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Electrospun Alumina Fibers Doped With Ferric and Magnesium Oxides

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Abstract:

It is well known that alumina possesses good mechanical and chemical properties. Nanofibers having α – alumina structure was used as reinforcement for metal, polymer and ceramic matrix composites. In this study, three series of nanofibers were prepared. The first series was made from 10 % water solution of the aluminium chloride hydroxide/polyvinyl alcohol with a mass ratio of 5:1. The other two series were made with the addition of 1 wt.% of $MgCl_2$ or 1 wt.% of $FeCl_3$ regarding the aluminium chloride hydroxide content. Nanofibers were prepared using the electrospinning technique and they were characterized by the TGA/DTA, XRD and FESEM methods. It was proven that addition of $FeCl_3$ into the initial spinning solution lowers the temperature for the corundum structure formation while the addition of $MgCl_2$ results if the formation of mixed oxides that eases the sintering process.

Keywords: *Nanomaterial; Electrospinning; Ceramic fibers.*

1. Introduction

Alumina is often used as a reinforcement in composites due to its high modulus of elasticity, chemical inertness and thermal stability. In the form of fibers alumina has good length to diameter ratio and is a material of choice for the reinforcement of polymer matrix composites [1]. There are different methods for the synthesis of nanofibers such as sol-gel method [2], hydrolysis and hydrothermal method [3], electrospinning method [4-6]. Electrospinning is used as a novel method for preparing inorganic and ceramic fibers with a diameter ranging from several micrometers to tens of nanometers [7, 8]. The temperature of transformation of alumina into its stronger form is rather high and any possibility to obtain this suiTab. structure at lower temperatures is carefully considered. α-Al_2O_3 (corundum), has been the subject of numerous investigations due to its important applications in advanced engineering materials. Hematite (α-Fe_2O_3) is added to alumina to reduce the temperature of the γ-α phase transition, which enables to produce α-Al_2O_3 with a smaller grain size [9]. The small addition of ferrous oxide to the composition enables the transformation to the corundum

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structure at lower temperatures while the obtained material maintains good mechanical properties. Main research for this type of materials is based on bulk materials. It was shown that as alumina and hematite have very similar structures, their crystals are well combined during the heat treatment of materials and the distribution of ferric atoms in the lattice of corundum is very good, especially when low concentrations of ferric atoms is considered [10]. The alumina and ferric oxide particles were good reinforcements in PE based composites when added in situ during the preparation of the polymer. Therefore the preparation of α-Al_2O_3 combined with α-Fe_2O_3 is crucial for the preparation of composites with good mechanical properties [11]. The fibers having this composition are also used as good sorbents for heavy metals [12].

Adsorption of nickel ions from aqueous solutions with nano aluminum oxide synthesized by sol-gel method, was found to exhibit 90 % removal at a lower concentration of adsorbate [13].

Magnesium oxide precursors are added into the alumina basis in order to ease sintering of the material. The sintering is easier and can be performed at lower temperatures due to the presence of spinel structure that occurs and eases the diffusion in the crystal [14].

2. Experimental procedure

Concentration of Fe_2O_3 in alumina was chosen so as to obtain the solid solution of the resulting oxides [15]. The added quantity of $MgCl_2$ was chosen to be comparable to that used as sintering additive.

2.1. Materials

Aluminium hydroxide chloride (Locron L; $Al_2(OH)5Cl•2,5\ H_2O$) was purchased in the crystallized state from the Clariant company. The PVA was purchased from Aldrich under label Mowiol 18 – 88 to 130000 of molecular weights.

2.2. Preparation of electrospun alumina fibers

The electrospinning procedure was used for the preparation of alumina based ceramic fibers. Three series of fibers were prepared. The first series is made from a 10 wt.% water solution of aluminium chloride hydroxide/polyvinyl alcohol with a mass ratio of 5:1 [16]. Into the second series 1 wt.% of $MgCl_2$ was added compared to aluminium hydroxide chloride content and third series had 1 wt.% of $FeCl_3$ compared to aluminium hydroxide chloride content. $MgCl_2$ and $FeCl_3$ were added in order to lower the temperature of the phase transformation. All solutions were stirred on the laboratory mixer for 1 h at 30 ºC. The solutions were then left for 2-3 days to rest in order to obtain clear solutions (i.e. to allow the air bubbles to escape). Electrospinner CH – 01 (Linari Engineering, Italy) was the electrospinning apparatus used for the experiments in this work. The solution was placed into the 20 ml plastic syringe having a needle of 0.8 cm orifice. The high voltage supply (SPELMANN PCM50P120, USA) capable of producing the 30 kV was used in experiments. The precursor solutions were used in supplied to the nozzles using syringe pumps of the R100E type (Razel Scientific Instruments, USA). The voltage applied in experiments varied from 28 kV (for the first series of fibers) to 30 kV (for the second and the third series of fibers). The mass flow varied from 0.3 ml/h for the first series of fibers to 0.1 ml/h for another two series of fibers. The distance between the needle and the collector was 15 cm. Aluminum foil was used as a collector. Obtained fibers were dried and then heat treated at 800 and 900 ºC during 2 h in air.

2.3. Characterization

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed simultaneously (30-1100 ºC range) on an SDT Q600 TGA/DSC instrument (TA instruments). The heating rate was 20 ºC/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. The X – ray powder diffraction was performed using a Bruker D8 Advance diffractometer in Bragg-Brentano transmission mode θ/θ with the primary germanium (Ge (111)) monochromator of Johannson type (CuKα1 radiation). Anodic voltage and anodic current were 40 kV and 30 mA, respectively. The diffraction data were collected by using scintillation counter of NaI (TI) type and the scan-step method in the range of 2θ diffraction angle from 10-90º, with step size of 0.05º and counting time of 6 s per step.
The morphology of the fibers was examined using the FESEM, MIRA 3 TESCAN electron microscope operated at 20 kV. The image analysis tool was used to obtain the fiber diameter distribution.

3. Results and discussion

The behavior of spun fibers during thermogravimetric measurement is shown in Fig. 1 together with the heat flow that was used to monitor the phase transitions of the material.

From the TG curves it could be concluded that the thermal behavior of spun fibers is almost identical in terms of PVA and water elimination from the structure. PVA is eliminated up to 400 °C and water loss is mostly finished at 600 °C. There is the phase transition between 800 and 900 °C that corresponds to the formation of corundum structure that is different in three specimens. The crystallization temperatures (from the DTA-curves) are very similar in all three cases (531.5, 550 and 532 °C, respectively). The temperatures of phase transformations are different: for pure fibers it is 830 °C, while for the doped fibers is much lower: 813 °C and 819 °C (with $MgCl_2$, or $FeCl_3$ respectively).

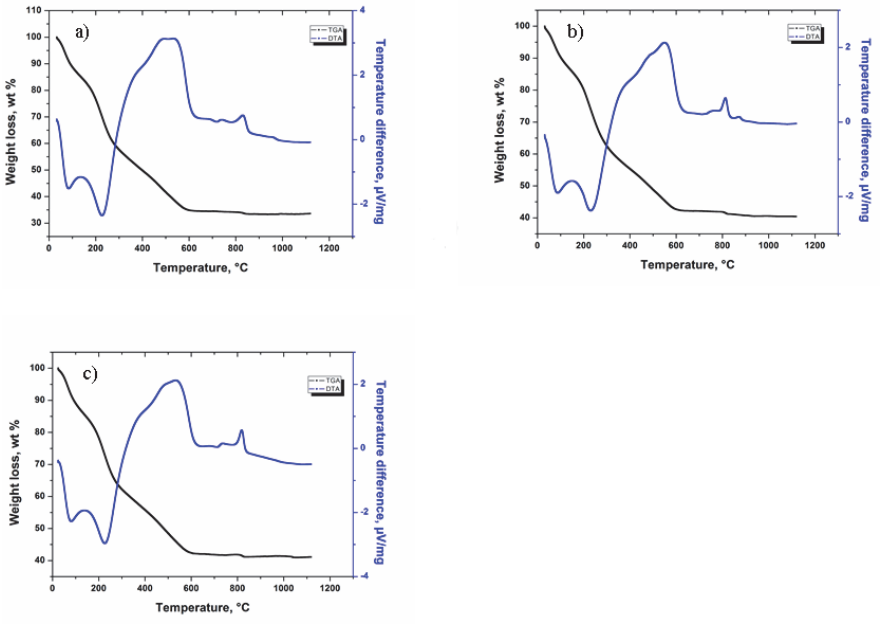

Fig. 1. The TGA and DTA curves of the as spun precursors a) pure alumina fibers, b) alumina fibers with the addition of $MgCl_2$ and c) alumina fibers with the addition of $FeCl_3$.

The fibers were heated at 800 and 900 °C in order to examine the crystal structure at temperatures under und over the phase transformation observed in DTA curves. X – ray powder diffraction data of synthesized samples are presented in Fig.s 2-4. The present phases in the samples were determined by means of X – ray structural phase analysis that was performed by using EVA 9.0 software. The XRD patterns of the undoped fibers are shown in Fig. 2 and the observed phases are marked. The dominant structure in samples without additives after heat treatment at 800 °C are γ – Al_2O_3 (PDF-2 79-1558) and AlO(OH) (PDF-2 72-1268). Diffraction peaks at 900 °C are better defined and have a slightly narrower half width. The phase present in the samples are γ – Al_2O_3 (PDF-2 79-1558), aluminum hydroxide (PDF-2 84-0175) and small amount of α - Al_2O_3 (PDF-2 74-1081) which indicate that the crystallization of corundum is started at this temperature.

The XRD patterns of nanofiber obtained from the precursor with the addition of $FeCl_3$ are shown in Fig. 3.

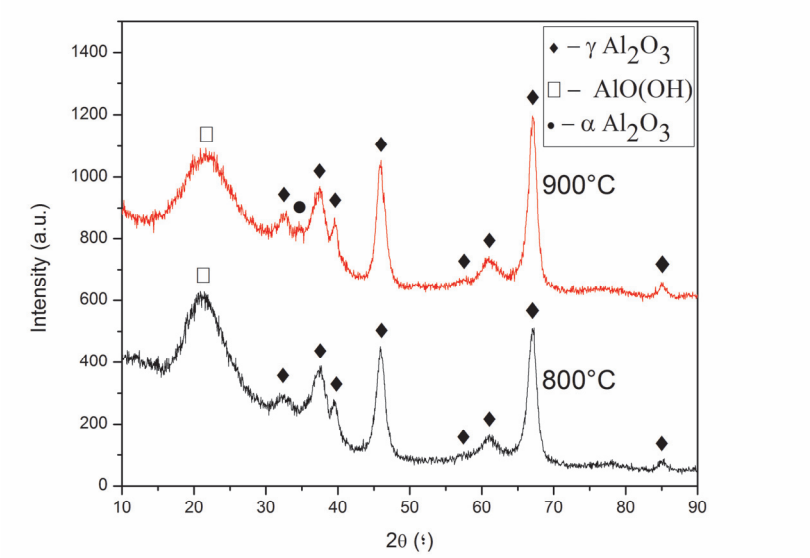

Fig. 2. XRD of the sample without additives after heat treatment at 800 and 900 °C.

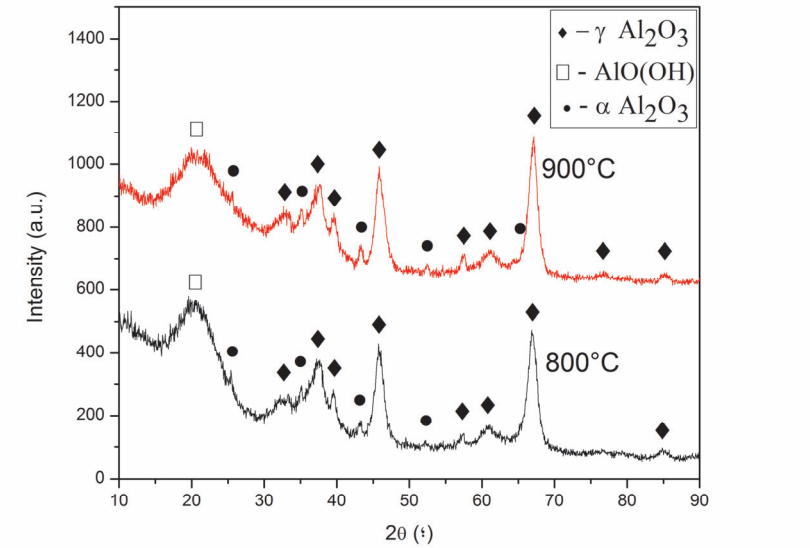

Fig. 3. XRD of the sample with the addition of $FeCl_3$ after heat treatment at 800 and 900 °C.

Sample with the addition of $FeCl_3$, has higher α - Al_2O_3 (PDF-2 74-1081) content, i.e. corresponding peaks are more prominent, particularly at 900 °C. The dominant phases are γ – Al_2O_3 (PDF-2 79-1558) and AlO(OH) (PDF-2 72-1268) as in undoped fibers. This indicates that the addition of ferrous oxide eases the formation of corundum.
The XRD patterns of nanofiber obtained from the precursor with the $MgCl_2$ addition are shown in Fig. 4.

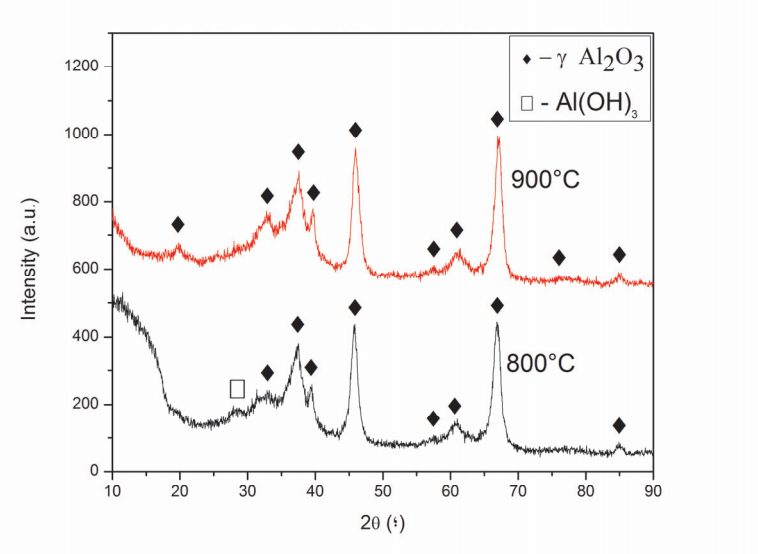

Fig. 4. XRD of a sample with addition of $MgCl_2$ in the precursor after heat treatment at 800 and 900 °C.

In the samples with addition of MgCl2 the alpha alumina is not detected but only γ – Al_2O_3 (PDF-2 79-1558) and $Al(OH)_3$ (PDF-2 77-0250). Those structures enable easier sintering of fibers in later stages of heat treatment.

The SEM micrographs of fibers and fiber diameter distribution are shown in Fig. 5. Statistical parameters characterizing fiber diameter distribution are given in Tab. I.

Tab. I Statistical parameters characterizing the measurement of fiber diameter.

Parameter	**PVA + $Al_2(OH)_5Cl \cdot 2.5\ H_2O$**	**PVA + $Al_2(OH)_5Cl \cdot 2.5\ H_2O$ + $MgCl_2$**	**PVA + $Al_2(OH)_5Cl \cdot 2.5\ H_2O$ + $FeCl_3$**
Mean (μm)	0.326	0.329	0.315
Median (μm)	0.277	0.352	0.302
Standard deviation (μm)	0.163	0.153	0.089
Sample Variance	0.027	0.023	0.008
Range	0.816	0.801	0.549
Minimum (μm)	0.143	0.101	0.124
Maximum (μm)	0.959	0.903	0.674
Count	138	115	132

The mean diameter of the fibers is smaller for fibers where a small amount of $FeCl_3$ is added. The calculated fiber diameters ranged from 101 to 959 nm and those are promising dimensions for fibers to be used either as reinforcement in polymer matrix composites or as absorbents.

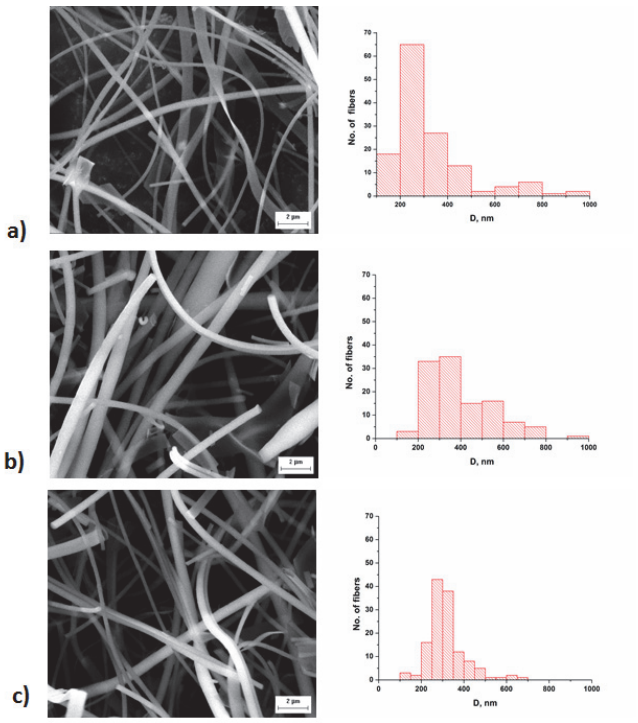

Fig. 5. The SEM micrographs of ceramic fiber obtained by the electrospinning method and fiber diameter distribution: a) PVA + Al_2 (OH)5Cl •2.5 H_2O, b) PVA + Al_2 (OH)5Cl •2.5 H_2O + $MgCl_2$, c) PVA + Al_2 (OH)5Cl •2.5 H_2O + $FeCl_3$.

4. Conclusion

Alumina chloride hydroxide/PVA fiber and fiber with the addition of $MgCl_2$ and $FeCl_3$ were produced using the electrospinning method. The calcination was done at 800 and 900 ºC. The temperature of the phase transformation is lower when alumina is doped and it is confirmed by the TGA/DTA. The crystallization temperatures are very similar while the temperatures of phase transformations and possible formation of corundum are different. The crystal structure in all three specimens at 800 °C are similar and consists mostly of γ-alumina with some other structures that explains the complexity of the obtained crystal structure. Corundum appears in the specimen with added ferrous oxide in significant quantity. In the specimen made of pure alumina precursors the corundum structure appears only in a small amount. The addition of magnesia in the structure of alumina results in the formation of spinel structures that will ease the sintering at sintering temperatures, but the presence of corundum structure is not important in this specimen. All the obtained fibers have submicrometer diameters when they are produced, so after the sintering the mean diameter will be finer and the obtained material should have a large surface area that enables both to be used as reinforcement in a composite material and as a sorbent. The fibers with the addition of $FeCl_3$ have a smaller average diameter and are thinner than the other two types of fibers.

Acknowledgements

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5. References

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Садржај: *Алуминијум оксид има добра маханичка и хемијска својства. Нановлакна, која имају структуру α – алуминијум оксида, коришћена су као ојачање за металне, полимерне и керамичко матричне композите. У овом истраживању направљене су три серије нановлакана. Прва серија направљена је од 10 % раствора алуминијум хидроксид хлорида и поли винил алкохола у масеном односу 5/1. У две друге серије је додато по 1 % $MgCl_2$ и 1 % $FeCl_3$ у односу на алуминијум хидроксид хлорид. Нановлакна су припремљена техником електропредења и карактерисана су TGA/DTA, XRD и FE-SEM методама. Доказано је да додавање $FeCl_3$ снижава температуру појаве корунд структуре, док додавање $MgCl_2$ резултује формирањем мешовитих оксида који олакшавају процес синтеровања.*

Кључне речи: *Наноматеријали; електропредење; керамичка влакна.*