Fabrication of transparent alumina (Al$_2$O$_3$) nanofibers by electrospinning

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Abstract

Transparent alumina nanofibers have been fabricated from a suitable inorganic–organic composite solution by spinning in an electric field (strength $\sim$70–90 kV/m) applied between the tip of a needle and the target plate. Upon firing and sintering under carefully pre-selected time–temperature profiles (heating rate, temperature and soak time), high-purity and crystalline alumina nanofibers retaining the morphological features of the electrospun composite fibers were obtained. Tools such as laser Raman spectroscopy, X-ray diffraction, scanning and transmission electron microscopy together with energy dispersive spectroscopy and selected area electron diffraction were employed to follow the systematic evolution of the ceramic phase and its morphological features in the fired fibers.

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1. Introduction

Electrospinning (e-spinning) is one of bottom-up approaches that are gaining increasing attention in recent years for the fabrication of ceramic nanostructures. The technique of e-spinning was discovered more than 90 years ago [1,2] and has been exclusively and successfully used for making polymer nanofibers for the past several decades [3–13]. The technique uses external electrical forces to produce polymeric fibers of diameters in the range of 50–500 nm, depending upon a number of process parameters such as the solution concentration, strength of the applied voltage between a drop of the precursor solution (or melt) and the collecting surface, deposition time and separation between the fiber tip and the collector [14–16]. When the electrical forces at the surface of the drop overcome the surface tension, the solution or melt is ejected as an electrically charged jet and shoots towards the oppositely charged electrode. Upon reaching the collector surface, it gets neutralized and collects as dry nanofibers.

The possibility of extending this concept to ceramic systems has opened a new era in nanoscale research during the past couple of years. It is envisaged that by controlling the jet orifice, one can control the diameter of the resulting nanofibrillar structures, thereby modifying their key properties such as structure, elasticity, strength and resistance to fracture, thermal and electrical conductivity, and optical characteristics, etc. [17–19]. Thus, it has seen its adaptation to ceramic systems and several papers and patents have since been published and issued [18–25]. The processing and structure relationships in the electrospun ceramic fibers have recently been reviewed [26]. Potential applications of this technology also include biological membranes for immobilized enzymes and catalysts, artificial blood vessels, anti-septic wound dressing materials, aerosol filters, to name a few. By using an orthogonal set up (electrospinning simultaneously at right-angles), a matty design of a given ceramic or two ceramic nanofibers can also be fabricated [27,28]; a possible application of such a design would be the clothing membranes for protection against fire burns, battlefield threat and environmental hazards.

Alumina (Al$_2$O$_3$) is a well-known structural material among functional ceramics – in the area of catalysis, microelectronics and optics [29,30] – both in pure or doped form as well as in combination with others. Its applications range from pure and transparent thin films as optical windows to particulates, platelets and fibers as strengthening reinforcements in lightweight ultra-strong metal matrix composites. Dai et al. [31] have reported the synthesis of alumina-borate composite fibers by electrospinning a viscous mixture (1:10 w/w) of boric acid-stabilized aluminum acetate in 10% aqueous solution of PVA. They obtained fibers thicker than 0.5 $\mu$m upon firing the composite up to 1400 $^\circ$C. Electrohydrodynamics (EHD) technique has...
been employed by Loscertales et al. [32] for making alumina nanofibers using hybrid organic/inorganic sols in a core-shell design whereby α-alumina fibers with diameter in the range of ~150 nm were obtained.

Giving due cognizance to the potential application of ceramic nanofibers in general and of alumina nanofibers in particular, we report in this communication the fabrication, processing and characterization of transparent one-dimensional alumina nanofibers via e-spinning. In the present work, target composition was first electrospun in the form of ceramic-polymer (‘cermer’) composite fibers from a suitable homogeneous mixture of a simple aluminum precursor solution and a polymer. The as-spun fibers were subsequently processed to yield the desired alumina ceramic. The transformation of cermer to ceramic was followed by a series of heat-treatment and the systematic phase evolution. The structural and morphological features of the products subsequent to each of such heat-treatments were verified by laser Raman spectroscopy (LRS), X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS) and transmission electron microscopy coupled with energy dispersive spectroscopy and selected area electron diffraction (TEM–EDS–SAED) techniques.

2. Experimental procedure

High-purity aluminum 2,4-pentanedionate [Al(CH$_3$COC-HCOCH$_3$)$_3$] from Alfa-Aesar, MA, USA (purity 99.995%) was used as the precursor for the synthesis of alumina fibers. Typical concentration of the aluminum pentanedionate solution (AP) used in this work was ~6.85 × 10$^{-2}$ mol l$^{-1}$ in ACS grade acetone (Alfa-Aesar, 99.5% +). Granular polyvinyl pyrrolidone (PVP, average molecular weight ~1.3 × 10$^6$, Alfa-Aesar) was used as the polymeric component and the solution. Fifteen weight percentage of PVP solution was made by dissolving PVP powder in reagent grade ethanol (Fisher Chemicals, PA, USA) under constant and vigorous stirring. Due to the pronounced volatility of ethanol during and after the preparation, and the tendency of the solution to dry out and leave a stiff gel in the container upon prolonged storage, the PVP solution was prepared only when electrospinning was to be carried out. However, the aluminum precursor solution in acetone could stay clear and last for much longer duration without forming any sol; it did not require any stabilization either.

For the electrospinning experiments, equal volumes of the precursor solutions (AP and PVP) were thoroughly stir-mixed into a homogeneous viscous solution, after which the mixture was drawn into a 5 ml capacity Benton-Dickenson clinical syringe (VWR International, IL, USA). A precision-tip 23 gauge stainless steel needle (EFD Inc., RI, USA) was attached to the syringe, which was mounted on a programmable syringe pump (KDS-100) that could be operated either in a horizontal or vertical configuration. The preferred orientation of the syringe pump in this work was horizontal (no difference was noted in the quality of the fibers produced in either configuration). A custom-made dc power supply with the high voltage system (30 kV maximum) from Ultra Volt (FL, USA) using a circuit design developed at NASA Glenn Research Center [33] was used for the fiber e-spinning. The circuit allows the application of a steady dc voltage in a gradual fashion between the fluid droplet and the neutralizer. One terminal of the power supply was connected to the needle, while the other was connected to the grounded collector plate.

Previously, we have used a collector plate made by folding several thicknesses of Al foil into 4 in. × 4 in.; for the ease of sample handling and subsequent processing, ceramic plates were also used where a small 1 in. × 1 in. Al foil was attached to the back of the dish with double-side tape and the electrode was hooked to the foil [34,35]. This allowed the fibers to be collected directly onto the ceramic plate. In the present work, a modified design of collector plates (shown in Fig. 1) was used to enhance the fiber collection area.

Two (4 in. × 4 in.) stainless steel plates were employed. The plates were kept about an inch apart and connected together to a common junction by soldering short lengths of electrical wires to the center of the plates at the back. This allowed the fibers to spread across the plates including the empty space between them. In order to minimize the electrostatic/electromagnetic induction effects, the use of metallic components in the vicinity of the e-spinning set-up was totally eliminated by supporting the collector plates against wooden stands held firmly in a porcelain base. The process variables were optimized after considerable simulation and several preliminary experiments.

Using the power supply, a voltage of 7–9 kV was applied between the needle and the collectors in order to initiate the e-spinning. After the voltage was turned on, the syringe pump was started. The voltage was tweaked precisely by adjusting the voltage knob in small steps in both the directions until the fibers began to form steadily and collect on the plates placed about 4 in. away from the tip of the needle. A flow rate of 0.03 ml/h was chosen and the cermer fibers were spun continuously with short intermittent interruptions of the run for periodic cleaning of the clogged needle-tip from time to time.

After spinning was complete, small amounts of the as-spun composite fibers were used for characterization by Raman spectroscopy and scanning electron microscopy. The remaining fibers were collected on zirconia crucibles and fired at 1000, 1300 and 1500 °C for 1 h in two stages. Various batches of dry cermer fibers were first heated slowly at a ramp rate of 0.5 °C/min up to 500 °C (soak time, 1 h) followed by a second firing up to...
to 1000, 1300 or 1500 °C for 1 h at the same heating rate of 0.5°/min. The small heating rates were chosen so as to ensure the removal of organic components without destroying the nanofibrillar morphological features in the end product and also to avoid the disintegration of the alumina fibers; it is well known that alumina exhibits rather poor thermal shock resistance, even in bulk. After the furnace was cooled, samples were collected for characterization by a host of analytical techniques, such as, Raman spectroscopy, X-ray diffraction, scanning and transmission electron microscopy, energy dispersive spectroscopy and selected area electron diffraction.

3. Results and discussion

Fig. 2 shows Al2O3-PVP cermer fibers formed in real-time on the twin collectors with a taut cloth-like distribution. Fig. 3 shows the scanning electron micrographs (acquired on a Philips XL30 FEG SEM) of the same. Identical morphological features of individual fibers with large aspect ratio can be easily seen.

The SEM pictures of the composite fibers fired for 1 h each at 1000 and 1300 °C are shown in Fig. 4. As can be readily seen, the fibrillar attributes observed in the as-spun composite are fully retained in the fired samples, with considerable decrease in the fiber diameter.

The energy dispersive spectrum (EDS) acquired on the fibers fired at 1000 °C for 1 h, shown in Fig. 5 indicates the presence of aluminum and oxygen alone. The elemental quantification (within the ±3% permissible error limit) performed by the standardless ZAF correction method yielded the average aluminum concentration to be 43.76 wt.% (31.57 at.%) which is in rather
large deviation from 52.93 wt.%, had the product been stoichiometric alumina (Al_2O_3) after this heat-treatment.

However, it is well known that the formation and crystallization of aluminum oxide goes through a number of phase transition schemes, one of which involves the formation of boehmite (aluminum hydroxy oxide) phase, AlO(OH), particularly in the case of aluminum hydroxide or other complex precursors. The most accepted pathway of dehydration followed by several sequential transitions from a polymeric, partially disordered state to the crystalline α-alumina via a number of intermediates can be represented as [36–38]:

\[ \text{AlO(OH)} \text{ (boehmite)} \rightarrow \gamma \text{-Al}_2\text{O}_3 \rightarrow \delta \text{-Al}_2\text{O}_3 \rightarrow \theta \text{-Al}_2\text{O}_3 \rightarrow \alpha \text{-Al}_2\text{O}_3 \]

The theoretical weight fraction of aluminum in boehmite is 45%, which is in good agreement with that obtained from the EDS analysis of the fibers fired at 1000 °C (Fig. 5). Thus, it is likely that at this stage, the aluminum precursor in the AP–PVP composite is reduced to boehmite instead of the target phase, alumina.

The transmission electron micrographs of the composite fired at 1500 °C are shown in Fig. 6; on average the fibers are ~150 nm across the diameter and are transparent.

The quantitative analysis of the TEM–EDS spectrum (shown in Fig. 7) of the fibers acquired after they were calcined at 1500 °C for 1 h yielded a value of 56.4 wt.% aluminum in the calcined fibers, thereby confirming that fibers possessing the morphology shown in Fig. 6 are indeed those of alumina.

It is natural to speculate the presence of carbon as an impurity in the fired samples as a result of the degradation of PVP in the as-spun composite upon heat-treatment. It is, however, rather hard to detect carbon if formed, by XRD, especially if it is present as trace impurity, but it is possible to identify it easily by Raman spectroscopy since carbon is strongly Raman active. The distinct D and G peaks of carbon are observed around 1332–1350 and 1560–1600 cm\(^{-1}\), respectively [39–41].
Fig. 7. EDS signature in the electrospun fibers fired at 1500 °C.

The laser Raman spectroscopy (LSR) data collected in the range 200–2000 cm\(^{-1}\) (LabRam, Jobin-Yvon Horiba Inc., laser excitation wavelength = 633 nm) on the AP–PVP composites fired at 1500 °C for 1 h was compared (after eliminating the background excitation) with that of commercial grade boehmite (from Sasol, TX, USA) and α-alumina powders (Alfa-Aesar). The Raman peaks of the fired fibers were identical to those registered for commercial α-alumina powder and are well documented for the Al–O bonds in alumina specimen [42,43]. Furthermore, there was no signal characteristic of D or G peak of carbon in the spectrum of the fired fibers. Thus, the carbon from the polymeric component as well as from the organic aluminum precursor is completely eliminated when the AP–PVP was fired at 1500 °C.

Fig. 8 shows the room temperature XRD pattern (Philips, PW 3050/60 X’pert Pro) of the fibers fired at 1500 °C, which conforms to that of α-alumina (ICDD card # 74-0323). The selected area electron diffraction (SAED) pattern shown in Fig. 9 also confirmed the evolved phase to be α-alumina.

The powder XRD data was also used to compute the approximate crystallite size in the fiber using Scherrer equation [44–46] that relates the full-width of the most intense peak at the center of the maximum height (FWHM) and the diffraction angle as follows:

\[
s = \frac{K\lambda}{\beta_{1/2} \cos \theta}
\]

where \(s\) is the crystallite size (Å), \(\lambda\) the wave length of the incident radiations, \(\beta_{1/2}\) the FWHM of the Bragg peak, \(\theta\) the Bragg angle of diffraction of the selected peak and \(K\) is the Scherrer constant whose value varies between 0.9 and 1.2 depending upon the shape of the particle under consideration (spherical, cubic or otherwise) [47–49]; we used a value of 0.94 for \(K\) [42] in the Scherrer equation for the two most intense diffractions, viz., (1 0 4) and (1 1 3), which yielded 2.5 nm as an average value for the crystallite size in the alumina fibers calcined at 1500 °C. The TEM picture of the debris of the same fibers (Fig. 10) shows alu-
mina grains to be in the size range of 3–5 nm; this is in contrast to the grain size up to 60 and 110 nm in the alumina-borate fibers calcined for 2 h at 1000 and 1200°C, respectively, reported by Dai et al. [31].

4. Conclusions

Transparent alumina nanofibers have been synthesized via electrospinning of a polymeric composite solution of aluminum 2,4-pentanedionate in acetone. The resulting cermet composites were calcined in a well-conceived temperature–time–heating rate profile at 1000–1500°C to understand the pathway of phase evolution in the ultimate ceramic product with the scope of retention of the fibrillar artifacts. Analytical tools, such laser Raman spectroscopy, X-ray diffraction, scanning and high resolution transmission electron microscopy in conjunction with energy dispersive X-ray spectroscopy and selected area electron diffraction were employed to carry out systematic structural and microstructural characterization of alumina fibers as a function of heat-treatment given to the as-spun material. This investigation showed that transparent α-alumina nanofibers of high structural quality possessing uniform diameter and high aspect ratios could be produced by electrospinning technique.

References