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Original Article

# Effect of heat treatment conditions on magnesium borate fibers prepared via electrospinning

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ABSTRACT

The influence of different heating rates as well as different atmospheres on magnesium borate fibers produced by electrospinning was investigated in this work. The green fibers were prepared from sol–gel precursors, using polyvinyl-pyrrolidone (PVP) as processing aid. Crystalline fibers with the typical necklace structure and average diameter in the range 300–500 nm were produced when heating up to 900 °C in air. The main phase detected by XRD analysis was in this case $Mg_2B_2O_5$. On the other hand, the fibers slowly heated in reducing atmosphere to 800 °C exhibited similar dimension but a different morphology. The crystalline grains were presumably smaller, hence the necklace effect was absent. This sample also revealed a much higher specific surface area in comparison to the samples calcined in air. $Mg_3B_2O_6$ was here the main crystalline phase, while a part of boron was lost during the thermal treatment.

## 1. Introduction

In the last years, bottom-up approaches such as electrospinning (hereafter referred as e-spinning) have received increasing attention for the development of nanoscaled materials. As the name suggests, this process depends on electrostatic forces to form "one-dimensional" shapes such as fibers, ribbons, filled and hollow tubes, all having large specific surface areas. The most important advantage of this technology is that it is relatively simple and inexpensive to produce nanofibers (NFs) with tunable properties for a broad range of applications. In addition, e-spinning generates continuous structures: this continuity offers the potential for alignment, direct writing, and spooling of the fibers. The process was first patented in 1934 by Formhals [1] and, for the last 70 years, was mainly used for making polymeric fibers. Ceramic nanofibers synthesized via e-spinning were only reported first in 2002. Since then, this new field and its application are rapidly growing. For example, electroceramic nanofibers can be used in nanostructured components such as gas sensors, piezoelectric tubing for nanofluidics, and catalysts. To date, it is clear that almost any ceramic system for which a sol–gel or co-precipitation precursor is available can be readily electrospun. In summary, the experimental steps for e-spinning of ceramics normally are the following:

1. Preparation of the e-spinning solution.
2. E-spinning and collection of the polymer/inorganic composite fibers/mat.
3. Calcination of the composite fibers to remove unwanted constituents and to obtain the desired ceramic phase.
4. Annealing (optional) for further modification of the fiber microstructure.

Most studies of ceramic e-spinning to date have reported fabrication and property evaluation. However, very little theoretical work has been published. The theory previously developed for polymers needs to be revisited, taking into consideration the enhanced conductivity of the ceramic precursor solution. A review of electro hydrodynamic (EHD) theory for e-spinning applied to ceramics has been proposed by Sigmund et al. [2]. Better control and prediction of fiber morphology and understanding of the kinetics of the calcination and annealing processes are essential for scale-up and commercialization efforts.

Magnesium borates, of different chemical compositions such as $Mg_2B_2O_5$, $MgB_4O_7$ and $Mg_3B_2O_6$, are remarkable functional materials. Among them, $Mg_2B_2O_5$ shows excellent mechanical properties combined with good heat and corrosion resistance: in recent years it has been widely used as an anti-wear material to reduce the friction coefficient [3,4]. Magnesium borates also have other potential applications

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such as catalysts for the conversion of hydrocarbons [5,6], thermo-luminescent phosphors [7–9], luminescent materials for cathode ray tube screens [10] and as fused cast refractories with high thermal shock resistance and good corrosion-erosion resistance in basic oxygen steelmaking environments [11].

In our previous work, magnesium borate fibers were prepared by e-spinning from sol–gel precursors in organic solvents followed by calcination in air. A stable jet was obtained, and fibers with random orientation and diameters in the range 200–500 nm were produced. However, the starting morphology was lost after heat treatment, with development of porous structures with a diameter of about 6 μm. Unusual shapes for electrospun nanofibers had already been reported, as for example ribbon shaped fibers [12]. In our case, coalescence of the fibers was observed already at 600 °C, after the decomposition of the PVP. We believe that this issue was related to the particular atmosphere in the furnace (with possible contaminants) or the employed heating rate. Therefore, in the present work three different heating rates were tested for the calcination of fiber mats in air. For consistency, the precursor solution and spinning parameters were kept exactly as described in [13]. In addition, one fiber sample was heat treated in reducing conditions to check the influence of the atmosphere on the final morphology and on the phase composition. In view of a possible application of electrospun fibers together with ceramic filters for steel melt filtration, this last treatment was the same required for the production of carbon-bonded alumina filters [14]. Fibers produced by electrospinning may be used as reactive coating, to capture the oxygen dissolved in the melt and prevent the formation of endogenous inclusions after casting [15,16].

## 2. Materials and methods

The precursors used for the preparation of magnesium borate fibers were boron ethoxide (liquid, purity ≥99%) and magnesium ethoxide (granular, purity ≥98%). Polyvinylpyrrolidone powder (PVP, average Mw = 1,300,000) was used to generate a fibrous precursor structure. Both alkoxides were dissolved in 2-Methoxyethanol (anhydrous, purity ≥99.8%), while PVP was dissolved in N,N-dimethylformamide (DMF, anhydrous, purity ≥99.8%). All raw materials and solvents were purchased from Sigma–Aldrich (Saint Louis, USA) and used as received.

The e-spinning solution was produced exactly as in our previous work [13]: first a 40 wt% precursor solution was prepared in 2-methoxyethanol using a magnetic stirrer. A 1:1 molar ratio between $C_4H_{10}MgO_2$ and $C_6H_{15}BO_3$ was chosen in order to obtain $Mg_2B_2O_5$ as the primary phase after heat treatment in air. This solution was then stored in a desiccator in order to prevent the hydrolysis of the precursors. Separately, a 25 wt% solution of PVP was prepared in DMF, again by means of magnetic stirring. Since 2-methoxyethanol and DMF are miscible in one another, the e-spinning solution (called 40-25 for simplicity) was obtained simply by mixing the precursor and the PVP solutions in a 2:1 weight ratio until homogenization.

The production of the fibers was performed in a NE100 unit provided by Inovenso (Istanbul, Turkey). The prepared e-spinning solution was loaded into a 10 ml syringe connected to a 0.8 mm diameter conductive brass needle and fed at 0.5 ml/h with a syringe pump (NE-300, New Era Pump Systems, USA). e-spinning was carried out at room conditions ($T \approx 21$ °C, R.H. ≈ 40%) and at a voltage of 15 kV using a DC power supply. An aluminum plate covered with aluminum foil was used as the collector, and the distance between nozzle and collector was 10–12 cm. After the e-spinning process the as-spun fiber mat was removed from the aluminum foil. Samples were then heat treated at 900 °C in air, or at 800 °C in reducing atmosphere. In the first case three different heating rates of 1, 5, and 10 °C/min, with a holding time of 1 h, were employed. The resulting samples were called, respectively, MB_1, MB_5 and MB_10. Separately, a fiber mat was treated in retorts filled with calcined petcoke (Müco, Germany) with a particle size between 0.2 and 2 mm, to approach reducing conditions. The maximum temperature of 800 °C was reached with a heating rate of 1 K/min, additional dwell steps of 30 min for every 100 °C, and a final holding time of 180 min (Fig. 1). In this way we applied the same heat treatment conditions that are used for the fabrication of carbon-bonded filters for steel melt filtration [14]. This sample was called MB_C. Finally, the deposition of fibers directly on a carbon-bonded alumina filter was attempted: in this case, the aluminum plate was replaced with a special sample holder and the substrate was connected with the grounding cable. The spinning parameters were left unchanged. After the formation of a very thin fiber mat on the external surface (approx. 20 s of spinning), the filter was removed from the holder and treated in reducing conditions (see above). Direct contact between the petcoke and the fiber mat was avoided by leaving a small gap above the top surface of the sample.

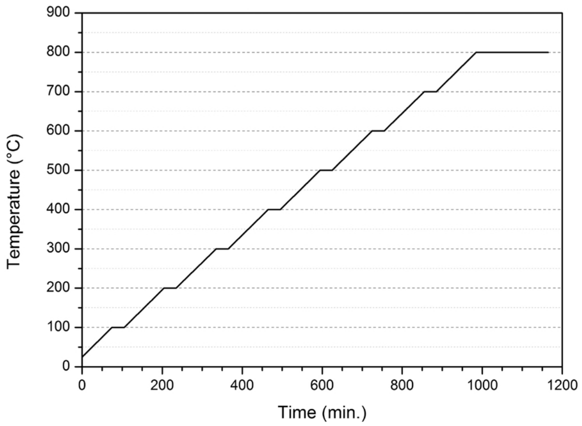

**Fig. 1.** Heat treatment schedule in reducing atmosphere (sample MB_C).

The microstructure evaluation before and after annealing/coking of the samples was carried out by means of optical microscopy (VHX-200 D, Keyence, Germany) and scanning electron microscopy (SEM XL30, Philips, Germany) in combination with energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy images of the MB_C sample were obtained using EFTEM Jeol 2200 FS microscope. The sample was prepared by drop casting of a suspension (1 mg/mL) on 200 mesh TEM grid. Elemental maps and EDS spectra were obtained by means of a SDD detector X-MaxN 80 TS from Oxford Instruments (England). X-ray diffraction analysis (XRD) was conducted after heat treatment to determine the phase composition of the samples. The instrument (X'Pert PRO MPD X-Ray Diffractometer 3040/60, PANalytical, Germany) operates in Bragg-Brentano geometry with a fixed divergence slit and a rotating sample stage. The parameters were standard Cu K$\alpha$ radiation ($\lambda$ = 1.54Å), a $2\vartheta$-range from 7.5 to 85° with a scan step size of 0.013° and a holding time of 30 s per step. This led to a total scan of 12 min. The X-ray source was operated at 40 kV and 40 mA. The analyses were done on ground fibers using the back loading technique to minimize preferred orientation.

The specific surface area of the samples was determined by $N_2$ adsorption–desorption measurements at 77 K. An automated Micromeritics ASAP 2020 (Norcross, USA) instrument was used: samples were first degassed at 90 °C for 30 min and then at 350 °C for 5 h under vacuum. The specific surface areas $S_{BET}$ were calculated from the linear form of the BET equation [17] taking the cross-sectional area of the nitrogen molecule to be $16.2 \cdot 10^{-20}$ m$^2$ (linearity region between 0.05 and 0.35 $p/p_0$). In general, it is possible to estimate the pore shapes and size distribution by using the multimolecular adsorption curve over its whole range of pressures. However, in the case of a fiber mat, gas may easily condensate in the regions between different fibers. For this reason, our analysis was focused on the determination of the BET specific surface. Since the phenomenon of capillary condensation only occurs at high pressure range, it does not affect the calculation of specific surfaces according to the BET theory [18]. A hot stage