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Journal of the European Ceramic Society 34 (2014) 465–473

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Synthesis and characterization of sol–gel derived continuous spinning alumina based fibers with silica nano-powders

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Received 11 June 2013; received in revised form 12 August 2013; accepted 15 August 2013
Available online 25 September 2013

Abstract

Silica nano-powders were used as the Si source to substitute acidic silica sol in the SiO_2–Al_2O_3 sol mixture for benefiting the sintering of the fibers at 1250 °C. With the increase of nano-silica, grain diameter and porosity of the fibers decreased firstly and increased subsequently, a minimum value of 35.86 nm and 0.86% was exhibited at the nano-silica content of 20%. The solid content, linear growth model and homogeneity of the precursor sol were not affected by the presence of nano-silica, although the continuous spinning length became low. NMR Analysis of ^{27}Al indicated that polymerization degree of the sol was enhanced by nano-silica. The nano-particle contributed to the reduced intermolecular distance of gel, so the appropriate content existed for resulting the reduced grain size and compact structure of the fibers.

Keywords: Alumina based fibers; Sol–gel; Silica nano-powders; Nano grains; Spinnability

1. Introduction

Alumina based fibers exhibit excellent properties, such as outstanding high-temperature strength, creep resistance, low thermal expansion coefficient, and good dielectric properties. Comparing with carbon fibers, SiC and other inorganic fibers, alumina based fibers are an attractive alternative because of their stability in oxidizing atmospheres up to 1000 °C.[1–4] It has been reported that alumina based fibers are mainly used in two major areas, as reinforcement of metals or ceramics in the form of continuous fibers and as high temperature insulating material in the form of mats, blankets, boards, etc.[5]

Two main manufacturing processes of ceramic fibers existed, including melt-spinning processes and sol–gel spinning processes. Conventionally, melt-spinning methods are adopted for the synthesis of ceramic fibers with low-melting point.[6,7] Correspondingly the sol–gel technique is employed to synthesize the high-melting point ceramic fibers.[8–12] This technique appears attractive owing to its several obvious advantages, such as low processing temperature, high homogeneity and purity of resulting materials.[13,14] The sol is hydrolyzed and polymerized, then condensed at a certain temperature until an appropriate viscosity ideal for spinning continuous long fibers is achieved. Essentially sol–gel processing is an approach of limiting and controlling physical chemical variability of the surface and interfaces within the material by the production of uniquely homogeneous structures or producing extremely fine-scale (10–100 nm) second phase.[15] Therefore in nature, it is feasible to add nanoparticles into target fibers by using the sol–gel technique.

It is known that materials have uniquely functional properties at nanometre-scale dimensions which could lead to novel engineering systems with highly useful characteristics.[16] Recent research on fibers containing nanoparticles mainly focuses on the organic functional material field and all utilize electrospinning processes. For example, polyethylene oxide (PEO)–ZnO composite photoluminescence fibers were prepared with zinc acetate, tetramethylammonium hydroxide and PEO by the electrospinning method, according to Sui et al.[17] Wang et al.[18] fabricated a kind of polyvinylpyrrolidone (PVP) fibers containing TiO_2 nanoparticles via coupling sol–gel method and electrospinning. Nevertheless inorganic fibers have a broader servicing environment and wider application fields. Currently there are a few researchers involved in this field. Hwang et al.[19] produced core–shell fiber electrodes using a dual

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http://dx.doi.org/10.1016/j.jeurceramsoc.2013.08.015

nozzle electrospinning in a scalable manner. The poly(methyl methacrylate) solutions containing Si nanoparticles and the polyacrylonitrile (PAN) solution were injected into the core and shell channels of the nozzle, respectively. After electrospinning and carbonization, fibers with nanoparticles in the core were wrapped by a carbon shell. However all of these researchers were limited by electrospinning to produce finely separated fibers. Research about electrospun oriented fibers is only at its infancy. Currently electrospinning produces low yield fibrous films, instead of mass manufactured continuous fibers. Sol–gel technique can completely eliminate this defect.

The work presented in this paper is based on the idea that: direct addition of nano-particles in the sol can enhance the solid content of the condensed sol, and will maintain the homogeneous level during the earliest stages of material preparation and be beneficial to the sintering stage. Thus silica nano-powders, instead of metal alkoxides, were directly used as the starting material of sol–gel method. In this work, we fabricated continuous spinning alumina based fibers with compact structure and nano grains using aluminum chlorohydrate (as Al source), acidic silica sol, silica nano-powders (as Si source) and polyvinyl alcohol (as spinning aids) in the water solvent system. With the replacement of SiO_2 sol by silica nano-powders, the Al_2O_3–SiO_2 sol and alumina based fibers were characterized by solid content, viscosity, nuclear magnetic resonance (NMR), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and field emission scanning electron microscopy (FESEM) to study its effect on the sol evolution and the grain growth of fibers.

2. Experimental procedure

About the starting materials, acidic silica sol (SiO_2, 20 nm, Chemical grade, Zhejiang YUDA, China) and nano-silica (SiO_2, 30 nm, Merck KGaA, Germany) were both used as Si source. Aluminum chlorohydrate ($Al_2(OH)_5Cl{\cdot}2H_2O$, ACH, daily chemical, YOTECH Chemical, China), PVA ($[C_2H_4O]_n$, Shanxi Sanwei Chemical Industry Co. Ltd., China) and distilled water (H_2O, Xi'an reagent factory, China) were used as Al source, spinning aids and co-solvent respectively.

Spinning sol was prepared as follows. First of all, ACH was mixed with distilled water at room temperature under vigorously stirring to obtain a transparent sol (transparent sol 1). Acidic silica sol and nano-silica were then mixed successively, stirring for about 3 h to give a transparent sol 2. The weight ratio of effective $[Al_2O_3]/[SiO_2]$ was 85:15 in the mixture sols. Concentrations of the SiO_2 nano-powders were varied by amount of 0, 10, 20, 30, 40, 50 and 60% of effective sum SiO_2. Finally, 5 wt.% PVA solution was added slowly into the sols mixture by magnetic stirring as a spinning aid (sol 3). The mass ratio of $[PVA]/[Al_3O_2]$ was 0.07. Firstly sol 3 was condensed at 60 °C using a water bath, and then was kept at room temperature until an appropriate viscosity was obtained which was suitable for spinning.

Spinning sol 4 was then spun using a laboratory miniature dry-spinning apparatus (self-made in lab), and collected by a bobbin winder. The gel fibers were dried at 40 °C for 2 h. The dried gel fibers were calcined in air at 1250 °C with a slow heating rate of less than 1 °C/min at low temperature, and also a fast rate of more than 10 °C/min was used for the temperature above 800 °C. The sintering time was 20 min. The processing steps are shown in Fig. 2.1.

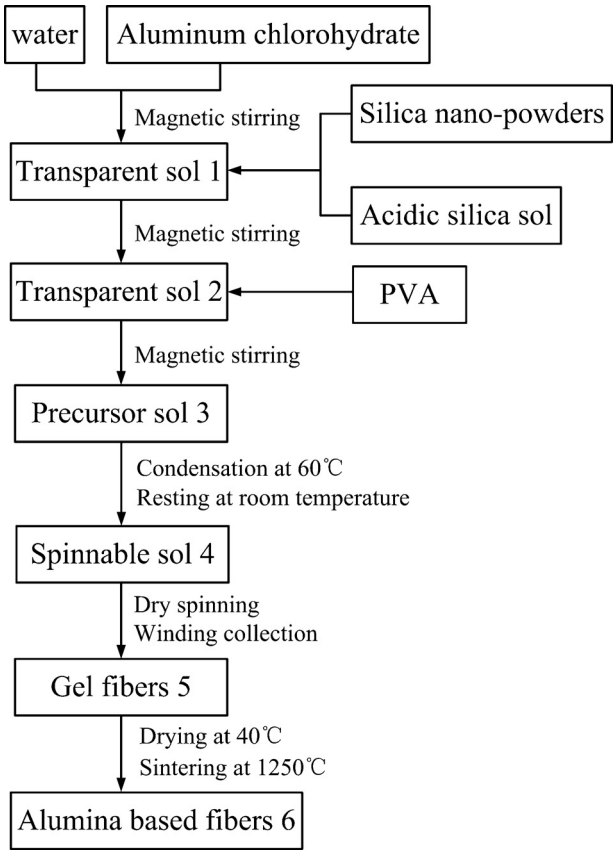

Fig. 2.1. Schematic view of the preparation route for sol–gel derived alumina based fibers.

Rheological and viscosity measurement of the spinning sols were carried out by using the HADV-2 viscometer (Shanghai Nirun Tech. Co. Ltd., Shanghai, China) at 25 °C at different shear rates (60, 80 and 100 rpm), and the average value was calculated. The prepared fibers were characterized by thermo-gravimetric analysis/differential scanning calorimetry (TG/DSC), X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM). The TG/DSC was measured on SDTQ600 (TA, USA) with a heating rate 10 °C/min and sample weight was about 15 mg. The XRD patterns were obtained on the D/max-3c diffractometer (Rigaku Co. Ltd., Japan) at 40 kV and 100 mA using Cu Kα radiation with a step width of 0.02° and a counting time of 0.3 s. The FESEM observation was done on S-4800 instrument (HITACHI, Japan). Measurements of the grains size and porosity of fibers were done on the FESEM photographs.

3. Results and discussion

3.1. Spinnability and spinnable mechanism of the sols

Continuous spinning length is one of the evaluation parameters of the spinnability of the sols. In this paper, the best