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Short communication

Preparation of low cost alumina nanofibers via electrospinning of aluminium chloride hydroxide/poly (vinyl alcohol) solution

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Abstract

Alumina nanofibers are very suitable materials for use as reinforcement in a great variety of high performance composite materials. Nanosized alumina fibers were prepared from the aluminum chloride hydroxide/poly (vinyl alcohol)/water precursor using the electrospinning technique. The mass ratio of aluminum chloride hydroxide/polymer was 5/1. The fibers were calcinated at 1100 °C. The fibers were characterized by the TGA/DTA, XRD and FESEM methods. Calcinated fibers had a mean diameter of 470 nm and corundum well defined crystal structure.

Keywords: Ceramic fiber; Electrospinning; Nanomaterial

1. Introduction

Alumina has good mechanical and chemical properties and has extensive use as refractory material [1]. Nanofibers having α-alumina structure are excellent candidates to be used as reinforcement for metal, ceramic or polymer matrix composites, as well as to prepare the nonwoven products having good chemical stability and desired microstructure [2]. When particles or fibers are fine, their influence on mechanical properties of the composite is very important, even if the quantity of the fibers added is rather small.

Aluminum oxide has several crystal forms, and corundum is one of the most desired forms for reinforcement of composite materials when mechanical properties are important. There are several methods of producing aluminum oxide fibers either from melt spinning or using precursor fibers that are further calcinated to obtain the desired crystal form. The precursor fibers can be obtained via several chemical concepts of the process, starting from different precursor materials such as alkoxides [3,4], salt solutions [5] or polymer solutions [6]. All these processes use alumina precursor materials that are several times more expensive compared to aluminum chloride hydroxide. Poly (vinyl alcohol), PVA, is a water soluble material and enables good rheological adjustment of solution properties for fiber drawing.

Electrospinning is the method appropriate to produce fine fibers. In the past decade [7], the number of publications concerning electrospinning is increasing and this method becomes very widely used due to the possibility to control the diameter of fibers by adjusting operation conditions of the apparatus. Therefore, electrospinning was chosen to prepare alumina ceramic precursor fibers.

2. Experiment

2.1. Materials

Aluminum chloride hydroxide (Locron L) was purchased from the Clariant company in the crystallized state of $Al_2Cl(OH)_5 \cdot 2.5H_2O$. This product contained 23.5% Al_2O_3, 8.18% Cl, corresponding to an Al/Cl, molar ratio of 2/1. The PVA used had 130,000 molecular weight, and was purchased under the label Mowiol 18-88 (Aldrich).

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All the chemicals were used for water solution preparation without further treatment.

2.2. Preparation of fibers

The procedure for fiber preparation was selected so as to enable preparation of mixtures having desired ratio of aluminum oxide bearing chemical to the polymer in the solution. The 10 mass% aqueous solution of polymer was prepared and adequate quantity of the aluminum chloride hydroxide was added in it. The desired mass ratio of aluminum chloride hydroxide to polymer in the mixture was 5/1. The solution was than stirred on the laboratory mixer for 1 h at 30 °C. The resulting solution contained air bubbles that disappeared after 24 h. The solution was used 2–3 days after preparation.

The electrospinning apparatus used for the experiments in this work was Electrospinner CH-01 (Linari Engineering, Italy). The solution was placed into the 20 ml plastic syringe having a needle of 0.8 mm orifice. The mass flow rate was of 1 ml/h. The high-voltage supply (SPELMANN PCM50P120, USA) capable of producing the 30 kV was used in experiments. The precursor solutions were supplied to the nozzles using syringe pumps of the R100E type (Razel Scientific Instruments, USA). The voltage applied in experiments varied from 20 kV to 28 kV and the mass flow varied from 0.5 to 3 ml/h. The voltage needed to obtain a stable process was of 28 kV and the flow rate was of 0.5 ml/h. The process was conducted in air at ambient temperature of 21 °C and relative humidity in the range 40–60%. The distance between the needle and the collector was fixed at 15 cm. Aluminum foil was placed at the bottom of the installation and over the foil the filter paper producing no ache during combustion was positioned in order to assure the collection of fibers. The fibers were heat treated at 1100 °C during 1 h in air.

2.3. Characterization

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed simultaneously (30–1100 °C range) on a SDT Q600 TGA/DSC instrument (TA Instruments). The heating rate was 20 °C/min and the sample mass was around 10 mg. The furnace atmosphere consisted of dry air at a flow rate of 100 cm^3/min. X-ray diffraction analysis was used to determine the crystallographic phase obtained in heat treated fibers. XRD pattern was recorded with an Ital Structure APD2000 X-ray diffractometer in a Bragg–Brentano geometry using CuKα radiation ($\lambda = 1.5418$ Å) and step-scan mode (range: 20–75° 2θ, step-time: 0.50 s, step-width: 0.02°).

The morphology of the fibers was examined using the FESEM, MIRA3 TESCAN electron microscope operated at 20 kV. The image analysis tool was used to obtain the fibers' diameters distribution of as spun and heat treated fibers.

3. Results and discussion

The behavior of as-spun raw fibers during heating is shown in Fig. 1. The first major step in TGA curve can be attributed to the loss of water that remained in the composition. Further, the significant weight loss in the interval 100–360 °C can be attributed to the removal of PVA that is evaporated up to 420 °C. The thermal degradation of PVA is achieved up to 460 °C and that corresponds to the third weight loss [8]. The last step in TGA curve up to 709 °C could be attributed to the final dehydration of alumina based component that precedes the crystallization at 579 °C [9], which is clearly shown as the first exothermic peak in the DTA curve. The second exothermic peak at 857 °C corresponds to the phase transition and formation of α-alumina structure.

The XRD pattern of nanofibers calcinated at 1100 °C is shown in Fig. 2. The corundum structure of the fibers is

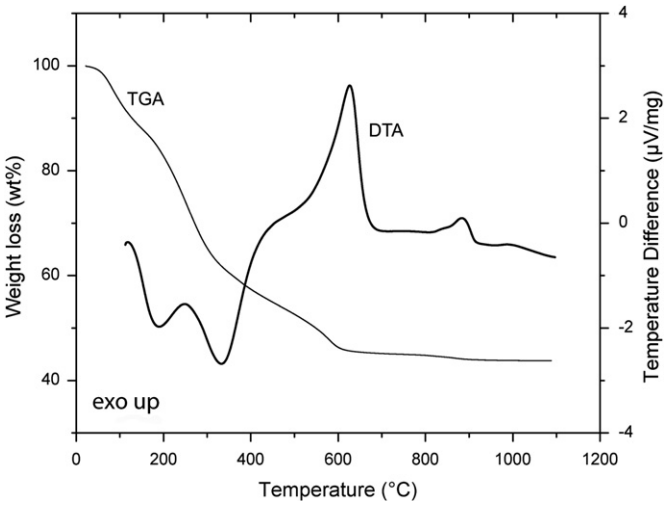

Fig. 1. TGA–DTA curve of the as-spun precursor alumina fibers.

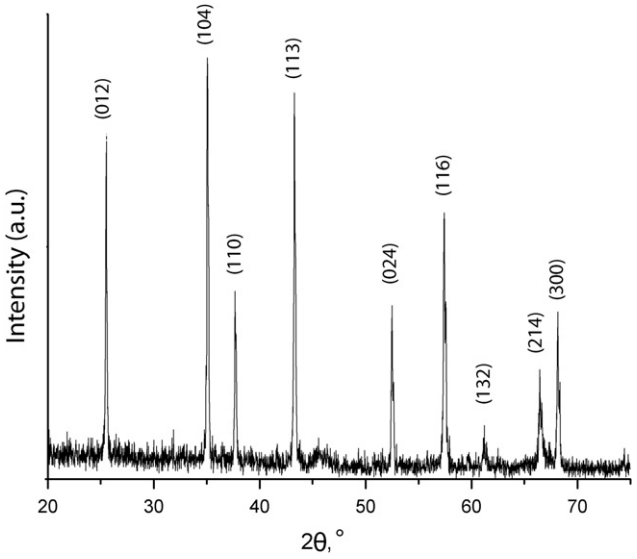

Fig. 2. XRD pattern of alumina nanofibers calcinated at 1100 °C.

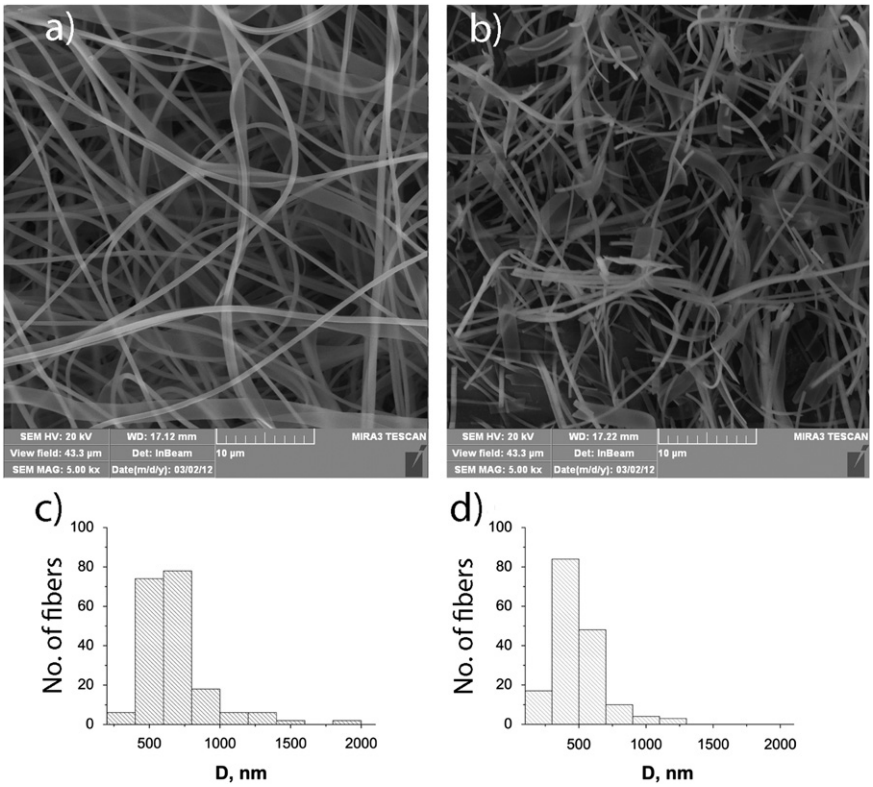

Fig. 3. SEM micrographs of ceramic fibers obtained using the electrospinning method, (a) raw fibers as drawn, magnification 5000 ×, (b) thermally treated fibers, magnification 5000 ×, (c) raw fibers diameter distribution, and (d) thermally treated fibers diameter distribution.

confirmed by comparison of the XRD data to the ICSD 93096 card. The program Powder Cell [10] was used for an approximate phase analysis. The unit cell parameters (a=0.4758 and c=1.2992 nm) of α-Al_2O_3 were obtained by the least-squares method using the program LSUCRIPC [11]. α-Al_2O_3 fibers had the mean crystallite size of around 207 nm. The mean crystallite size was estimated from two most intense diffraction peaks of the α-Al_2O_3 (104) and (113) planes by the Scherrer formula [12] using the appropriate instrumental resolution function for ZnO as a standard.

In addition, XRD pattern of the nanofibers calcinated at 800 °C confirmed that the material under these conditions is of low crystallinity. Only γ-Al_2O_3 phase (ICSD 30267) was recognized in the sample, but there were several broad peaks which could be attributed to boehmite like phase [13].

Fig. 3 shows the FESEM micrographs of the obtained fibers. Raw fibers produced in the experiment and the thermally treated fibers were presented in Fig. 3a and b, respectively. From the observation of these micrographs, it is clear that the fibers are well formed and that the conditions enabled the formation of fibers without the presence of drops in the product morphology. The distributions of fiber diameters obtained from FESEM images are presented in Fig. 3c and d. Statistical parameters characterizing fibers diameters distribution are given in Table 1. The mean diameter of the fibers was reduced to 32% during heat treatment due to the loss of PVA and the shrinkage of the alumina.

Table 1
Statistical parameters characterizing the measurement of the fiber diameter.

Parameter	As spun fibers	Calcinated fibers
Mean (μm)	0.702	0.479
Median (μm)	0.663	0.444
Standard deviation (μm)	0.295	0.179
Sample variance	0.087	0.032
Range (μm)	1.628	0.805
Minimum (μm)	0.364	0.205
Maximum (μm)	1.992	1.010
Count	188	166

4. Conclusion

Aluminum chloride hydroxide/PVA composite fibers were produced using the electrospinning method. The process included the water soluble polymer and aluminum chloride hydroxide that gave the starting mixture suitable for fine fiber formation. The obtained raw fibers did not have the crystalline structure recognizable at the XRD. The calcination was done at 1100 °C and the fibers having average diameter of 470 nm and well defined corundum structure were obtained. The calcinated fibers diameters ranged from 20 to 1010 nm. The control of the fibers diameters and the stability of the process will be the subject of further studies.

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