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EUN JU JEON*,**, NU SI A. EOM*, JIMIN LEE**, BIN LEE*, HYE MI CHO*,
JI SUN ON*, YONG-HO CHOA**, BUM SUNG KIM*,***#

MULTISTEP HEAT-TREATMENT EFFECTS ON ELECTROSPUN Nd-Fe-B-O NANOFIBERS

Neodymium-Iron-Boron (Nd-Fe-B) magnets are considered to have the highest energy density, and their applications include electric motors, generators, hard disc drives, and MRI. It is well known that a fiber structure with a high aspect ratio and the large specific surface area has the potential to overcome the limitations, such as inhomogeneous structures and the difficulty in alignment of easy axis, associated with such magnets obtained by conventional methods. In this work, a suitable heat-treatment procedure based on single-step and multistep treatments to synthesize sound electrospun Nd-Fe-B-O nanofibers of Φ572 nm was investigated. The single-step heat-treated (directly heat-treated at 800°C for 2 h in air) samples disintegrated along with the residual organic compounds, whereas the multistep heat-treated (sequential three-step heat-treated including three steps;: dehydration (250°C for 30 min in an inert atmosphere), debinding (650°C for 30 min in air), and calcination (800°C for 1 h in air)) fibers maintained sound fibrous morphology without any organic impurities. They could maintain such fibrous morphologies during the dehydration and debinding steps because of the relatively low internal pressures of water vapor and polymer, respectively. In addition, the $NdFeO_3$ alloying phase was dominant in the multistep heat-treated fibers due to the removal of barriers to mass transfer in the interparticles.

Keywords: Nd-Fe-B, nanofibers, electrospinning, heat treatment

1. Introduction

High energy density magnets have been of immense significance in many engineering applications. Nd-Fe-B magnets are considered to have the highest energy density compared to Sm-Co or ferrite-based magnets [1-3]. These magnets find applications in electric motors, generators, magnetic separators, micro motors, etc. Recently, the miniaturization of equipment has necessitated the requirement of magnets with a high energy density in a small volume [4]. The most conventional methods to obtain Nd-Fe-B magnets are powder metallurgy processes involving rapid quenching and sintering. [5,6]. The magnetic particles were firmly adhered to each other; it is therefore difficult to align the easy magnetization axis without applying a proper magnetic field [7]. Solution-based magnetic nanoparticles have been investigated to solve these problems [8-10]. However, the homogenously structured magnetic nanoparticles also have the limitation of shape anisotropy. A well-aligned fiber structure with a high aspect ratio has the potential to overcome the limitations of permanent magnets [11].

In this study, the heat treatment conditions were investigated to obtain one-dimensional (1-D) Nd-Fe-B-O nanofibers that need to be reduced to Nd-Fe-B nanofibers, which will be a part of our future study. These nanofibers have a high aspect ratio and their easy magnetization axis can be matched with the longer axis. It is also expected that this shape anisotropy will lead to the enhancement of magnetic properties of Nd-Fe-B nanofibers. The most facile method to fabricate 1-D nanofibers is electrospinning with an electromagnetic field produced by applying an appropriate voltage to overcome the surface tension of solutions [11-15]. Electrospinning was used to obtain Nd-Fe-B-O nanofibers, which have large specific surface area, high aspect ratio, and dimensional stability. Furthermore, the optimization of the heat-treatment parameters of the electrospun fibers is important in order to retain the fibrous morphology along with perfect alloying and crystallization [16,17]. The objective of this work is to optimize the heat-treatment conditions with comparisons and analysis between single-step and multistep heat treatments after the electrospinning of precursor solutions. The single-step heat-treatment method refers to direct heat-treatment at 800°C for 2 h in air, whereas multistep heat-treatment refers to the sequential process of dehydration (at 250°C for 30 min in an inert atmosphere), debinding (at 650°C for 30 min in air), and calcination (at 800°C for 1 h in air).

* KOREA INSTITUTE FOR RARE METALS, KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY, 9F TOWER TO GET PEARL GAEBEOL-RO 12 [SONGDO-DONG], YEONSU-GU, INCHEON, 21999, REPUBLIC OF KOREA
** FUSION CHEMISTRY ENGINEERING, HANYANG UNIVERSITY, ANSAN, KOREA
*** CRITICAL MATERIALS AND SEMICONDUCTOR PACKAGING ENGINEERING, UNIVERSITY OF SCIENCE AND TECHNOLOGY, DAEJEON, SOUTH KOREA
# Corresponding author: bskim15@kitech.re.kr

2. Experimental

The synthesizing process for Nd-Fe-B-O nanofibers consisted of the following steps.

A polymeric solution was prepared for electrospinning. The starting raw materials were neodymium nitrate hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$, 99.9%, Sigma Aldrich), iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98.0%, Junsei), and boric acid (H_3BO_3, 99.5%, Sigma Aldrich). A polyvinylpyrrolidone (PVP, M_w = 1,300,000, Sigma Aldrich)) solution was prepared using the solvent mixture of deionized water and ethyl alcohol. The metal salts Nd nitrate, Fe nitrate, and boric acid were added in the PVP solution with the target stoichiometric composition of $Nd_2Fe_{14}B$. The electrospinning solution was obtained by mixing the polymeric precursor solution using vortex mixers (Vortex-Genie2) for 30 min. Electrospinning was then performed using the precursor solution to prepare fibers with a needleless electrospinning apparatus (Nanospider, Elmarco). The applied voltage in electrospinning was fixed at 50 kV. The as-spun fibers produced by this electrospinning process had uniformly dispersed Nd, Fe, and B composites.

The as-spun fibers were heat-treated to remove organic components and obtain metal alloy oxides. Two types of heat treatments were applied: the single-step heat treatment and the multi-step heat treatment. The single-step treatment is a direct heat treatment at temperatures ranging from 600°C to 900°C for 2 h in air. The multistep heat treatment involves a three-step process with three different atmosphere conditions: dehydration at 250°C for 30 min in Ar, debinding at 650°C for 30 min in air, calcination at 800°C for 1 h in air.

To identify the phases of the fibers, X-ray diffraction (XRD, Cu K_α radiation, MODEL Bruker) was performed. The morphologies of the fibers were analyzed using scanning electron microscope (SEM, MODEL JEOL). Fourier transform infrared (FT-IR, PerkinElmer) spectroscopy was carried out in the ATR mode to explore the existence of organic components of fibers with infrared spectra.

3. Results and discussion

3.1. Effects of single-step heat treatment

The effects of single-step heat treatment of nanofibers on phases, morphologies, and infrared spectra were observed. Fig. 1 reveals the phases obtained in the as-spun fibers (Fig. 1a) and single-step heat-treated fibers for various heating temperatures ranging from 600°C to 900°C (Fig. 1b-e). The XRD patterns of the as-spun fibers, as shown in Fig. 1a, showed a non-crystalized phase. In the case of single-step heat treated fibers, 600°C was apparently not a high enough temperature for crystallization due to the presence of residual organic compounds. After the fibers were single-step heat treated at 700°C, according to Fig. 1c, crystallization peaks were observed. As the heat-treatment temperature was increased, the degree of crystallization increased simultaneously. The as-spun fibers heat-treated at 800°C are shown in Fig. 1d, and revealed Fe_2O_3 as the predominant phase. However, the $NdFeO_3$ phase became dominant in the fibers single-step heat-treated at 900°C (Fig. 1e). It is observed that at low temperatures, the Fe_2O_3 phase was dominant. At relatively high temperatures, the intensity of the Nd-Fe-oxide phase was higher than that of the Fe_2O_3 phase.

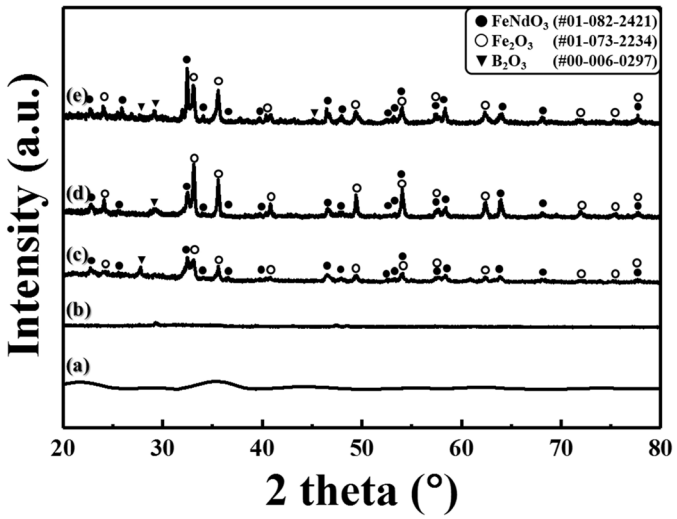

Fig. 1. XRD patterns of single-step heat-treated fibers; (a) as-spun, (b) 600°C, (c) 700°C, (d) 800°C, and (e)900°C for 2 h in air

In order to investigate the presence of organic compounds, the fibers single-step heat-treated at 800°C were compared with the as-spun fibers based on the FT-IR spectra shown in Fig. 2. The strong absorption peaks of the as-spun fibers ranging from 650 to 3600 cm^{-1} can be observed in Fig. 2a, and are attributed to the stretching and bending vibrations of PVP [18]. The band ranging from 2850 to 3450 cm^{-1} is responsible for the absorption peak of the O-H stretching or bending vibration of water molecules.

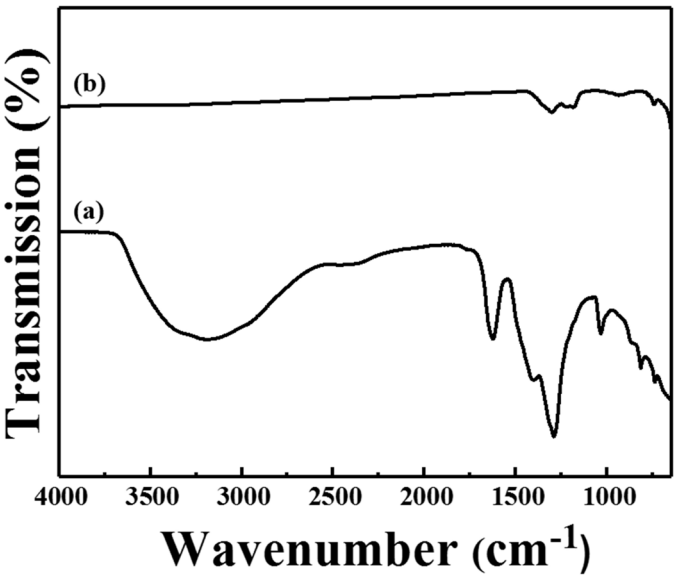

Fig. 2. FT-IR spectrums of single-step heat-treated fibers; (a) as-spun and (b) 800°C for 2 h in air

All the peaks of water disappeared in the fibers heated at 800°C (Fig. 2b), and most of the organic peaks disappeared due to the decomposition of PVP. However, there were still residual peaks that seemed to correspond to the remaining PVP that decomposed the compounds. The existence of residual organic peaks can be attributed to the entrapment of residual organic compounds between the metallic ions.

Figure 3 presents the SEM images of the as-spun fibers after single-step heat-treatment at various temperatures ranging from 600 to 900°C. The as-spun fibers had a diameter of about 1.4 μm. The as-spun fibers single-step heat-treated at 600°C (Fig. 3b) retained their fibrous morphology. The fibers single-step heat-treated at 700°C also had a fibrous structure, as shown in Fig. 3c. However, disintegration of fibers started occurring over 800°C, with the maximum disintegration at 900°C. As explained in Fig. 2, the organic compounds remained in the fibers up to 700°C. These compounds were responsible for holding the structure of the nanofibers intact. However, at 800°C, Fig. 2b shows that the organic compounds were more or less removed from the fibers, which created surface pores. These pores seemed to be responsible for disintegrating the particles. In addition, the rapid evaporation of water vapor and polymer induced high internal pressures in the fibers. The fiber structures thus disintegrated due to the high internal pressures over 800°C.

The results discussed above based on Fig. 1, Fig. 2b, and Fig. 3b-e demonstrated that single-step heat-treatment is not a feasible method to synthesize Nd-Fe-B-O nanofibers. In a phase study, to obtain the Nd-Fe-oxide alloy phase, a temperature as high as 900°C is required. Additionally, residual organic compounds were present when the as-spun fibers were single-

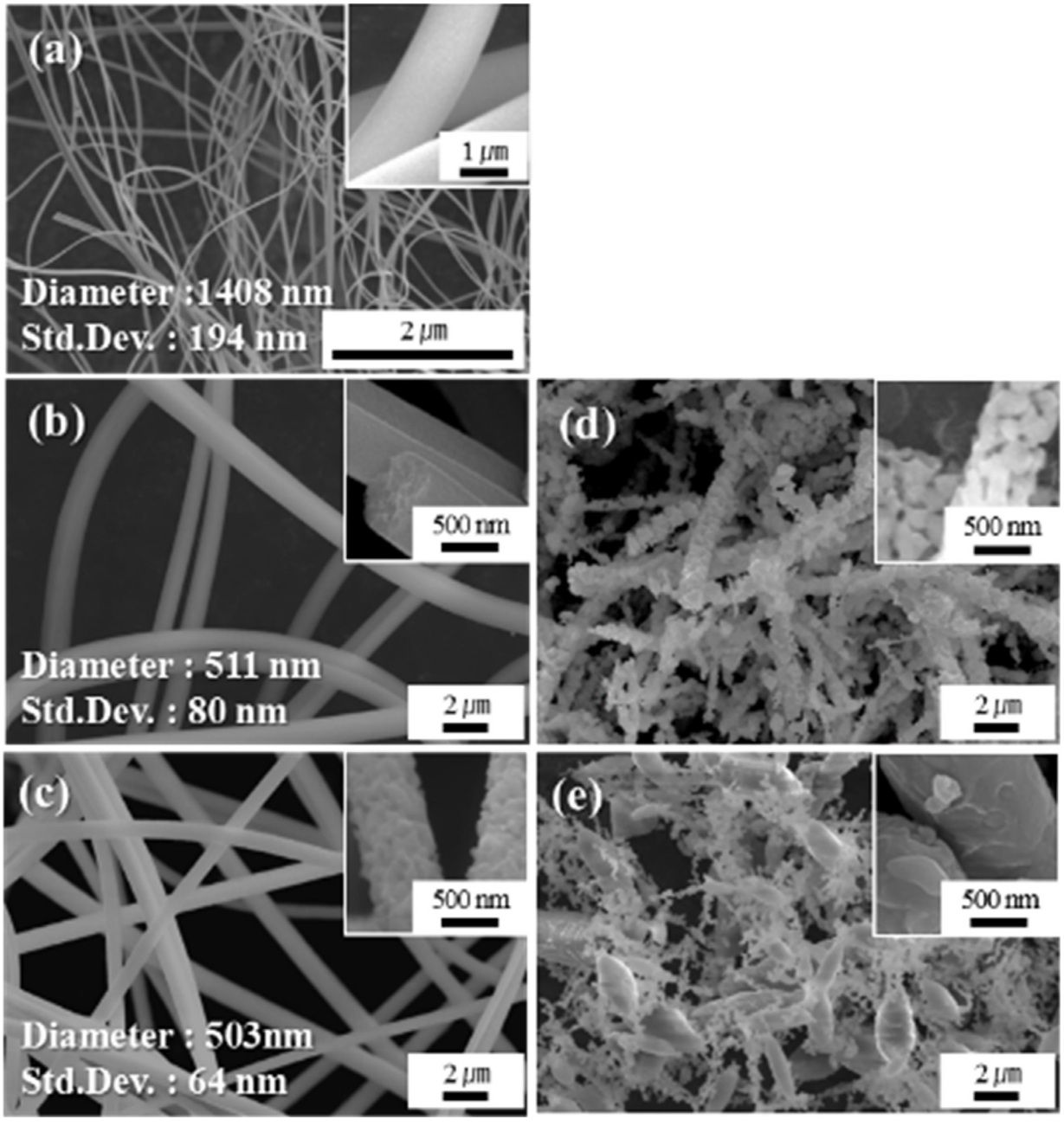

Fig. 3. Microstructures of single-step heat-treated fibers; (a) as-spun, (b) 600°C, (c) 700°C, (d) 800°C, and (e) 900°C for 2 h in air

step heat-treated at 800°C. To maintain the fiber structures, the heat-treatment temperature should be below 700°C. Either the surface integrity or the retention of organic compounds must be compromised, but with single-step heat-treatment neither objective could be achieved. Consequently, the single-step heat-treatment process was not considered relatively feasible for the synthesis of Nd-Fe-B-O nanofibers. A new method of multistep heat treatment was introduced to obtain 1-D fibrous structured nanofibers, with a dominant Nd-Fe-oxide-based alloy with minimum quantities of organic components.

3.2. Effects of multistep heat treatment

The multistep heat-treatment procedure involved three steps: dehydration, debinding, calcination. Dehydration was carried out at 250°C for 30 min in an inert atmosphere to evaporate the hydrates in the fibers. Debinding was then performed at 650°C for 30 min in air to remove organic compounds. Through dehydration and debinding, calcination proceeded at 800°C for 1 h in air for crystallizing and alloying the metal oxides of the fibers in the absence of any organic compounds. Fig. 4 to Fig. 6 present the effects of multistep heat-treatment of the as-spun fibers in terms of infrared spectra, phases, and micrographs.

Compared to the spectra of the as-spun fibers, shown in Fig. 4a, the O-H peaks ranging from 2850 to 3450 cm^{-1} disappeared after dehydration, as shown in Fig. 4b. All the hydrates of the dehydrated fibers seemed to be evaporated. This is because the evaporation rate was sufficient to vaporize the water in a stable state. Fig. 4c illustrates the spectra of the debinded fibers that had no peaks corresponding to organic compounds. It also appeared that the organic compounds were able to evaporate given sufficient time. The final calcined fibers had no reasonable residual organic peaks (Fig. 4d). It is found that the multi-step heat-treatment process effectively removed water and organic compounds during dehydration and debinding, respectively.

The XRD patterns of the dehydrated fibers seemed to reveal non-crystallization (Fig. 5a). The debinded fibers also had non-crystalized phases (Fig. 5b). The main phase of the multistep heat-treated (calcined at 800°C) fibers was $NdFeO_3$, as shown in Fig. 5c, which was unlike the XRD patterns of the fibers single-step heat-treated at 800°C (Fig. 1e). This is because in single-step heat-treatment the residual polymer acted as barriers between iron oxide and neodymium oxide interparticles. By multistep heat-treatment through dehydration (Fig. 5a) and debinding (Fig. 5b), PVP was almost removed before calcination; mass transfer was promoted in the absence of polymer barriers in the interparticles. The multistep heat treatment process could improve the $NdFeO_3$ phase in the fibers.

One of the most important factors is to ensure sound fiber formation following heat treatment. The SEM images of the fibers multi step heat-treated are shown in Fig. 6. Fig. 6a shows the fibrous structure of dehydrated fibers about 874 nm in diameter. The debinded fibers (Fig. 6b) revealed a fine morphology, with a diameter of about 632 nm. Even though the debinding

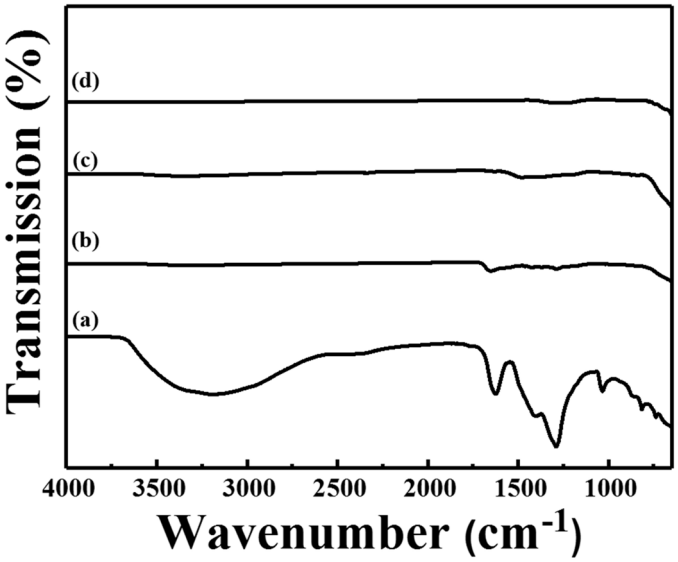

Fig. 4. FT-IR spectrums of multistep heat-treated fibers; (a) as-spun, (b) dehydrated at 250°C for 30 min in Ar, (c) debinded at 650°C for 30 min in air, and (d) calcined at 800°C for 1 h in air

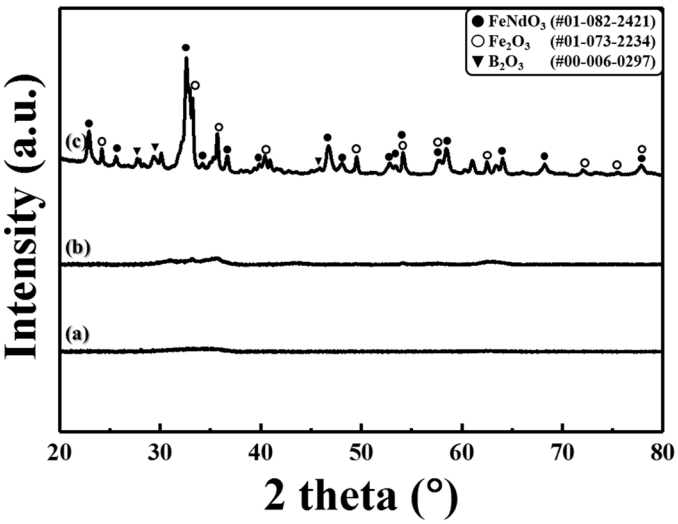

Fig. 5. XRD patterns of multistep heat-treated fibers; (a) dehydrated at 250°C, (b) debinded at 650°C, and (c) calcined at 800°C

temperature (650°C) was similar to single-step heating (700°C) (Fig. 3c), the debinded fibers showed an even better fibrous 1-D morphology. The fibers calcined at 800 °C successfully retained the 1-D nanofiber morphology, with a diameter of about 572 nm, as shown in Fig. 6c. The relatively slow evaporation during heat treatment restrained the internal pressure of the fibers, assisting the formation of a stable fiber structure, compared to single-step heat-treatment at 800°C.

The multistep heat treatment process including dehydration, debinding, and calcination proved to be effective in synthesizing fibers consisting of an Nd-Fe-oxide rich phase without any organic compounds. The three steps resulted in the complete evaporation of PVP. Therefore, in a phase study, the removal of organic compounds accelerated mass transfer, resulting in Nd-Fe-oxide alloy phase growth. Further, the gradual removal

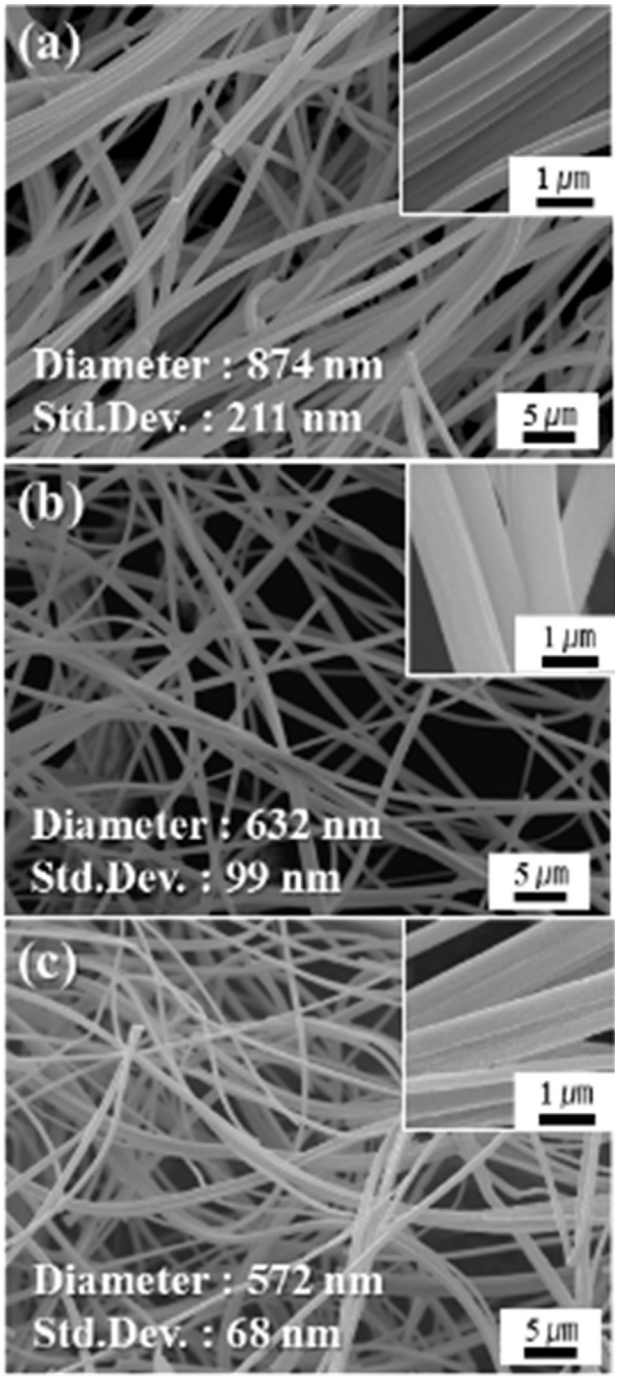

Fig. 6. Microstructures of multistep heat-treated fibers (a) dehydrated at 250°C, (b) debinded at 650°C, and (c) calcined at 800°C

of organic compounds and water did not allow high internal pressures to develop inside the structures, and therefore, a smooth morphology of the nanofibers was obtained.

4. Conclusions

In this investigation, Nd-Fe-B-O nanofibers with a high aspect ratio and large specific surface area was successfully synthesized by electrospinning and multistep heat treatment. After single-step heat-treatment at 900°C, the proportion of the $NdFeO_3$ phase increased. However, the fiber structure disintegrated due to the presence of residual organic compounds as a result of the internal pressures of water vapor and polymer. The multistep heat treatment process resulted in a high proportion of the $NdFeO_3$ alloying phase without any organic impurities in the fibers. The fibers could also maintain their sound fibrous 1-D morphology (diameter 572 nm), while the diameter of the as-spun fibers was about 1408 nm. The Nd-Fe-O nanofibers, which can be used to make Nd-Fe-B magnets through subsequent reduction, were synthesized through optimized multistep heat-treatment.

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