

Formation of niobium oxide and carbide nanofibers from poly(vinyl alcohol)/niobium oxide composite nanofibers

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Abstract Poly(vinyl alcohol)-niobium oxide (Nb_2O_5) composite nanofibers (precursors) were formed by electrospinning employing water as a solvent for the spinning solution. The precursors were converted into Nb_2O_5 or carbide (NbC) nanofibers by heating them in air or Ar. Hexagonal Nb_2O_5 nanofibers with high-specific surface area were obtained by heat-treatment of the precursors in air. NbC nanofibers could be obtained below theoretical temperatures calculated from thermodynamics data, indicating that the precursor is a nano-scale mixture of Nb and carbon sources.

Introduction

Many kinds of inorganic nanofibers have been obtained by heat-treatment of organic–inorganic composite precursor nanofibers formed by electrospinning (ES) [1, 2]. Almost all of the inorganic nanofibers obtained from the precursors are metal oxide nanofibers [3–6], but the reports of metal carbide or nitride nanofibers have increased gradually in recent years [7–10].

We focused on the formation of niobium oxide (Nb_2O_5) and niobium carbide (NbC) nanofibers. Nb_2O_5 is widely used in catalysts, oxygen sensors, electrochromic devices, optical filters, and so on [11]. There are some reports about the formation of Nb_2O_5 nanofibers from organic–inorganic composite precursor nanofibers obtained by ES. Poly(vinyl acetate)/ Nb_2O_5 (obtained by sol–gel reaction of niobium ethoxide) [12] and poly(vinyl pyrrolidone) (PVP)/niobium

ethoxide composites were used as the precursors to form the Nb_2O_5 nanofibers [13, 14]. These precursors were prepared by using organic solvents (ethanol or acetone) as the spinning solutions. On the other hand, NbC is used as structural materials resistant to high temperatures (the melting point of NbC is 3600 °C [15]) and corrosive atmospheres, abrasives, superconductors, and high-performance permanent magnets. NbC nanowire arrays have been synthesized via biotemplate method [16]. The nanowires have a length of 1–50 μm and a diameter of 30–100 nm. The growth of the nanowire arrays attributed to a vapor–liquid–solid growth mechanism. However, the formation of NbC nanofibers using ES has not been reported. If the NbC nanofibers can be developed, they would be applied as a super-refractory filter and a constructional material for nuclear facilities as alternate materials for commercially available SiC fibers (SiC is a low activation material).

In this study, we formed poly(vinyl alcohol) (PVA)/ Nb_2O_5 particle composite nanofibers by ES using water as a solvent of the spinning solution and used the nanofibers as a new precursor to form Nb_2O_5 and NbC nanofibers. The structure of the nanofibers obtained was also investigated.

Experimental

Materials

Poly(vinyl alcohol) (PVA; degree of polymerization: 1500) was obtained from Wako Pure Chemicals Ind., Ltd., Japan. Nb_2O_5 sol was a kind gift from Taki Chemical Co., Ltd., Japan (Nb-G6000, content: Nb_2O_5 6 %, NH_4OH , under 1 %, dispersed particle size: ca.15 nm, disperse media: water).

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Formation of PVA/Nb₂O₅ composite nanofibers (precursors) by ES

PVA (14 wt%) aqueous solution was prepared. Nb₂O₅ sol was added to the PVA solution to produce transparent PVA/Nb₂O₅ mixed solution (spinning solution).

The mixed solution was loaded into a plastic syringe (2 ml) equipped with a needle (needle diameter: 0.7 mm). The solution extrusion rate was 0.5 ml/h. A voltage of 17 kV was applied to the needle, and the PVA/Nb₂O₅ (70/30 wt%) composite nanofibers were then deposited on a collector at a room temperature (23.5 °C). The collector (copper plate) was grounded, and the distance between the tip of the needle and the collector was 15 cm. The nanofibers obtained were used as a precursor to form Nb₂O₅ and NbC nanofibers.

Formation of Nb₂O₅ and NbC nanofibers by heat-treatment of the precursors

The PVA/Nb₂O₅ composite nanofibers were heated to a given temperature in an alumina tube furnace (Asahi Rika Seisakusyo Co., Ltd., AHRF-30KC-9P, Japan) at 500–1500 °C for 3 h in air or Ar gas flow, and Nb₂O₅ or NbC nanofibers were obtained. The flow rate of Ar gas was 3.5 l/min.

Apparatus and procedure

The structure of the nanofibers was observed with a scanning electron microscope (SEM) (Keyence VE-9800, Japan) and transmission electron microscope (TEM) (JEOL JEM-2100, Japan). Using a digitizer on the enlarged SEM images, the fiber diameter and its standard deviations at each nanofiber were estimated. X-ray diffraction (XRD) measurement was taken using CuK_α with a Ni filter (30 kV, 15 mA) (Rigaku MiniFlex II, Japan). Nitrogen adsorption isotherms (−196 °C) of the nanofibers were measured with Micromeritics TriStar 3000, USA.

Results and discussion

Formation of Nb₂O₅ nanofibers by heat-treatment of PVA/Nb₂O₅ composite nanofibers

Many beads (size: ca. 1 μm) were observed in the nanofibers when the spinning solutions with greater than Nb₂O₅ 40 wt% were used. Thus, the PVA/Nb₂O₅ composite nanofibers (PVA/Nb₂O₅ = 70/30 wt%) were selected as the precursor to obtain well-formed inorganic nanofibers (The viscosity of the spinning solution is 242 mPa s at 23.5 °C). Figure 1a, b shows SEM and TEM images of the

PVA/Nb₂O₅ (70/30 wt%) composite nanofibers (precursors) obtained by ES. The average fiber diameter of the nanofibers is ca. 170 nm. From Fig. 1b, we found that the

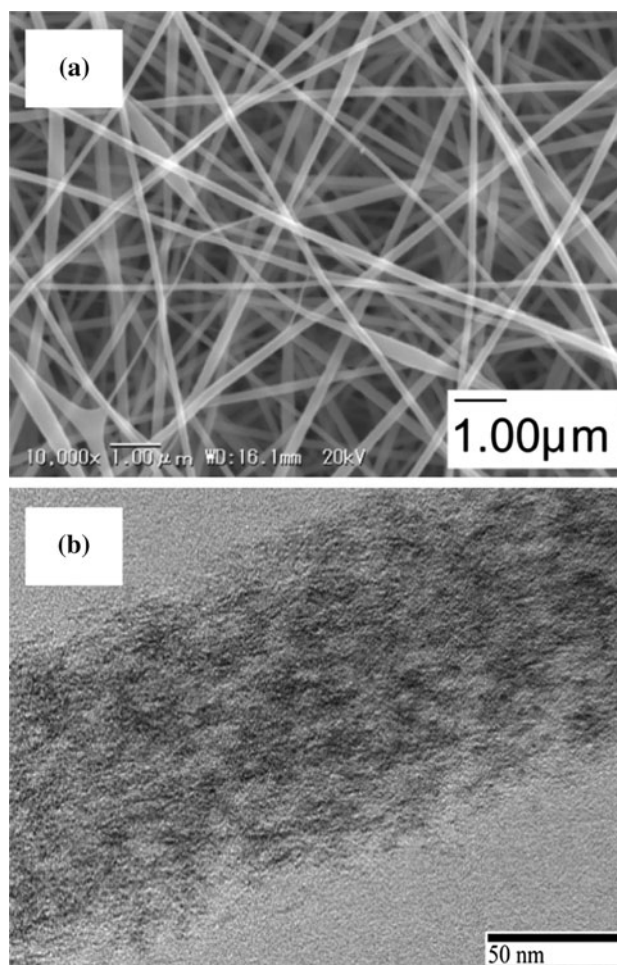


Fig. 1 a SEM and b TEM images of PVA/Nb₂O₅ (70/30 wt%) composite nanofibers (precursors) obtained by ES



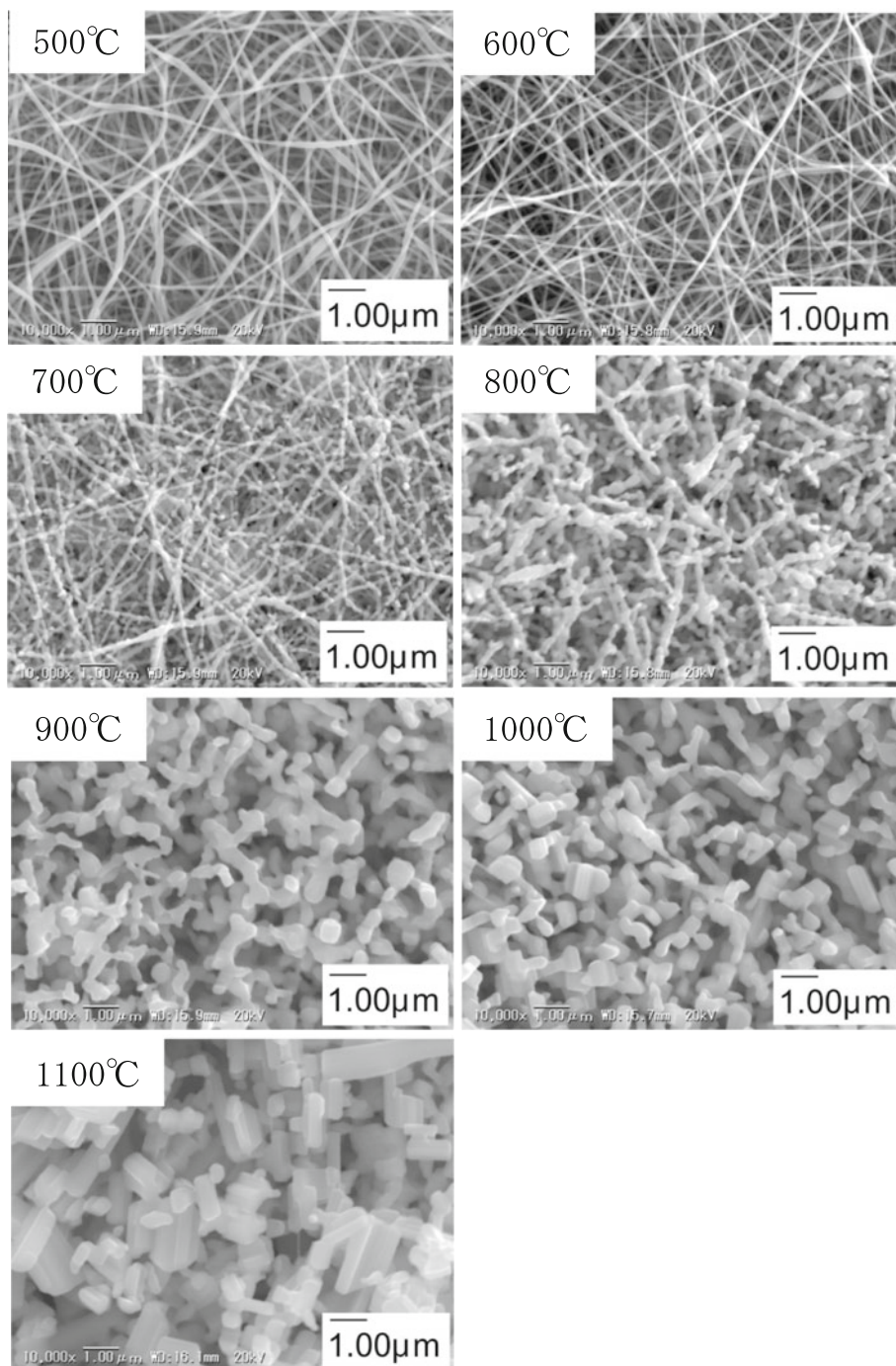
Fig. 2 A view of the precursor nanofiber mat heated at 500 °C

Nb_2O_5 particles were dispersed homogeneously in the PVA matrix because a dark contrast was observed throughout the fiber.

White and brittle mats were obtained after heat-treatment of PVA/ Nb_2O_5 composite nanofiber mats at 500–1100 °C for 3 h in air. Figure 2 shows a view of the mat heated at 500 °C. Figures 3 and 4 show SEM images and XRD curves of the Nb_2O_5 obtained. In Fig. 3, the Nb_2O_5 nanofibers were obtained below 700 °C. But it changes shape from nanofiber to granular component above

800 °C. The average diameters of the nanofibers heated at 500, 600, and 700 °C were 102, 89, and 101 nm, respectively. It is likely that the diameter did not depend on the heating temperature. These values are lower than that of the diameter of the precursor nanofiber (170 nm) because of the shrinkage of the fibers due to the thermal decomposition of PVA. In Fig. 4, the hexagonal Nb_2O_5 is formed at 500–600 °C. Moreover, the orthorhombic and the monoclinic Nb_2O_5 are formed at 700–800 °C and 900–1100 °C, respectively. Thus, the morphology change

Fig. 3 SEM images of Nb_2O_5 obtained after heat-treatment of PVA/ Nb_2O_5 composite nanofibers at 500–1100 °C for 3 h in air



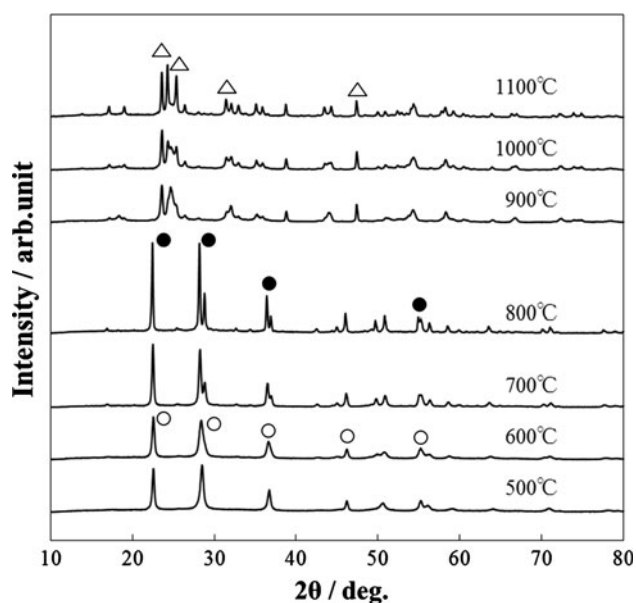


Fig. 4 XRD curves of Nb_2O_5 obtained after heat-treatment of PVA/ Nb_2O_5 composite nanofibers at 500–1100 °C for 3 h in air (open circle hexagonal Nb_2O_5 , filled circle orthorhombic Nb_2O_5 , open triangle monoclinic Nb_2O_5)

of Nb_2O_5 in Fig. 3 would be caused by the crystal structure transformation from hexagonal-type (and orthorhombic-type) to monoclinic-type.

The specific surface area and the pore volume of the Nb_2O_5 nanofiber heated at 500 °C for 3 h were 26.8 m^2/g and 0.0507 cm^3/g , respectively. Considering the report of Zhou et al. [11], the highly porous Nb_2O_5 nanofibers could be obtained in this study due to the thermal decomposition of PVA in the precursors. Each value gradually decreased with increasing heating time due to the sintering; for example, the values were 15.5 m^2/g and 0.0324 cm^3/g after heat treatment at 500 °C for 24 h. On the other hand, the porosity of the nanofibers rapidly decreased with increasing heating temperature. The specific surface area and the pore volume of the Nb_2O_5 nanofibers heated at 800 °C for 3 h

were 3.94 m^2/g and 0.0045 cm^3/g , respectively, and it is likely that the nanofibers became nonporous material.

Formation of NbC nanofibers by heat-treatment of precursors

The precursor nanofibers were heated at 800–1500 °C in Ar gas flow for 3 h. Figure 5 shows the SEM images of the residues after the heat-treatment at various temperatures in Ar. The nanofibers were retained after each heating temperature. Figure 6 shows the effect of heating temperature on the average fiber diameter of the nanofibers obtained by the heat-treatment in Ar. The diameters of the resultant nanofibers decrease with increasing heating temperature up to 1100 °C, and then they keep constant (~ 110 nm) up to 1500 °C.

Figure 7 shows the XRD curves of the nanofibers after the heat-treatment in Ar gas flow. In Fig. 7, the peaks of NbC are observed from 800 to 1000 °C, but other peaks such as Nb_2O_5 and NbO_2 are also observed in the curves. Oxygen and carbon would be supplied from thermal decomposition of PVA. The peaks of NbC became sharp with increasing heating temperature, and the peaks of niobium oxide disappeared at 1100 °C. Thus, we confirmed that NbC nanofibers could be formed above 1100 °C.

The carbonization will typically proceed as follows [17, 18]:



The Gibbs free energy change, ΔG° , for the reaction was given using the available thermodynamic data [19]. If the $\Delta G^\circ < 0$, the reaction will proceed. The initial carbonization (NbC) temperature calculated from thermodynamics data is 1229 °C. This temperature is higher than observed temperature, 1100 °C (as shown in Fig. 7), indicating that the precursor is a nano-scale mixture of Nb and carbon sources, and thus the reaction formula (1) would proceed effectively, or another reaction route might be created.

Fig. 5 SEM images of residues after heat-treatment of PVA/Nb₂O₅ composite nanofibers at 800–1500 °C for 3 h in Ar

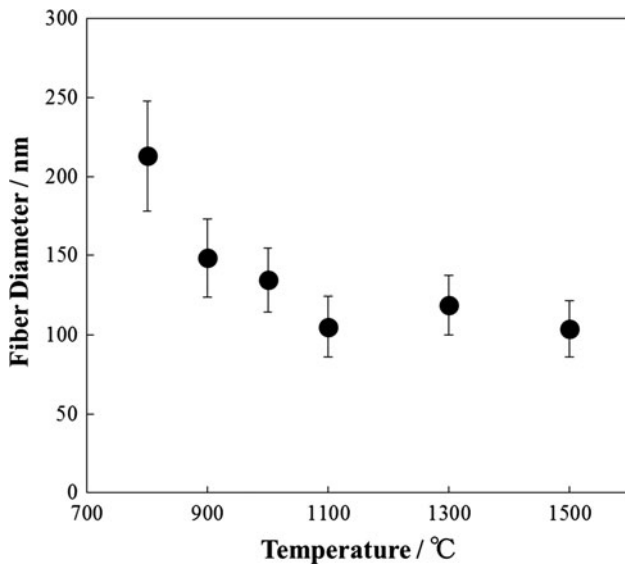
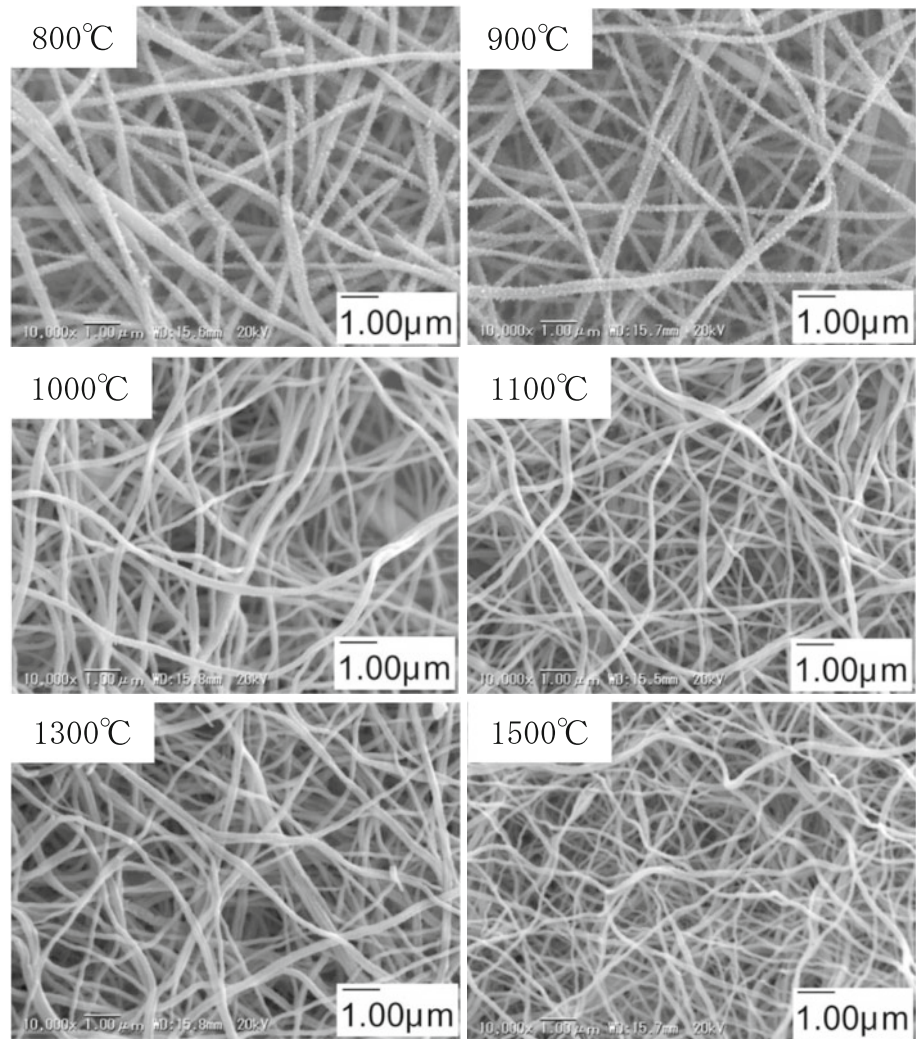


Fig. 6 Effect of heating temperature of the precursors on the average fiber diameter of the nanofibers obtained by heat-treatment of PVA/Nb₂O₅ composite nanofibers in Ar

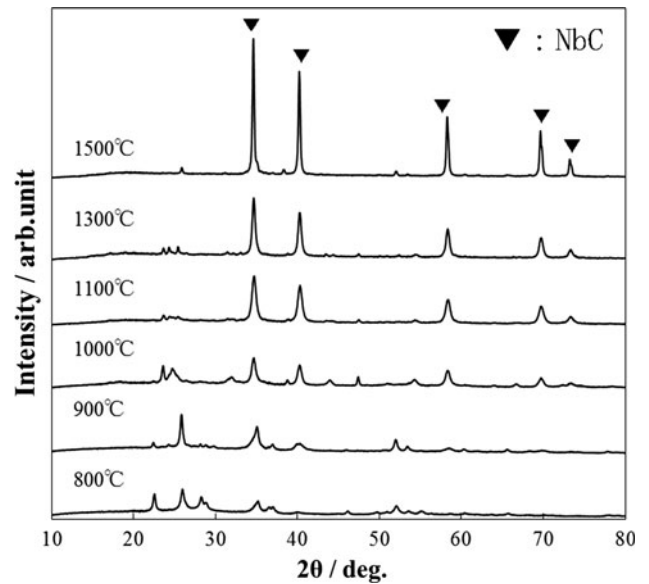


Fig. 7 XRD curves of the nanofibers after the heat-treatment of PVA/Nb₂O₅ composite nanofibers at 800–1500 °C for 3 h in Ar

Conclusions

PVA/Nb₂O₅ composite precursor nanofibers were formed by ES using PVA/Nb₂O₅ nanoparticles aqueous solution as a spinning solution. Hexagonal Nb₂O₅ nanofibers were easily obtained by heat-treatment of the precursors in air. The nanofibers obtained were highly porous materials. NbC nanofibers could be formed at low temperatures by heating the precursors under Ar gas flow. Highly pure and highly crystalline NbC nanofibers will be formed by optimizing the heating conditions of the precursors in the next step.

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