Highly aligned continuous mullite nanofibers: Conjugate electrospinning fabrication, microstructure and mechanical properties

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Abstract

Continuous mullite nanofibers with highly aligned structure were fabricated by conjugate electrospinning technique combined with the sol-gel method. Aluminum acetate stabilized with boric acid and tetraethyl orthosilicate (TEOS) were used as raw materials. Aligned and continuous as-spun nanofibers were prepared first. After calcining at 1000 °C, the obtained mullite nanofibers retained decent alignment and continuous structure despite the decomposition of PVP and other organics. Such fibers were composed of Al_b2O_9 phase and amorphous SiO_2. The elastic modulus of a single mullite nanofiber was 12.27 ± 1.77 GPa and the tensile strength of the aligned mullite nanofiber bundle was 32.21 ± 3.73 MPa.

1. Introduction

Mullite fibers, with outstanding physical and chemical stabilities, are widely used in areas of filtration, catalyst, insulation and also used as reinforcements for resins, metals and ceramics [1–3]. They have been converted into textiles, such as yarn, sleeves or fabrics, to expand their applications [1,4]. In order to produce mullite textiles, continuous mullite fibers with aligned structure are required. In recent years, extensive researches has been focused on ceramic nanofibers due to their better flexibility, larger surface-area, lower thermal conductivity and other superior properties, compared with the commercial ceramic fibers [5–7]. Therefore, it is an effective approach to use mullite nanofibers to produce mullite textiles with improved performance. And consequently, preparing aligned and continuous mullite nanofibers with good flexibility and high tensile strength is of great significance.

In the past two decades, electrospinning has drawn increasing attention for its unique advantages in producing continuous ceramic nanofibers [8,9]. Compared to other modified devices of electrospinning, conjugate electrospinning is more effective to prepare aligned nanofibers [10,11]. During conjugate electrospinning, two oppositely placed metal needles are connected to positive and negative voltages, respectively. Positively and negatively charged fibers eject from the two needles will attract and stick to each other. Continuous and aligned fibers are obtained after collecting the merged fibers using a rotating drum. Based on the previous literatures, little research work has been done regarding fabricating the aligned continuous mullite nanofibers, especially by the means of conjugate electrospinning. Thus, the current work was focused on such a topic. The microstructure and mechanical properties of the aligned continuous mullite nanofibers were investigated.

2. Experimental procedure

Aluminum acetate stabilized with boric acid (Al(OH)_2(OOCCH_3))_1/3H_3BO_3 and tetraethyl orthosilicate (TEOS) were used as the sources of alumina and silica. Deionized water and alcohol were used as the solvents. Polyvinyl pyrrolidone (PVP, Mn = 130,000) was used as the polymer additive. Aluminum acetate, TEOS, deionized water and ethanol with the corresponding mass percentages of 15, 7.2, 38.9 and 38.9 wt% were mixed and stirred for 12 h at 40 °C to prepare the precursor sol. A 16% PVP alcohol solution and the precursor sol were mixed with a mass ratio of 3:1 to obtain the spinning solution.

Fig. 1 shows the schematic diagram of the conjugate electrospinning setup for collecting aligned as-spun nanofibers. The angle...
The distance between the two needles equipped on the syringes was 120°. The distance between the needle tips was 20 cm. During electrospinning, the positive and negative voltages were kept at +3.5 and −3.5 kV, respectively. The feeding rate of each syringe was 0.45 ml/h. The rotating drum with a linear velocity of 1.8 m/s was used to collect as-spun nanofibers (shown in the right in Fig. 1). The fibers were heated to 800 °C at a heating rate of 5 °C/min and maintained for 1 h, and then were calcined at 1000 °C for an extra 1 h to obtain the mullite nanofibers. For tension test, as-spun fibers were converted into fiber bundle along the alignment before calcination.

Fiber morphology was observed by scanning electron microscopy (SEM) (Quanta FEG 250, FEI). X-ray powder diffraction (XRD) data was recorded by a diffractometer (D8 Advance, Bruker). Fourier transform infrared (FT-IR) absorption spectrum was recorded using a spectrometer (Model 6700, Nicolet). The grain structure was observed by transmission electron microscopy (TEM) (JEM-2100F, JEOL). The elastic modulus of a single nanofiber was measured using atomic force microscope (AFM) (Multimode 8, Veeco) by the three-point bending method as reported by Ding [12]. The tensile strength of the nanofiber bundles was measured using a fiber tensile tester (XS (08) XT-3, Xusai).

3. Results and discussion

Fig. 2(a) shows that highly aligned continuous as-spun nanofibers with an average diameter of 1152 nm were obtained. Though a small fraction of fibers were in disordered patterns, as evidenced in SEM micrographs with lower magnifications, the integral perspective was good. After calcining at 1000 °C (Fig. 2(b)), the average fiber diameter decreased to 589 nm due to the decomposition of PVP and other organics, but these reactions exerted little influence on the decent alignment and continuous structure. These results revealed that fabricating highly aligned continuous mullite nanofibers by conjugate electrospinning was effective.

As mentioned, a large proportion of boron was introduced by aluminum acetate. In Al2O3-SiO2-B2O3 ternary system, Al2O3 tended to react with B2O3 to form γ-Al2O3 or reacting with SiO2 to form mullite [13]. Thus, it was reasonable that the diffraction peaks in the XRD pattern in Fig. 2(c) were identified as Al4B2O9 phase. Besides, the broad hump between the 2θ of 13° and 29° was detected as amorphous SiO2. Such phase composition was confirmed by the FT-IR results (Fig. 2(d)). The insert in Fig. 2(d) listed the absorption bands and the corresponding assignments [13,14]. Structural units of BO3, AlO4 and AlO6 were the main components of Al4B2O9 phase and the absorption band at 1099 cm−1 was due to the stretching vibration of Si–O–Si in amorphous SiO2. TEM micrograph in Fig. 2(e) revealed that the Al4B2O9 grains (< 20 nm) were disconnected since they were normally surrounded by amorphous SiO2. Thus, the grain growth would be limited and the fibers structure at high temperatures would be stable. The interplanar spacings displayed in Fig. 2(f) were 0.53 nm and 0.34 nm, corresponded to the (1 1 0) and (2 1 0) crystal planes of the Al4B2O9 phase, respectively. The insert ED pattern further confirmed the above analyses. Additionally, a thin amorphous layer was observed on fiber surface, indicating that the crystal grains had not grew to the surface layer.

Fig. 3(a) and (b) display the 3D image of a single nanofiber with a diameter of 612 nm suspended over a groove and a representative force curve obtained by AFM. The elastic modulus was calculated to be 12.27 ± 1.77 GPa, which was much smaller than that of the micron-scale mullite fibers. This difference was attributed to the higher surface-to-volume ratio and the tiny cracks of the nanofibers [15]. The low modulus value indicated the good flexibility of the nanofibers. This was confirmed in Fig. 3(c) since the aligned mullite nanofibers could be easily wrapped on a glass rod without any breakage. One reason for the good flexibility was that the small Al4B2O9 grains had minor effect to impede deformation. Another reason should be that the atoms in amorphous SiO2 were less constrained and their bond energy was not too strong, thereby making the nanofibers easy to deform.

The schematic diagram and photograph showing the tension test of the aligned fiber bundle is illustrated in Fig. 3(d) and a typical stress-strain curve was displayed in Fig. 3(e). The elastic region was not smooth due to the slippages of inner fibers. The post-failure region was not straightly down because of the incomplete
fracture of the fiber bundle (shown in the insert in Fig. 3(e)). Such features were caused by the disordered nanofibers discussed above. However, the tensile strength of the fiber bundles, which measured to be 32.21 ± 3.73 MPa, was still much higher than that of the random electrospun ceramic fiber mats reported in Ref. [6]. Beyond the aligned structure, the fracture morphology of a single fiber (Fig. 3(f)) revealed that few defects existed in the fiber, which also contributed to the high tensile strength.

4. Conclusions

This study presented the fabrication, microstructure and mechanical properties of the highly aligned continuous mullite nanofibers. Conjugate electrospinning was confirmed to be an effective fabrication method. $\text{Al}_4\text{B}_2\text{O}_9$ formed, instead of $\text{c-Al}_2\text{O}_3$ or mullite phase, due to the presence of $\text{B}_2\text{O}_3$. The good flexibility was attributed to the fine $\text{Al}_4\text{B}_2\text{O}_9$ grains and the
presence of amorphous SiO2. The high tensile strength was ascribed to the aligned structure and the defects-free feature of the nanofibers.

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References


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