Mullite fibers prepared by a sol-gel method using tartaric acid

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Long mullite fibers were prepared by a sol-gel method using aluminum nitrate, tartaric acid and tetraethylorthosilicate (TEOS). Thermogravimetry-differential scanning calorimetry (TG-DSC), Fourier transform infrared (FTIR) spectrometer, 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 were obtained by sintering at 1200 °C, and theirs main phase was indentified as mullite.

Key words: Mullite, Fibers, Sol-gel method, Tartaric acid.

Introduction

Mullite (3Al₂O₃·2SiO₂) has been recognized as an outstanding ceramic material, for its high temperature strength, creep resistance, thermal and chemical stability, low thermal expansion coefficient and good dielectric properties [1]. An important potential application of mullite is as fiber reinforcement of metals, ceramics and resins. In the Al₂O₃-SiO₂ system, only mullite exists as a stable compound, which occupies the structure of edge-shared AlO₆ octahedral chains parallel to the c-axis bounded by aluminum and/or silicon tetrahedral [2].

The main processes for the manufacture of ceramic fibers can be classified as melt-spinning processes and sol-gel spinning processes [3]. Usually, the melt-spinning method has been adopted for the synthesis of ceramic fibers with a low melting point. So, this method is not suitable for the preparation of mullite fibers, since mullite has a high melting point of 1850 °C.

Many successful processes have been reported in the preparation of mullite fibers by the sol-gel method [4, 5]. In most of the starting materials, aluminum isopropoxide (AIP) was selected as the Al source, because its polymerization was responsible for the appropriate spinning viscosity. On the other hand, since the expensive AIP was involved in the synthesis process of mullite fibers, the process was limited in applications, although mullite fibers are obtained, with smooth surfaces and dense microstructures. Zhang [3] fabricated mullite fibers using aluminum nitrate (Al(NO₃)₃·9H₂O), tetraethylorthosilicate (TEOS) with commercial grade polyvinyl butyral (PVB) as the binder. But the fiber length was about 40 cm. It is desirable to fabricate long fibers of mullite using an Al source low in cost with high fiber quality.

In the dissertation, long mullite fibers were prepared by a sol-gel method using aluminum nitrate (AN), tartaric acid and tetraethylorthosilicate (TEOS) as raw materials. The process, crystallization phase and surface morphology were also investigated in detail.

Experimental procedure

Preparation of samples

The starting materials used were aluminum nitrate (Chemicals grade, Xi’an reagent factory, Xi’an, China), tartaric acid (Chemicals grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), TEOS (Chemicals grade, Tianjin kermel chemistry Co. Ltd., Tianjin, China) and ethanol (Chemicals grade, Xi’an reagent factory, Xi’an, China).

The mullite fibers were prepared according to the processing steps shown in Fig. 1. The alumina sol was prepared by mixing H₂O, aluminum nitrate and tartaric acid with a molar ratio of 10:1:1.5, followed by heating in a water bath (80 °C). The viscous sol was then dissolved in absolute alcohol. Then, a proper amount of TEOS was added to the alumina solution to obtain a stoichiometric Al/Si ratio of 3:1. Then, the precursor solution was concentrated to obtain a spinning sol in a 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 gel fibers were then sintered at various temperatures between 800 and 1200 °C for 1 h with a heating rate of 1K·minute⁻¹.

Characterization techniques

For the gel fibers, their thermal behavior was measured by a TG/DSC instrument (SDT Q600, TA
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Instrument, American) with a heating rate of 10 K·minute⁻¹ in flowing air, and Fourier transform infrared (FTIR) spectra was recorded on a infrared spectrometer (6700, Nicolet Magna, American) with the samples as KBr pellets. X-ray diffraction analysis was carried out on a X-ray diffractometer (D/max2400, Rigaku, Japan) using CuKα radiation, and a step size of 0.05 ο/second. The morphologies of heat treated fibers were characterized by scanning electron microscopy (JSM-6390 LV, JEOL, Japan). All tests were done at room temperature.

Results and Discussion

The alumina sol was prepared by a synthesis and hydrolysis reaction which took place between aluminum nitrate and tartaric acid in an aqueous solution during the stirring and heating. The main chemical reactions may be simplified as the following equations (1), (2) and (3), although the actual reactions were complex [6, 7]:

\[
\begin{align*}
\text{Synthesis:} & \quad 3\text{C}_4\text{H}_6\text{O}_6 + 2\text{Al} (\text{NO}_3)_3 \rightarrow \text{Al}_2(\text{C}_4\text{H}_6\text{O}_6)_3 + 6\text{HNO}_3 \\
& \quad \text{HNO}_3 \rightarrow 1/2\text{H}_2\text{O} + 1/4\text{O}_2 \uparrow + \text{NO}_2 \uparrow \\
\text{Hydrolysis:} & \quad \text{Al}_2(\text{C}_4\text{H}_6\text{O}_6)_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{C}_4\text{H}_6\text{O}_6
\end{align*}
\]

TEOS was hydrolyzed under an acidic condition, and then condensation polymerization took place when the precursor solution was concentrated in a water bath (60 °C). Then, a sol of spinnable alumino-silicate was obtained, mainly because the hydroxyl groups and carboxyl groups of tartaric acid could react with the Al and Si ions or particles, and an organic–inorganic hybrid structure was formed. The overall reactions can be written as equation (4):

\[
\text{Hydrolysis:} & \quad \text{Al}_2(\text{C}_4\text{H}_6\text{O}_6)_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{C}_4\text{H}_6\text{O}_6
\]

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

Fig. 2. Photograph of the precursor gel fibers.

The maximum length of the gel fibers achieved was about 20 cm. The length of fibers can be increased only by the addition of suitable spinning additives in the sol, e.g., polyvinyl butyral (PVB), polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), etc [3, 8]. The length of the gel fibers can achieve about 80 cm by adding 20 wt% PVB as a spinning additive (Fig. 2). The long fibers were obtained because the hydroxyl groups and ester groups of PVB react with the alumino-silicate sol and an organic-inorganic hybrid structure was formed [3]. These overall reactions can be written as:

\[
\begin{align*}
\text{Synthesis:} & \quad 3\text{C}_4\text{H}_6\text{O}_6 + 2\text{Al} (\text{NO}_3)_3 \rightarrow \text{Al}_2(\text{C}_4\text{H}_6\text{O}_6)_3 + 6\text{HNO}_3 \\
& \quad \text{HNO}_3 \rightarrow 1/2\text{H}_2\text{O} + 1/4\text{O}_2 \uparrow + \text{NO}_2 \uparrow \\
\text{Hydrolysis:} & \quad \text{Al}_2(\text{C}_4\text{H}_6\text{O}_6)_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{C}_4\text{H}_6\text{O}_6
\end{align*}
\]

(4)

(5)
The length and diameter of fibers were influenced by the viscosity and surface tension of the spinning sol, the speed of hand drawing, etc. Further research about these factors is being followed.

The TG/DSC curves of the precursor gel fibers are shown in Fig. 3 with a heating rate of 10 K·minute⁻¹. The DSC curve of the gel fibers exhibited two endothermic peaks at about 90 °C and 360 °C, and two exothermic peaks at about 420 °C and 998 °C. The endothermic peaks are assigned to the evaporation of the residual ethanol and the decomposition of hydroxides in the gel fibers, whereas the two exothermic peaks are assigned to the decomposition of the organic component and crystallization of mullite [3], respectively. The TG curve of the gel fibers showed a weight loss around 62 wt% at 800 °C, while almost no further weight loss appeared with increasing temperature.

In the above thermal analysis, the most interesting phenomenon is the exothermic peak at 998 °C. The exothermic peak indicated better homogeneity of the Al and Si components at a molecular scale [9, 10], which will be beneficial for obtaining a mullite phase at lower temperature.

The FTIR spectra of alumina gel and precursor gel fibers are shown in Fig. 4. As can be seen, the bands at 3400 cm⁻¹ and 1630 cm⁻¹ are assigned to the O-H stretching modes and bending modes of adhesive and constitution water as well as tartaric acid and alcohols, respectively. The band at 2500 cm⁻¹ is assigned to the O-N stretching mode of nitric acid. The bands at 1310 cm⁻¹ and 820 cm⁻¹ may be assigned to the C-O stretching mode and bending mode, respectively. The bands at 1430 cm⁻¹ and 1380 cm⁻¹ are assigned to the CH₂ and CH bending modes. As can be seen, a little nitric acid was present in the samples.

The alumina gel was obtained by condensation of alumina sol in a water bath (80 °C). As shown in Fig. 4(a), the band observed at 1400 cm⁻¹ corresponds to Al-OH bonding mode [11]. The stretching modes of the Al-O-Al linkage are observed at 620 cm⁻¹ and 820 cm⁻¹ [12]. When the alumina solution was condensed, polycondensation could occur. So, the stretching modes of Al-O-Al linkage are observed [5].

As shown in Fig. 4(b), the bands at 1100 cm⁻¹ and 480 cm⁻¹ are assigned to the stretching and bending modes of Si-O-Si in the network. TEOS hydrolysed under an acidic condition, and condensation polymerization took place when the sol was concentrated. So, the Si-O-Si linkages are obtained [5]. The band at 580 cm⁻¹ has a shoulder at 720 cm⁻¹, which maybe assigned to the (Si, Al)-O-(Si, Al) linkages bending mode [13]. The (Si, Al)-O-(Si, Al) linkages were obtained because the condensation polymerization reaction between aluminum and silicon hydroxide occurred simultaneously [5].

The X-ray diffraction patterns of gel fibers sintered at 800, 1000, and 1200 °C are shown in Fig. 5. Only an amorphous phase was present when the fibers were sintered at 800 °C. The mullite phase was obtained in the samples sintered at 1000 °C, while only the mullite phase was observed in the sample sintered at 1200 °C. From the DSC and XRD results, it can be concluded that mullitization of the gel occurred at a temperature of about 1000 °C.

The formation temperature of the mullite nucleation sites (Al₂O₃ sites) is close to 1000 °C, together with the further densification by the growth of particles and clusters to exceed the critical size of mullite nuclei, resulted in rapid mullitization with a very high nucleation density [14].

Fig. 3. TG and DSC curves of mullite precursor gel fibers.

Fig. 4. FT-IR spectra of (a) alumina gel and (b) mullite precursor gel fibers.
The mullitization temperature was considered to be an important criterion in the assessment of the mixing scale of the Al and Si components in the gels. Temperatures in the range of 1600-1700 °C are required to achieve complete mullitization by mixing alumina and silica particles in the micrometre size range. Complete mullitization temperatures of 1000-1100 °C can be attained for a mixing scale at the molecular level [15].

SEM micrographs of mullite fibers sintered at 1200 °C are shown in Fig. 6. The fibers had a diameter of about 50–60 µm.

Conclusions

Long mullite fibers were prepared using aluminum nitrate, tartaric acid and TEOS as raw materials, with a molar ratio of 3:4.5:1. The length of the gel fibers achieved was about 80 cm by adding PVB as a spinning additive. The main phase was mullite in the samples sintered at 1000 °C, without other crystal phases present. Mullite fibers were obtained when the gel fibers were sintered at 1200 °C.

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References