel	No

The viscosities of alumina sols prepared from aluminum chloride and aluminum nitrate, respectively, are shown as a function of aging time in Figs. 1 and 2. The alumina sol mainly consists of particles with various shapes and sizes dispersed in water [Maki and Sakka, 1988]. As the sol becomes concentrated

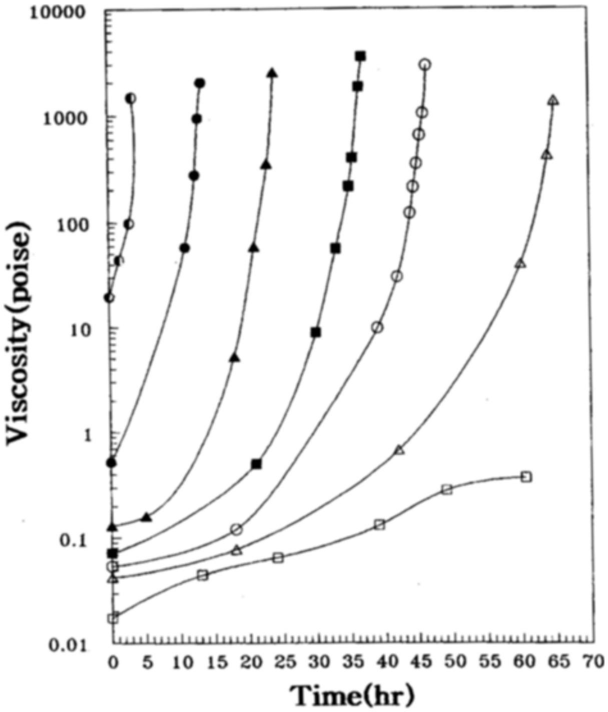


Fig. 1. Viscosities of alumina sols prepared from the $AlCl_3$ system as a function of aging time. Viscosity was measured at a shear rate of 10S^{-1}.
Marks indicate the samples of Table 1: (□) sol 1; (△) sol 2; (○) sol 3; (■) sol 4; (▲) sol 5; (●) sol 6 and (◐) sol 7.

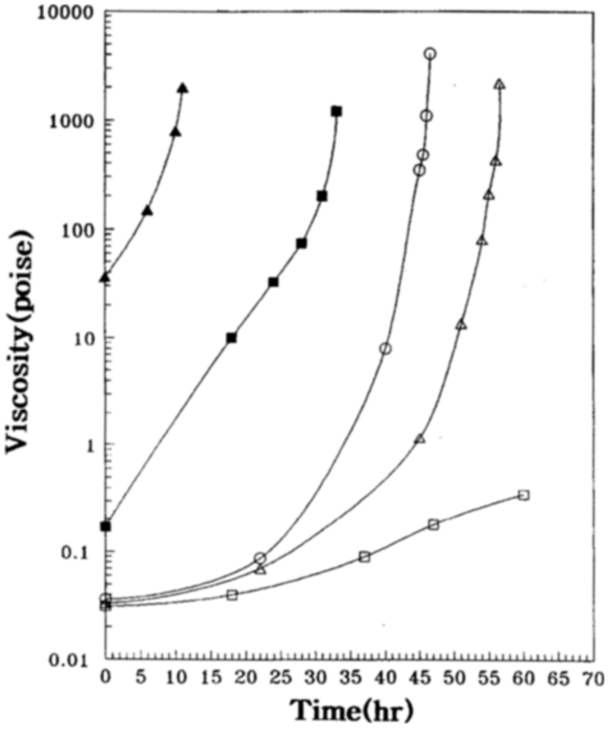


Fig. 2. Viscosities of alumina sols prepared from the $Al(NO_3)_3$ system as a function of aging time. Viscosity was measured at a shear rate of $10S^{-1}$.
Marks indicate the samples of Table 2: (□) sol 8; (△) sol 9; (○) sol 10; (■) sol 11 and (▲) sol 12.

through the evaporation of water, the particles in the sol tend to aggregate with each other and the sol viscosity increases [Song and Chung, 1989a, b]. Thus, the viscosities of the sols in Figs. 1 and 2 increase gradually in the initial stage, then increase strikingly near the gelling point. Sols prepared without the addition of Al powder (sols 1, 8) do not show a rapid increase of viscosity with aging time. This means that aggregation between particles does not happen in these sols because no particles are formed during refluxing. Gelling time can be defined as the aging time at which the viscosity of the solution increases rapidly [Song and Chung, 1989a]. It is seen from these figures that the gelling time is dependent on the dissolved content of Al powder. The more Al powder is dissolved, the shorter the gelling time becomes.

Fiber drawing from the viscous solutions was possible in the high viscosity ranges of 350-3,000P in both systems. A photomicrograph of the drawn fibers is shown in Fig. 3, depicting gel fibers which are several meters long and 10-100 μm in diameter. The average diameter of the gel fibers is related to the viscosity of the solution at the time of fiber drawing. That is, fibers have a small diameter when drawn from low viscosity solutions, but they have a large diameter when drawn from high viscosity solutions.

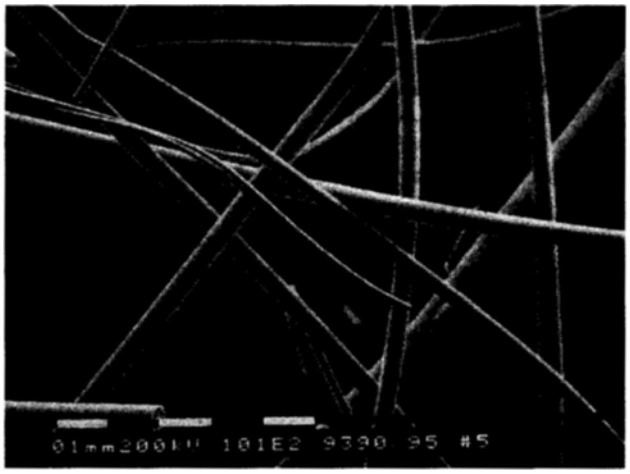


Fig. 3. Photomicrograph of gel fibers.

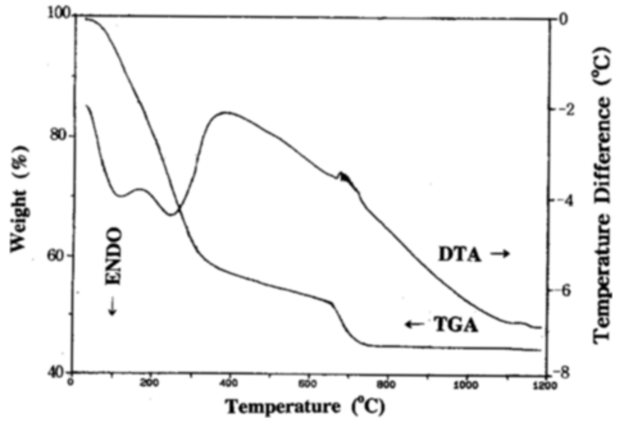


Fig. 4. DTA/TGA curves of gel fibers prepared from $AlCl_3$ system (sol 5 in Table 1).

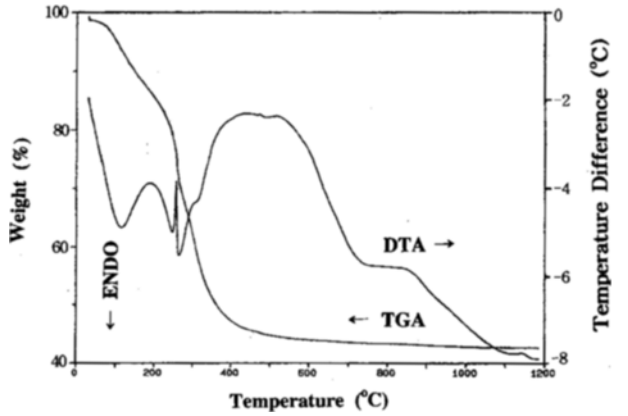


Fig. 5. DTA/TGA curves of gel fibers prepared from $Al(NO_3)_3$ system (sol 10 in Table 2).

2. Changes in Properties of Gel Fibers at Different Calcination Temperatures

Figs. 4 and 5 show the DTA/TGA curves of gel fibers from aluminum chloride (sol 5 in Table 1) and aluminum nitrate (sol 10 in Table 2) systems, respectively. The DTA/TGA curve shown in Fig. 4 indicates that most weight loss occurs below 700 °C and that the total weight loss is 55 % in the aluminum chloride system. The exothermic peak with weight loss near 670 °C may be due to thermal decomposition of chloride groups in the gel fibers, while the exothermic peak without weight loss at 1,130 °C is due to transformation to α-alumina [Li and Thomson, 1990]. On the other hand, the DTA/TGA curve shown in Fig. 5 indicates that there is a weight loss of 56 % between 30 ° and 400 °C, and no additional significant weight loss in seen up to 1,200 °C in the aluminum nitrate system. The exothermic peak with large weight loss near 260 °C is due to thermal decomposition of nitrate groups in the gel fibers. From the above thermal analysis it is seen that thermal decomposition in the aluminum nitrate system is completed at a lower temperature than in the aluminum chloride system, which supports that thermal decomposition of Cl^- is more difficult than that of NO_3^-.

Figs. 6 and 7 show comparisons of X-ray diffraction (XRD) patterns with calcination temperatures obtained from gel fibers of the aluminum chloride (sol 5 in Table 1) and the aluminum nitrate (sol 10 in Table 2) systems, respectively. Fibers of the aluminum chloride system are amorphous at room temperature (RT) and the phase transformation to γ-alumina begins at 600 °C. At 900 °C, both γ-alumina and α-alumina peaks are observed in the XRD diagram in Fig. 6. Above 1,000 °C, γ-alumina is completely transformed into α-alumina. On the other hand, the XRD patterns for fibers of the aluminum nitrate system at RT and 600 °C, which are shown in Fig. 7, do not show any crystalline peaks. At 800 ° and 900 °C the peaks assigned to γ-alumina are observed, then further heating above 1,000 °C results in disappearance of the γ-phase and growth of α-alumina. From the above XRD patterns we can know that the phase transformation of amorphous gel fibers to γ-alumina, then to α-alumina in the aluminum chloride system takes place at a lower temperature than in the aluminum nitrate system.

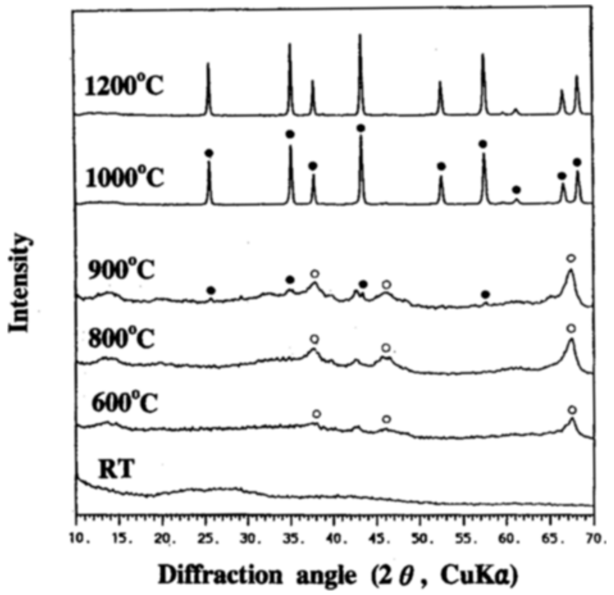


Fig. 6. X-ray diffraction patterns of gel fibers from the $AlCl_3$ system (sol 5 in Table 1) heat-treated at various calcination temperatures for 2 hrs.

Marks indicate the peaks of alumina crystals: (○) γ-alumina and (●) α-alumina.

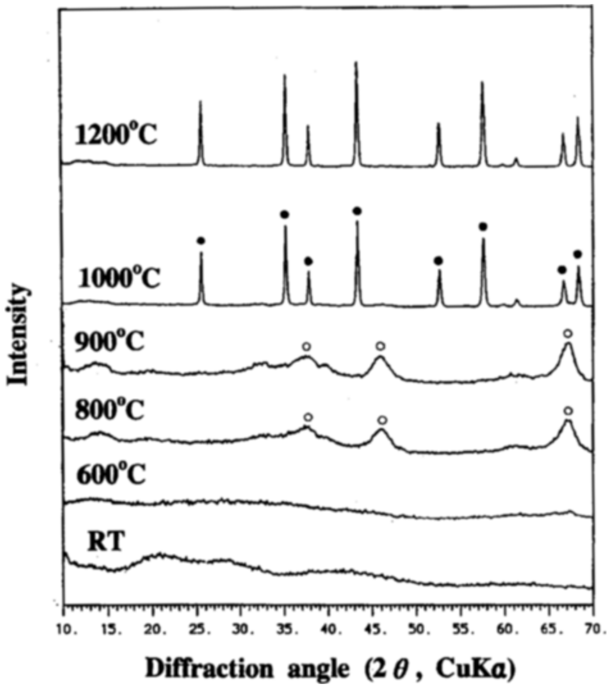


Fig. 7. X-ray diffraction patterns of gel fibers from the $Al(NO_3)_3$ system (sol 10 in Table 2) heat-treated at various calcination temperatures for 2 hrs.

Marks indicate the peaks of alumina crystals: (○) γ-alumina and (●) α-alumina.

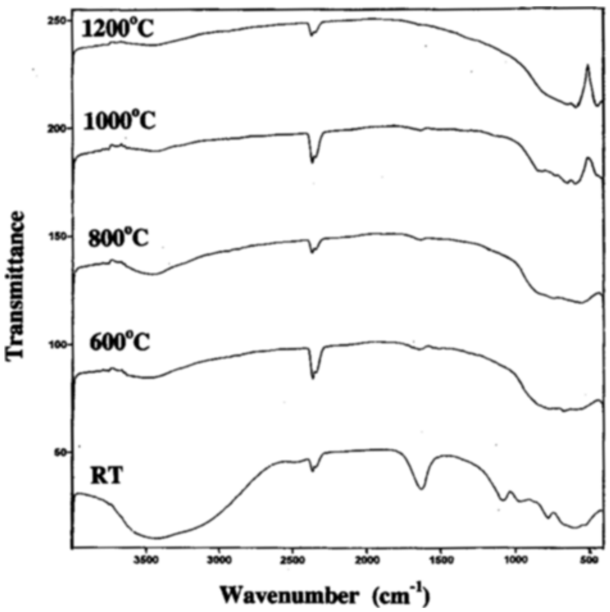


Fig. 8. FT-IR spectra of gel fibers from the $AlCl_3$ system (sol 5 in Table 1) heat-treated at various calcination temperatures for 2 hrs.

Figs. 8 and 9 show changes in the FT-IR spectra with calcination temperatures of gel fibers prepared with aluminum chloride (sol 5 in Table 1) and aluminum nitrate (sol 10 in Table 2), respectively. Peaks resulting from absorption of molecular water (either pore water, hydration water, or absorbed water) are observed at 1,640 and 3,420 cm^{-1} in fibers heat-treated at RT in Figs. 8 and 9. The former peak is due to H-O-M bending vibrations and the latter peak is due to O-H stretching vibrations [Gadsden, 1975]. The peaks at 1,640 and 3,420 cm^{-1} are significantly reduced when the fibers are calcined at 600 °C. This is attributed to the evolution of water. The peak near 470 cm^{-1} at 1,000° and 1,200 °C in Figs. 8 and 9 is assigned to Al-O vibration in the AlO_6 octahedra [Sacks et al., 1984]. This indicates the formation of α-alumina and corresponds to the XRD results in Figs. 6 and 7. In the aluminum nitrate system shown in Fig. 9, the strong gel fiber (RT) absorption peak at 1,380 cm^{-1} is caused by NO_3^- ion, corresponding to N-O stretching vibration [Bellamy, 1975]. IR results of fibers calcined at 400 °C show that most nitrate ions disappear due to thermal decomposition of nitrate groups in gel fibers at 260 °C, as seen in the DTA curve of Fig. 5.

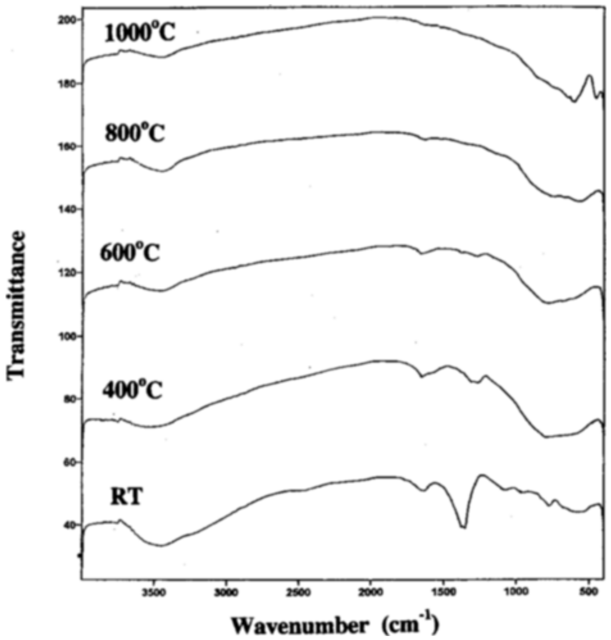


Fig. 9. FT-IR spectra of gel fibers from the $Al(NO_3)_3$ system (sol 10 in Table 2) heat-treated at various calcination temperatures for 2 hrs.

3. Changes in Microstructures of Fibers at Different Calcination Temperatures

SEM photomicrographs of fiber cross-sections from the aluminum chloride (sol 5 in Table 1) and aluminum nitrate (sol 10 in Table 2) systems at various calcination temperatures are shown in Figs. 10 and 11, respectively. In order to transform gel fibers into alumina fibers, gel fibers are heated in air from room temperature to 1,200 °C at a heating rate of 5 °C/min. As shown in Fig. 10, the cross-section of gel fiber from the aluminum chloride system is circular. The fibers contain no pores and show a dense structure. However, cross-sections of fibers calcined at 800°, 1,000°, and 1,200 °C show broken structures with large cracks. As temperature is increased above 800 °C, more cracks are observed. These broken structures are caused by phase transformations of amorphous gel fibers to γ-alumina fibers and α-alumina fibers during calcination. Since crystallization of ceramics is followed by an abrupt shrinkage in volume, cracks are produced in cross-sections of fibers calcined. These cracks cause deterioration of the mechanical strength of the fibers. Thus, better conditions for heat treatment, such

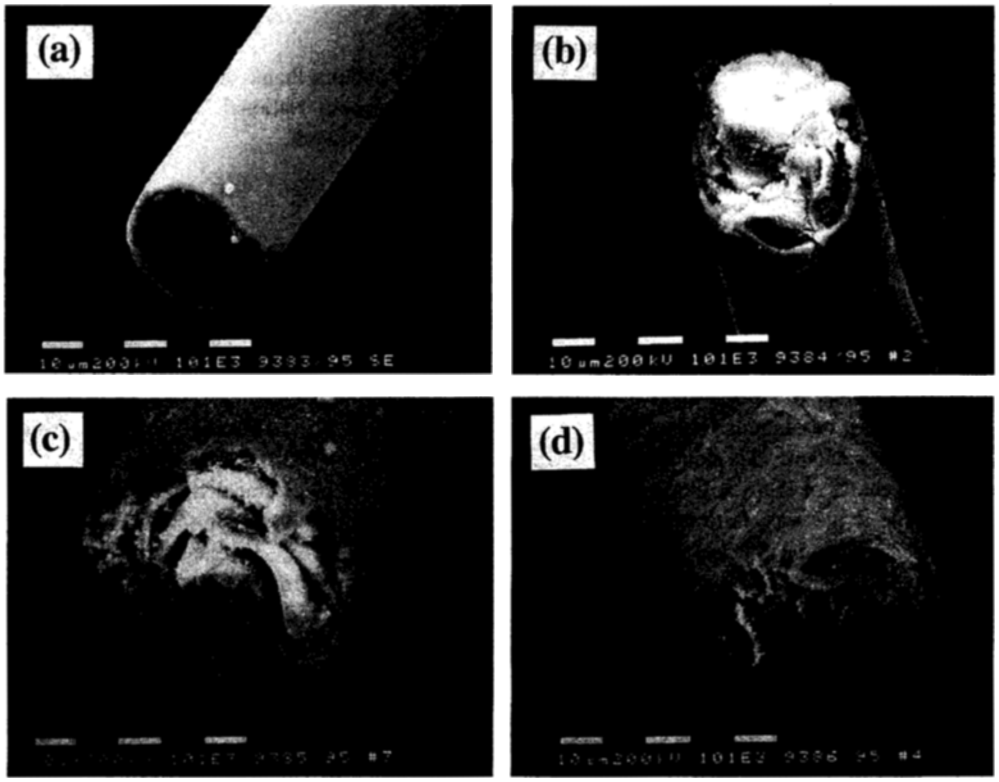


Fig. 10. SEM microstructures of fiber cross-sections from the $AlCl_3$ system (sol 5 in Table 1) heat-treated at various calcination temperatures for 2 hrs.

(a) room temperature; (b) 800 °C; (C) 1,000 °C and (d) 1,200 °C.

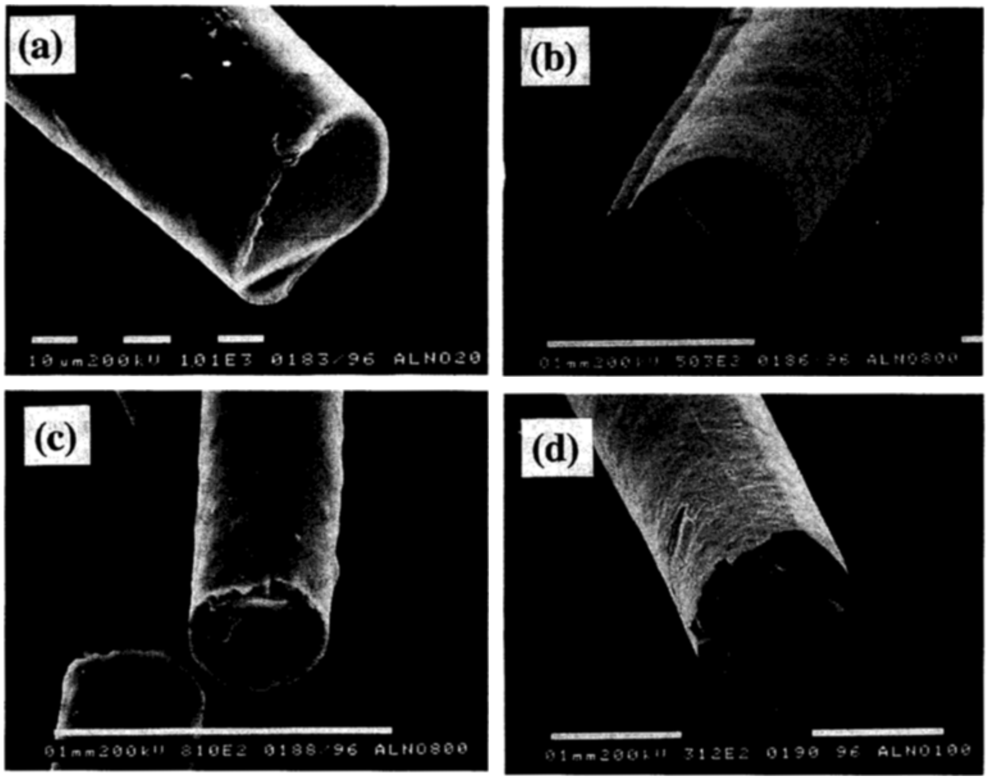


Fig. 11. SEM microstructures of fiber cross-sections from the Al(NO_3)$_3$ system (sol 10 in Table 2) heat-treated at various calcination temperatures for 2 hrs.
(a) room temperature; (b) 800 °C; (C) 1,000 °C and (d) 1,200 °C.

as heating rate, heating temperature, heating time, and the atmosphere used in the treatment, are needed in the aluminum chloride system in order to produce denser fibers with higher mechanical strength. On the other hand, when calcined above 800 °C, fibers of the aluminum nitrate system, shown in Fig. 11, show less broken structures with fewer cracks in cross-section than fibers of the aluminum chloride system.

CONCLUSIONS

Alumina fibers were synthesized by the sol-gel method using the two aluminum salts: aluminum chloride and aluminum nitrate. The spinnability of solutions was determined by the dissolved content of Al powder. In the aluminum chloride system, gel fibers were obtained from solutions in a composition range of Al powder/$AlCl_3$ molar ratios of 2 to 5. In the aluminum nitrate system, the spinnable range was narrower than that in the aluminum chloride system. Thermal changes of the two systems were studied by DTA/TGA and SEM analyses. The TGA curve of the aluminum chloride system showed weight loss up to 700 °C, while that of the aluminum nitrate system showed no weight loss above 400 °C, which indicates that thermal decomposition of Cl^- is more difficult than that of NO_3^-. In the aluminum chloride system fibers calcined above 800 °C exhibited broken microstructures with many cracks. When calcined above 800 °C, fibers of the aluminum nitrate system showed less broken microstructures with fewer cracks than fibers of the aluminum chloride system.

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