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Microstructure and elastic modulus of electrospun Al_2O_3-SiO_2-B_2O_3 composite nanofibers with mullite-type structure prepared at elevated temperatures

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ABSTRACT

In the present work, Al_2O_3-SiO_2-B_2O_3 composite nanofibers with mullite-type structure were prepared using electrospinning technique. The microstructure and elastic modulus of the composite nanofibers obtained at elevated temperatures were studied. The results showed that $Al_4B_2O_9$ phase formed at 900 °C and then transformed to $Al_{18}B_4O_{33}$ at 1100 °C. Mullite was also detected in the nanofibers prepared at 1100 °C. Amorphous SiO_2 existed in all samples even the calcination temperature reached up to 1400 °C. The continuous and uniform structure of the composite nanofibers was kept after calcining at different temperatures, while rougher surface was evident due to the growth of the grain caused by the elevated temperature. An increase of elastic modulus of the samples from 9.47 ± 1.91 GPa to 27.30 ± 2.61 GPa was observed when calcination temperatures increased from 800 °C to 1400 °C.

1. Introduction

Continuous mullite ($3Al_2O_3{\cdot}2SiO_2$) fibers, as a kind of promising ceramic materials, have been used in various areas, including insulation, filtration, catalyst and reinforcement of metals, ceramics and resins due to their outstanding dielectric properties, chemical stability, low thermal conductivity and excellent high temperature properties [1–3]. Amongst all the physical properties of ceramic fibers, good flexibility is essential to allow the fiber products to be converted into required shapes and forms, and expands their applications eventually [1,4]. With respect to mullite fibers, a serious problem is their relatively high elastic modulus [4], which lead up to a low flexibility and restrict their applications consequently.

To date, researches prove that diminishing the grain sizes is an available approach to improve the flexibility of mullite fibers [1,5]. To achieve this purpose, adding B_2O_3 into the mullite was investigated. EA Richards et al. [5] found that B_2O_3 is the most effective additive to decrease the grain sizes of mullite fibers compared with P_2O_5, Cr_2O_3 and their mixture. They also confirmed that small grain size was correlated with high tensile strength of the fibers. Though the addition of B_2O_3 significantly decreased the mullite formation temperature, the boron doped mullite fibers still showed enormous advantages when they were converted into textiles (i.e. yarn, sleevings or fabrics) owing to their relatively high flexibility. Currently, the most widely known flexible commercial ceramic fibers in Al_2O_3-SiO_2-B_2O_3 ternary system are Nextel™ 312 fibers produced by 3 M Company (USA) [4,6]. The chemical composition of the fibers in wt.% is 62% Al_2O_3, 24% SiO_2 and 14% B_2O_3. The filament tensile modulus of Nextel™ 312 fibers is about 150 GPa, which is the smallest among the Nextel™ ceramic oxide fibers, indicating the best flexibility and lowest weaving difficulty. Nextel™ 440 fiber is another type of Al_2O_3-SiO_2-B_2O_3 composite fiber with lower B_2O_3 content (2 wt.%) and a higher modulus (190 GPa) [4]. With the exception of the good flexibility, the introduction of B_2O_3 also decreases the density of mullite fibers. This feature is benefit to reduce the total weight of those objects which the Al_2O_3-SiO_2-B_2O_3 ternary ceramic fibers are used in large amount.

For ceramic fibers, which involve mullite fibers undoubtedly, reducing their diameters was also a meaningful method to improve their flexibility [1,7]. Particularly, ceramic nanofibers, apart from the good flexibility, are also gifted with larger surface area to volume, lower density, lower conductivity of heat and other superior properties, and have drawn a lot of attention [8,9]. Obviously, the smaller diameters of ceramic fibers are related to the disparate preparation technology. The conventional techniques used to prepare ceramic fibers are melt extraction [10], melt spinning [11,12], pyrolysis of cured polymer fiber [13] and sol-gel processing [14–16], etc. However, such methods are

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still not available to produce ceramic fibers in nano-scale independently as investigated previously. Consequently, the method of a combination of electrospinning and sol-gel processing was developed in the past two decades to prepare continuous ceramic nanofibers. Dai et al. [17] prepared ultra-fine alumina-borate oxide fibers for the first time using this method. Soon afterwards, other ceramic nanofibers such as SiO_2 [18], Al_2O_3 [19], ZrO_2 [20] and so on were derived. As to electrospinning technique, it involves the use of a high voltage to charge the surface of a polymer solution droplet through a spinneret, and then a liquid jet ejects. The jet is stretched to form continuous and ultrafine fibers due to the electric field force acting on them. While fabricating ultrafine ceramic fibers using this method, precursor sol is initially added into a polymer additive solution to acquire the composite spinning solution. Then the spinning solution is electrospun to obtain the as-spun composite nanofibers and the as-spun fibers are calcined to produce the desired products. To summarize, this method has been demonstrated to be an effective way to generate various kinds of ceramic nanofibers with high purity, good homogeneity, fine grain sizes and sufficiently small diameters, and has been regarded as a promising technique in generating continuous ultrafine ceramic fibers in the future.

As has been introduced, mullite nanofibers were also prepared by electrospinning combined with sol-gel method. Wu et al. [21] prepared high purity polycrystalline mullite nanofibers with diameters of about 200 nm using aluminum nitrate (AN), aluminum isoproxide (AIP) and tetraethyl orthosilicate (TEOS) as raw materials. They focused on the influence of the PVP content on the morphology development of mullite nanofibers and they observed that large grains formed in the fibers after heat treatment at 1200 °C. M. Mohammad Ali Zadeh et al. [22,23] also studied the impact of the proportions of polymer additives on the properties of spinning solution and morphology of mullite precursor nanofibers, but their fiber products were not uniform and could not retain a stable structure under high temperature. Chen et al. [24] fabricated mullite fibers with diameters ranging from 400 nm to 10 um using electrospinning technique. They considered that the most convenient way to obtain fibers with well-controlled diameters was to control the solid concentration and the rheology of the mullite sol. Peng et al. [25] prepared uniaxially aligned mullite fibers by electrospinning, but the average diameter of the fibers calcined at 1300 °C was 1.78 um, which were not in nanoscale apparently. Based on these introductions it can be seen that researchers are still focusing on fabricating pure mullite without the additions of second phases, which means that continuous mullite nanofibers with B_2O_3 added synthesized by electrospinning have not raised much interest yet. S. Tanriverdi et al. [26] once prepared electrospun ceramic nanofibers in Al_2O_3-SiO_2-B_2O_3 ternary system with a Al_2O_3:SiO_2:B_2O_3 ratio of 1:8:1. But the fibers could hardly be regarded as a type of mullite fibers since SiO_2 had crystallized at 1000 °C due to its large amount and the final products lost fiber-like structure after calcined at temperatures beyond 1000 °C. Apart from that, the synthesis of Al_2O_3-SiO_2-B_2O_3 composite nanofibers has never been reported. Thus, it is meaningful to prepare the Al_2O_3-SiO_2-B_2O_3 composite nanofibers with mullite-type structure. Additionally, little attention has been paid on the mechanical properties of the electrospun mullite nanofibers and little research has been done regarding the relationship between elastic modulus and calcination temperatures. Consequently, the aim of the present work was to prepare mullite-type nanofibers in Al_2O_3-SiO_2-B_2O_3 ternary system with good flexibility. The phase transformation, microstructure evolution and room temperature elastic modulus of the composite nanofibers after calcining at elevated temperature were investigated.

2. Experimental

2.1. Synthesis of stable spinning solution

Aluminum acetate ($Al(OH)_2(OOCCH_3)\cdot 1/3H_3BO_3$) purchased from Strem Chemicals, Inc. (Boston,USA) was used as the sources of alumina and boron oxide. Boric acid contained in the aluminum acetate acts as a stabilizer. Tetraethyl orthosilicate (TEOS) with a SiO_2 content of 28 wt. % offered by Xilong Chemical Co., Ltd. (Guangzhou, China) was used as the silica source. Deionized water and pure ethanol were used as the solvent to prepare the composite precursor sols. The molar ratio of Al:Si:B of the target nanofibers was designed to be 3:1:1. To obtain homogeneous precursor sols, aluminum acetate stabilized with boric acid, TEOS, deionized water and pure ethanol were mixed together simultaneously. The mass percentages of the four materials in the mixture were 15, 7.2, 38.9 and 38.9 wt.%, respectively. The mixture solution was stirred at 40 °C for 12 h to obtain the composite precursor sol. Polyvinyl pyrrolidone (PVP, Mw = 1,300,000) provided by Bodi Chemical Reagent Plant (Tianjin, China) was applied as the polymer additive. It was added into alcohol and stirred at room temperature for 3 h to acquire a 16 wt.% PVP alcohol solution. Then the PVP solution was mixed with the precursor sol with a mass ratio of 3:2 and stirred for 1 h to obtain a composite spinning solution which was homogeneous and suitable for electrospinning.

2.2. Electrospinning and calcination

The composite spinning solution was transferred into a plastic syringe equipped with a metallic needle. The needle was connected to a negative voltage supply. During electrospinning, the voltage supply was set to generate a voltage of −7.45 kV and the feeding rate controlled by a syringe pump was kept at 0.45 ml/h. A piece of aluminum foil was used as the collector and the distance between the needle tip and the collector was 15 cm. After electrospinning, the as-spun composite nanofibers mats were dried by an oven at 50 °C for 5 h to remove the residual solvent. The dried fiber mats were put in Al_2O_3 plates and calcined in a muffle furnace from room temperature to 800 °C in air circumstance with a heating rate of 5 °C/min. After calcining at 800 °C for 1 h, PVP and organic matters existed in the as-spun fibers were basically decomposed and removed. Then the nanofibers were calcined at temperatures varied from 800 to 1400 °C for an extra 1 h to obtain the Al_2O_3-SiO_2-B_2O_3 composite nanofibers.

2.3. Characterization

The X-ray powder diffraction (XRD) data of calcined samples were recorded by a diffractometer (D8 Advance, Bruker, German) with CuKα radiation in the region of $10 < 2\theta < 80^{\circ}$. Diffraction peaks were indexed with Jade 6.0 software. Fourier transform infrared (FT-IR) absorption spectra of the calcined nanofibers were recorded using a spectrometer (Model 6700, Nicolet, USA) at wave number ranged from 400 to 1500 cm^{-1}. The calcined fibers were ground to powders to prepare KBr pelltes for FT-IR measurements. The morphology of the nanofibers was examined by scanning electron microscopy (SEM) (Quanta FEG 250, FEI, USA) and transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan). To prepare SEM samples, the as-spun nanofibers should not be exposed to air for too long to avoid the absorption of the moisture and protect the fiber morphology. The calcined nanofibers were sputtered with relatively thicker gold layer due to the low conductivity. The diameters of the nanofibers were calculated using the image analysis software Image J. As to the samples to be detected by TEM, calcined fibers were placed into ethanol and treated by ultrasonic subsequently. The suspensions with separated nanofibers were obtained and then were dripped on carbon-coated copper grids, where the nanofibers were left for TEM examination. The elastic modulus of a single ceramic nanofiber was measured using the three-point bending method by atomic force microscope (AFM) (Multimode 8, Veeco, USA) under the force mode. For AFM samples preparation, Al_2O_3-SiO_2-B_2O_3 nanofibers were placed into ethanol and ultrasonic treated for 30 min to obtain a suspension. The suspension was dropped on a customized silicon wafer with many etched grooves, each of which