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Preparation of mullite-silica-enstatite composites fibers by sol-gel method

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ABSTRACT

Mullite-silica-enstatite composites fibers were prepared using aluminum nitrate, magnesia and tetraethyl orthosilicate as raw materials, lactic acid as complexing agent. Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD), and scanning electron microscopy (SEM) analysis were used to characterize the properties of the gel and ceramic fibers. The composites fibers were obtained by sintering gel fibers at 1200°C for 2h, with a smooth surface and dense microstructure. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Mullite-silica-enstatite
composites;
Fibers;
Sol-gel method.

INTRODUCTION

Mullite ($\text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$) 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]. In the Al_2O_3 - SiO_2 system, only mullite exists as the stable compound, which occupies the structure of edges-shared AlO_6 octahedron chains parallel to c-axis bounded by aluminum and/or silicon tetrahedron^[2]. Mullite displays various Al to Si ratios referring to the solid solution $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10+x}$, with x ranging between about 0.2 and 0.9 (about 55 to 90 mol% Al_2O_3). The compositional variation is based on the exchange of $\text{O}^{2-} + 2\text{Si}^{4+} \rightarrow 2\text{Al}^{3+} + \square$, which introduces one oxygen vacancy^[3]. The properties of mullite may be affected by the exchange. Further research continues to define better these correlations.

An important potential application of mullite is used as fiber reinforcement. Main processes for the manu-

facture of ceramic fibers can be classified as melt-spinning processes and sol-gel spinning processes^[4]. Usually, the melt-spinning method was adopted for the synthesis of ceramic fibers with low melting point, so it was not suitable for the preparation of the mullite fibers.

Many successful processes have been reported for the preparation of mullite fibers by the sol-gel method^[5-7]. In most of starting materials, aluminum isopropoxide (AIP) was selected as Al source. On the other hand, since the AIP which is expensive was involved in the synthesis process of mullite fibres, the process is limited to its widespread applications, although mullite fibers are obtained, with smooth surface and dense microstructure^[4].

The Al_2O_3 - SiO_2 system had a lowest melting point when the content of alumina was 9wt%. The liquid phase could be obtained in the rich silica system at low temperature. The liquid phase could help mullite firing, and mullite fibers with a dense microstructure could be ob-

tained. Otherwise, one of the directions of modification of ceramics in order to attain desirable properties is creating a secondary crystalline phase^[8]. It is desirable to fabricate the mullite fibers contained silicon and magnesium phases, with high quality using low-cost Al source.

Recently, the composites fibers were prepared by sol-gel method using aluminum nitrate, magnesia and tetraethyl orthosilicate (TEOS) as raw materials, lactic acid as complexing agent. The results indicated that the composites fibers contained mullite, silica and enstatite ($Mg_2[Si_2O_6]$) phases by sintering at 1200°C for 2h.

EXPERIMENTAL PROCEDURE

Preparation of samples

Starting materials used were aluminum nitrate (Chemically grade, Xi'an reagent factory, Xi'an, China), magnesia (Chemically grade, Tianjin kernel chemistry Co. Ltd., Tianjin, China), lactic acid (Chemically grade, Xi'an reagent factory, Xi'an, China), absolute ethanol (Chemically grade, Xi'an reagent factory, Xi'an, China) and TEOS (Chemically grade, Tianjin kernel chemistry Co. Ltd., Tianjin, China).

The mullite based composites fibers were prepared as the processing steps shown in Figure 1. The aluminum-magnesium lactate (AML) sol was prepared by mixing H_2O , aluminum nitrate, magnesia and lactic acid with molar ratio of 10:1:0.25:3, followed by heated in water bath (60°C). The AML sol was then dissolved in absolute alcohol to obtained AML solution. And, a proper amount of TEOS was added in the solution to obtain stoichiometric Al/Si ratio as 0.80. Then, the precursor solution was concentrated to obtain spinning sol in water bath (60°C), and the gel fibers were prepared by pulling a thin glass rod slowly from the sol after immersing. Afterwards the obtained gel fibers were dried at 60°C for 24 h in an oven. The dried gel fibers were then sintered at various temperatures between 800 and 1200°C for 2h with a heating rate of 1°C/min.

Characterization

For the gel fibers, Fourier transform infrared (FTIR) spectra were recorded on 6700 Infrared Spectrometer (Nicolet Magna, American) with the samples as KBr pellets. X-ray diffraction analysis was carried out

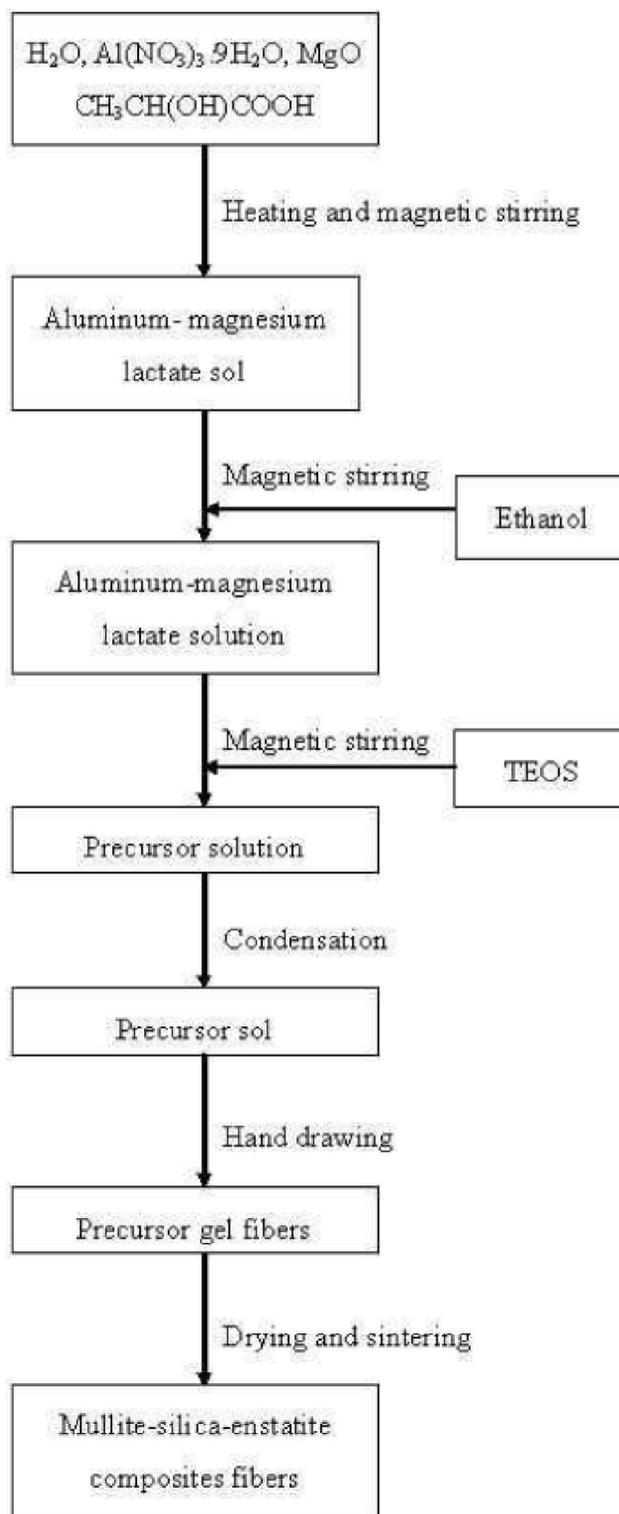


Figure 1 : Schematic view of the production route for mullite-silica-enstatite composites fibers

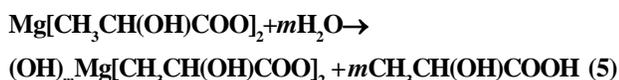
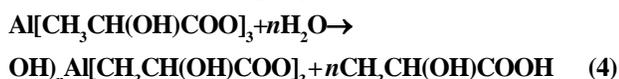
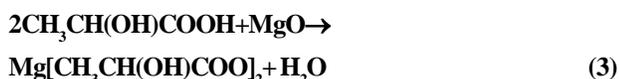
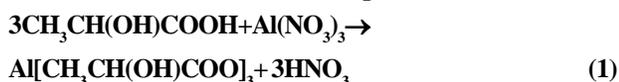
on a DX-2500 X-ray Diffractometer (Dandong Fangyuan, Dandong, China) using CuK α radiation, with a step width of 0.05°/s. Morphologies of heat treated fibers were characterized by scanning electron micros-

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copy (JSM-6390LV, JEOL, Japan). All tests were done at room temperature.

RESULTS AND DISCUSSION

Aluminum-magnesium lactate sol was prepared while the reaction took place between aluminum nitrate, magnesia and lactic acid in aqueous solution during the stirring and heating. The main chemical reactions can be simplified as the following equation (1)-(5), though the actual reactions were complex^[9-11]:



Where n are 0, 1, 2, or 3; m are 0, 1, or 2.

TEOS hydrolysis under the acidic condition (AML solution), and condensation polymerization took place when the sol was concentrated.

According to these hydrolysis and condensation polymerization reaction, the spinning precursor sol was obtained.

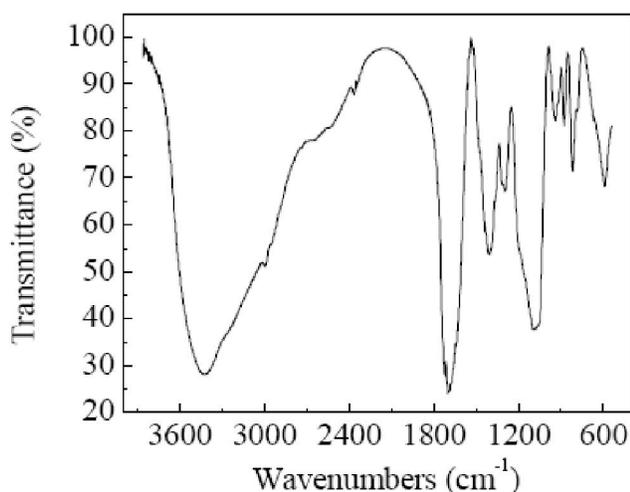


Figure 2 : FT-IR spectra of the precursor gel fibers

The FTIR spectra of precursor gel fibers are shown in Figure 2. As can be seen, the bands at 3430cm^{-1} and 1100cm^{-1} are assigned to the O-H stretching modes

and bending modes of adhesive and constitution water as well as lactic acid and ethanol OH, respectively. The band at 2650cm^{-1} maybe be assigned to the O-N stretching mode of nitric acid. The bands at 1680cm^{-1} is assigned to the C=O stretching mode. The band at 940cm^{-1} is assigned to the C-C stretching mode. The bands at 1300cm^{-1} and 880cm^{-1} may be assigned to the C-O stretching mode and bending mode, respectively. As can be seen, a little of nitric acid and some lactic acid was present in the samples.

As shown in Figure 3, the band observed at 1420cm^{-1} corresponds to Al-OH bonding mode^[12]. The stretching modes of Al-O-Al linkages are observed at 620cm^{-1} and 820cm^{-1} ^[13]. When AML solution was condensed, hydrolysis and condensation polycondensation could occur. So, the stretching modes of Al-O-Al linkages are observed. The band at 1050cm^{-1} is assigned to the stretching mode of Si-O-Si of the network. The condensation polymerization of TEOS also took place when the sol was concentrated. But, the Mg-O mode is not observed.

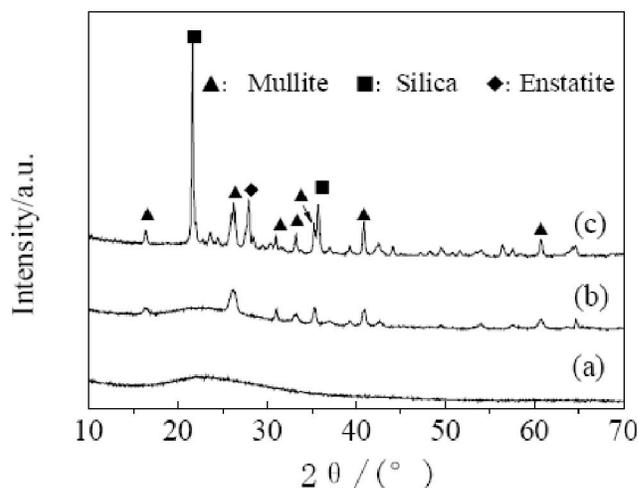


Figure 3 : XRD patterns of the precursor fibers heated at (a) 800, (b) 1000 and (c) 1200°C for 2h

The X-ray diffraction patterns of precursor gel fibers sintered at 800, 1000 and 1200°C are shown in Figure 3. The main phase was amorphous in the samples after being sintered at 800°C. Mullite phase was obtained after being sintered at 1000°C. Otherwise, silica and enstatite phase were observed after being sintered at 1200°C.

Usually, the formation of mullite by sol-gel methods starts at 1000°C and no other phase remains in the

samples after full reaction^[14-16]. The formation of the mullite nucleation sites (AlO_5 sites) closes to 1000°C , moreover, the further densification by the growth of particles and clusters exceeds the critical size of mullite nuclei, which results in rapid mullitization with a very high nucleation density.

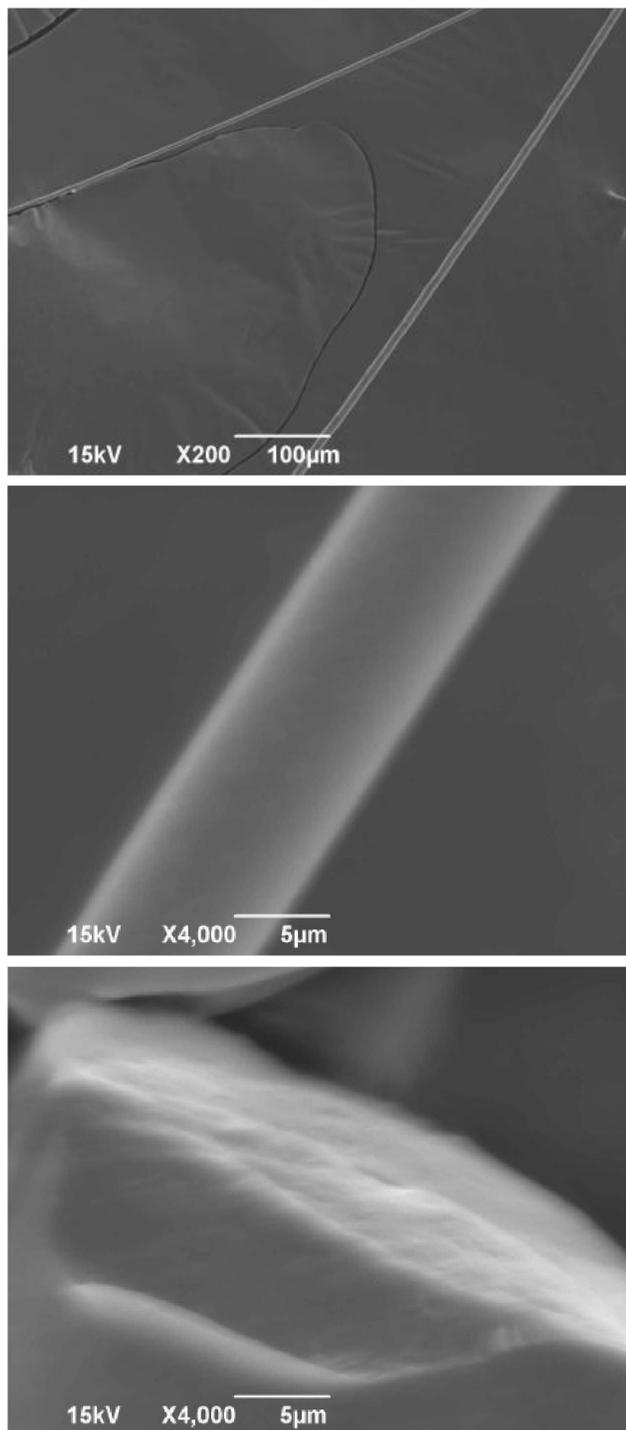


Figure 4 : SEM microstructures of the precursor fibers heated at 1200°C for 2h

SEM micrographs of precursor fibers sintered at 1200°C for 2h are shown in Figure 4. The fibers had a diameter ranged from 20 to 40 μm , with a smooth surface and uniform diameter.

CONCLUSION

The composites fibers were prepared by sol-gel method using aluminum nitrate, magnesia and tetraethyl orthosilicate (TEOS) as raw materials, lactic acid as complexing agent. Mullite phase was obtained after being sintered at 1000°C . Silica and enstatite phase were observed after being sintered at 1200°C . The composites fibers were obtained by sintering at 1200°C for 2h, with a smooth surface and uniform diameter.

ACKNOWLEDGMENTS

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REFERENCES

- [1] S.Li, H.Du, A.Guo; Preparation of self-reinforcement of porous mullite ceramics through in situ synthesis of mullite whisker in flyash body [J]. *Ceramics International*, **38(2)**, 1027-1032 (2012).
- [2] R.Naghizadeh, F.Golestani-fard, H.R.Rezaie; Stability and phase evolution of mullite in reducing atmosphere [J]. *Materials Characterization*, **62(5)**, 540-544 (2011).
- [3] A.Douy; Crystallisation of amorphous spray-dried precursors in the Al_2O_3 - SiO_2 system [J]. *Journal of the European Ceramic Society*, **26(8)**, 1447-1454 (2006).
- [4] Y.Zhang, Y.Ding, J.Gao; Mullite fibers prepared by sol-gel method using polyvinyl butyral [J]. *Journal of the European Ceramic Society*, **29(6)**, 1101-1107 (2009).
- [5] K.C.Song; Preparation of mullite fibers from aluminum isopropoxide-aluminum nitrate-tetraethylorthosilicate solutions by sol-gel method [J]. *Materials Letters*, **35(5-6)**, 290-296 (1998).
- [6] X.T.Chen, L.X.Gu; Sol-gel dry spinning of mullite fibers from AN/TEOS/AIP system[J]. *Materials Research Bulletin*, **44(4)**, 865-873 (2009).

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- [7] X.Chen, L.Gu; Structural evolution of sol-gel derived mullite fibers with different solid contents during sintering [J]. *Journal of Materials Processing Technology*, **209(8)**, 3991-3998 (2009).
- [8] E.Medvedovski; Alumina-mullite ceramics for structural applications [J]. *Ceramics International*, **32(4)**, 369-375 (2006).
- [9] A.Apelblat, E.Manzurola, J.Krieken; Solubilities and vapour pressures of water over saturated solutions of magnesium-_L-lactate, calcium-_L-lactate, zinc-_L-lactate, ferrous-_L-lactate and aluminum-_L-lactate [J]. *Fluid Phase Equilibria*, **236(1-2)**, 162-168 (2005).
- [10] L.Zhang, H.Eckert; Multinuclear NMR studies on the sol-gel preparation of sodium aluminophosphate glasses [J]. *Solid State Nuclear Magnetic Resonance*, **26(3-4)**, 132-146 (2004).
- [11] L.Zhang, C.C.Araujo, H.Eckert; Aluminum lactate-an attractive precursor for sol-gel synthesis of alumina-based glasses [J]. *Journal of Non-Crystalline Solids*, **353(13-15)**, 1255-1260 (2007).
- [12] J.Chandradass, M.Balasubramanian; Sol-gel processing of alumina fibers [J]. *Journal of Materials Processing Technology*, **173(3)**, 275-280 (2006).
- [13] P.Padmaj, G.M.Anilkumar, P.Mukundan; Characterisation of stoichiometric sol-gel mullite by fourier transform infrared spectroscopy [J]. *International Journal of Inorganic Materials*, **3(7)**, 693-698 (2001).
- [14] H.Tan, Y.Ding, J.Yang; Preparation of mullite fibres by sol-gel processes using aluminum carboxylates and tetraethylorthosilicate [J]. *Materials Science and Technology*, **27(2)**, 568-572 (2011).
- [15] X.T.Chen, L.X.Gu; The sol-gel transition of mullite spinning solution in relation to the formation of ceramic fibers[J]. *Journal Sol-Gel Science and Technology*, **46(1)**, 23-32 (2008).
- [16] X.T.Chen, L.X.Gu; Spinnability and structure characterization of mullite fibers via sol-gel ceramic route[J]. *Journal of Non-Crystalline Solids*, **355(48-49)**, 2415-2421 (2009).