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Simplified procedure for Al_2O_3 microfibers preparation by the method of electrospinning

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Inorganic micro-fibers of alumina are successfully produced by the method of electrospinning. A simplified procedure of the solution preparation is applied. It is based on single organic precursor dissolved alcohol and excludes the use of assisted polymer usually added to facilitate further fiber formation. Thermal treatment of the as-spun fibers is applied to remove the rests of organic components and for final inorganic mat synthesis.

The morphology of the as-spun and thermally treated fibers is imaged by scanning electron microscopy. Their phase composition is studied by XRD and SAED. The potential for ecology applications of the mat prepared is discussed.

Keywords: alumina fibers, electrospinning, catalytic materials

INTRODUCTION

Al_2O_3 is known as a functional material in many applications, due to its exceptional physical and chemical properties like high electronic conductivity of some alumina phases, chemical inertness and mechanical stability. Thin films, nanoparticles, micro- and nanofibers of Al_2O_3, together with the bulk material, are applied in electrical and electronics industries, catalysis, medicine, ecology etc. [1-4].

The method of electrospinning is discovered at the beginning of the 20 century by Zeleny [5,6]. Now, it is one of the main bottom – up approaches, used for the nanomaterials preparation. The electrospinning is the most versatile and simplest one between all methods for preparing micro- and nanofibers, as drawing with a micro-pipette, template synthesis, phase separation, chemical vapor deposition, and melt blowing [7-9]. It is also potentially scalable and requires little equipment.

In the method, a precursor solution of the fiber material is enclosed in a syringe, putted in a mechanical pump, ensuring a uniform supply of the solution. A high voltage is applied between the needle of the syringe and a metal plate, serving as a fibers collector. The electric field charges the solution. At certain value of the electric force, the surface tension of the precursor solution is overcome, the drop elongates and a jet is formed. The jet dries during the flight to the opposite electrode and solid fibers are collected on it. The process of fiber formation could be controlled by several essential parameters – solution concentration and viscosity, strength of the applied voltage, distance between the drop and the collector, ambient temperature and humidity.

In the years, the method of electrospinning has been applied for preparation of fibers of polymers, hybrid materials and inorganic substances. In the last decade many experiments have been carried out for the production of ceramic fibers by this method: Al_2O_3 [10], ZrO_2 [11], TiO_2 [12], SiC [13], ZnO [14], CaP [15]. The classical receipt for inorganic fibers preparation by the method of electrospinning includes from one side a precursor solution of the Al and from the other - a polymer component, aiming to facilitate the fiber formation process. For preparation of Al_2O_3 fibers, Azad et al. use Al 2,4-pentanedionate and polyvinylpyrrolidone in ethanol as a polymer component of the electrospinning solution [16]. In other research, Panda and Ramakrishna apply two different precursors — aluminium acetate and aluminium nitrate, as well as two types of polymers — polyvinyl alcohol and polyethylene oxide in the process of the Al_2O_3 fibers formation [17].

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The aim of the present work is to synthesize successfully Al_2O_3 fibers, using only an organic precursor for Al. Thus, we eliminate the additional polymer component, used by other authors and simplify the procedure for Al_2O_3 fibers formation.

EXPERIMENTAL

High purity (99.995%) aluminum sec-butoxide ($Al(OCH[CH_3]C_2H_5)_3$) from Sigma-Aldrich Co, USA was used as a precursor for the synthesis of Al_2O_3 fibers. As the viscosity of the pure butoxide was very high, thus obstructing the electrospinning process, a butanol ($CH_3(CH_2)_3OH$, Sigma-Aldrich, 99.9%) was added as a solvent. Experiments were carried out with 3 different solvent to precursor mixing ratios: 3:1, 5:1 and 7:1. In all 3 cases, a stirring for few minutes with a magnetic stirrer was applied and homogeneous solutions were prepared. After that the solutions were drawn into 5 ml syringes, supplied with stainless steel needles. The syringes with the different butoxide contents were mounted successively on the mechanical pump of the electrospinning installation and different mats were collected.

The electrospinning apparatus is home made vertical realization of the set-up. It consists of three main parts – a DC power supply with maximal voltage 30 kV, mechanical mechanism for pumping the solution with constant rate and grounded collector electrode from aluminum foil. At the beginning of the electrospinning process, the pump is started. The piston moves and presses uniformly the solution in the syringe. When the high voltage is not applied yet, the liquid from the syringe drops on the collector. After connecting the needle to one terminal of the power supply and the collecting electrode to the other, under the voltage of about 15 kV, the drops from the electrospinning solution transform into a long jet. When the distance between the tip of the needle and the collecting plate is big enough, the jet accomplishes a movement by spiral trajectory and dries. At the end of its path on the collector, it was completely transformed in a solid fiber. The totality of fibers form so-called non-woven mat. One part of the as-spun fibers is separated for different analysis – Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray difractometry (XRD). The remaining fibers are thermally treated in a programmable oven Dentamatic 6000, Tokmet -TK Ltd. and also analyzed after calcination.

The calcination procedure of the fibers, produced from aluminum sec-butoxide aims to eliminate definitively the rest of the organic precursor and solvent, to stabilize the fibers, to increase their crystallinity and to create predominantly one or another of the crystalline phases of the alumina, depending on the temperature. The as-spun fibers are thermally treated up to 800°C, starting from room temperature and following a special three-step procedure. At the first stage the samples are heated at 120°C in order to eliminate the volatile organic compounds. Fibers calcination is accomplished during the second stage when they are held at 360°C. The third step leads to complete crystallization of the fibers applying thermal treatment at 800°C. Duration of each stage is one hour and the heating rate from one to other stage is 1.6°C/min. The fibers annealing is carried out in a quartz tube with pure dry air flow for better elimination of the volatile components and for complete oxidation of the aluminum to alumina.

The study of the fibers morphology is performed by digitalized scanning electron microscope Philips 515 at accelerating voltage 25 kV. The microstructure of the fibers is carried out by transmission electron microscope JEOL JEM 2100 at accelerating voltage 200 kV. The phase composition of the mat is determined by X-ray powder diffractometer Philips PW 1710/00 and by selected area electron diffraction (SAED) mode of the transmission electron microscope.

RESULTS AND DISCUSSION

Three types of electrospinning solutions, with butoxide to butanol ratios: 3:1, 5:1 and 7:1 were examined. Visually, the best quality fibers and the best electrospinning process were produced at the ratio 5:1. All further results presented in this paper - morphology, microstructure and phase composition, will be referred to this ratio.

Except the properties of the solution, the process of the electrospinning and the quality of the fibers produced depend on the electric field parameters. The SEM micrographs of the as-spun fibers, prepared at three different strengths of the electric field: E<1 kV/cm, E=1 kV/cm and E>1 kV/cm are presented in Fig. 1 a), b) and c), respectively. It is seen that when the strength is E<1 kV/cm or E=1 kV/cm, the fibers growth defectless, while at E>1 kV/cm, the defects like beads appear in the structure of the fibers. More over, in the last case, the fibers are fragile and crushed. In all these experiments, the applied voltage is kept at 15 kV,

but the distance between the needle tip and the fibers collector is varied. At the beginning it is equal to 20 cm, thus ensuring a strength of the electric field E<1 kV/cm. After that, the distance is diminished consecutively to 15 cm and 10 cm for E=1 kV/cm and E>1 kV/cm, respectively. The distance of 10 cm is insufficient for the solvent to leave completely the jet of the solution. Its evaporation continues and after that the jet reaches the collector, thus causing the formation of crushed web.

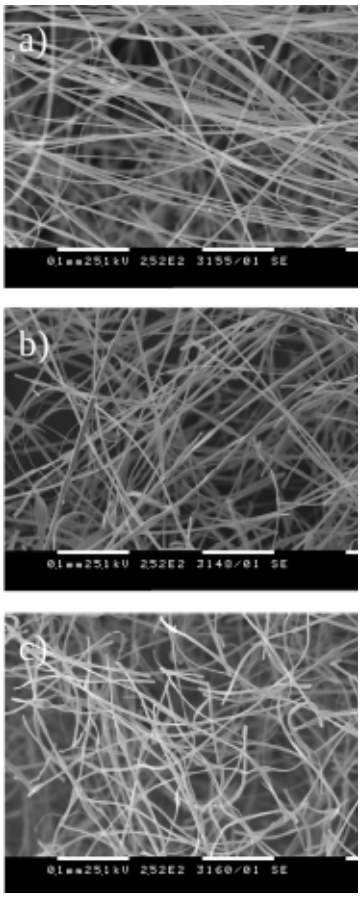

Fig. 1. SEM micrographs of as-spun fibers, prepared at strengths of the electric field: a) E<1 kV/cm, b) E=1 kV/cm and c) E>1 kV/cm.

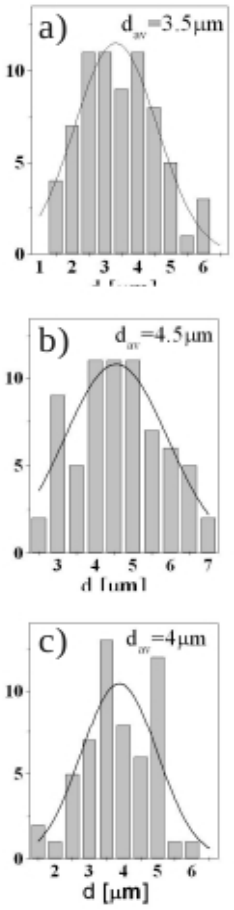

Fig. 2. Diameter distribution of as-spun fibers, prepared at electric field: a) E<1 kV/cm, b) E=1 kV/cm and c) E>1 kV/cm.

The morphology of the fibres after additional thermal treatment at 800°C during 1 hour is imaged in Fig. 3. The micrographs for the different strengths of the electric field are presented, as follows: a) E<1 kV/cm, b) E=1 kV/cm and c) E>1 kV/cm. The fibrillose morphology is stable and remains unchanged after the thermal treatment which indicates that the applied scheme of annealing is suitable for the samples studied.

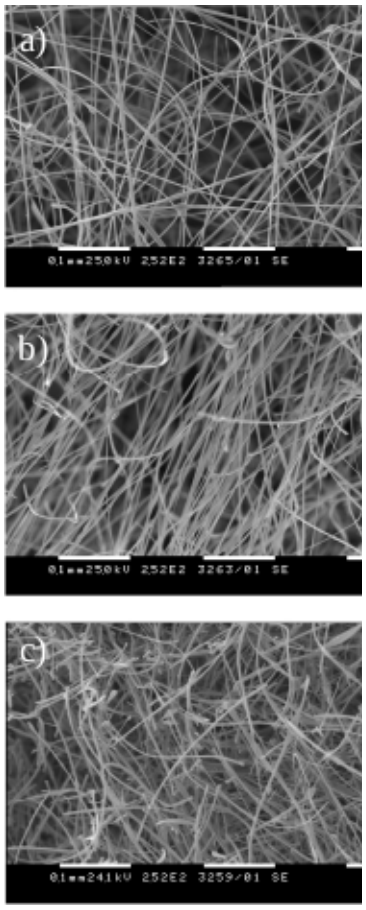

Fig. 3. SEM micrographs of annealed at 800°C fibers, prepared at strengths of the electric field: a) E<1 kV/cm, b) E=1 kV/cm and c) E>1 kV/cm.

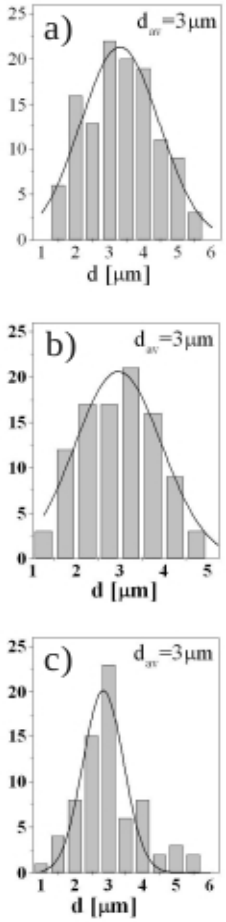

Fig. 4. Diameter distribution of annealed at 800°C fibers, prepared at electric field: a) E<1 kV/cm, b) E=1 kV/cm and c) E>1 kV/cm.

The micrographs in Figs. 1 and 3 are processed with the computer program ImageJ [18] and the distribution of the fibers diameters is presented as histograms in Figs. 2 and 4, respectively. The diameters of the as-spun fibers lie in the interval from 1.5 to 7 μm. Their mean values d_{av}, differ for the different strenght of the applied electric field. When E<1 kV/cm, d_{av} = 3.5 μm, at E=1 kV/cm, d_{av} = 4.5 μm and at E>1 kV/cm, d_{av} = 4.0 μm. The diameters of the fibers annealed at 800°C are situated in the interval from 1 to 5.5 μm. For the annealed fibers, the values of the mean diameter at the three strengths of the electric field are equal to 3 μm. It is seen that, as a result of the thermal treatment, the fibers fold and the values of their diameters diminish with 15% - 25%.

The XRD pattern of the annealed at 800°C Al_2O_3 fibers, prepared at electric field E>1 kV/cm is presented in Fig. 5. The peaks are identified and a presence of the θ-Al_2O_3 with crystalline structure, characterized by monoclinic lattice and lattice parameters a=11,79Å, b=2,91 Å, c=5,62 Å, ß=103,79° [19] is established. These results coincide with the data of other authors [20]. The fibers, studied by XRD are subjected to TEM

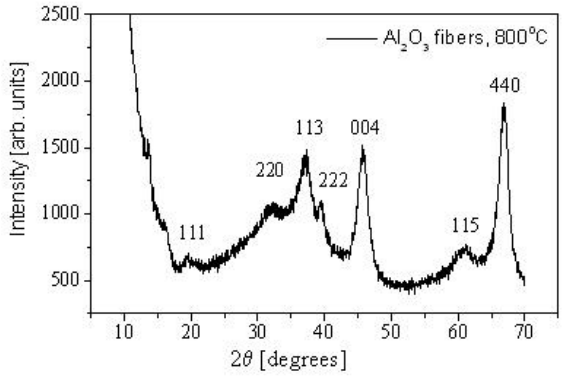

Fig. 5. XRD spectra of annealed at 800°C Al_2O_3 fibers, prepared at electric field E>1 kV/cm.

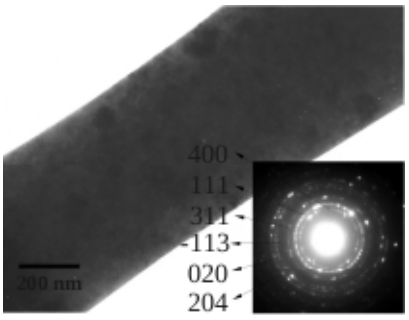

Fig. 6. TEM and corresponding SAED patterns of annealed at 800°C Al_2O_3 fibers, prepared at electric field E>1 kV/cm.

analysis. The TEM micrograph and the corresponding SAED patterns are presented in Fig. 6. The indexation of the polycrystalline diffraction patterns confirms the formation of θ-phase Al_2O_3. This phase of Al_2O_3 is suitable for catalytic application as catalyst support, due to its low surface energy. Combined with suitable metal or ceramic nanoparticles, Al_2O_3 fibers could be used as catalyst in ecological monitoring.

CONCLUSION

Al_2O_3 fibres were successfully produced by the method of electrospinning. A simplified procedure for preparation of the initial solution was proposed. The surface morphology, microstructure and phase composition of the fibers were examined by scanning and transmission electron microscopy and X-ray difractometry. The diameter distribution of the fibers was presented. It was demonstrated that the applied procedure leads to the formation of stable, free of structural defects and well defined Al_2O_3 fibers with diameters below 10 μm. After a precise thermal annealing, catalytically active Θ – phase was identified, that is a prerequisite for potential ecological applications of the fibers.

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ОПРОСТЕНА ПРОЦЕДУРА ЗА ПОЛУЧАВАНЕ НА МИКРОВЛАКНА ОТ АЛУМИНИЕВ ОКСИД ПО МЕТОДА НА ЕЛЕКТРООВЛАКНЯВАНЕ

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(Резюме)

Успешно са получени неорганични влакна от алуминиев оксид по метода на електроовлакняване. За целта е приложена опростена процедура за приготвяне на предилния разтвор. Тя се основава на разтварянето в алкохол на органичен прекурсор, без да се добавя асистиращ полимер, служещ за улесняване образуването на влакната. За отстраняване на остатъци от органичната компонента в получените влакна и за превръщането им в неорганичен мат е приложено термично третиране.

Морфологията на получените влакна, както и на термично третираните е визуализирана със сканираща електронна микроскопия. Фазовият състав на влакната е изследван с помощта на прахова рентгенова дифракция и електронна дифракция. Дискутирана е възможността за приложение на така получените матове от алуминиев оксид за екологични цели.