

Magnetic property and crystallinity of a Ni-P hollow microfiber affected by immersion in a NaOH aqueous solution

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An amorphous nickel-phosphorus (Ni-P) hollow microfiber is prepared by template-synthesis with a hydrogen-bonded fibrous supramolecular template by Pd-promoted electroless deposition. To let the Ni-P microfiber show conductivity and magnetic property in this study, we carried out thermal annealing at 500 °C under an argon atmosphere in different two ways. One is the annealing after template removal with a 1 mol dm⁻³ NaOH aqueous solution. Another is the annealing without template removal, which was intended to reduce fabrication procedures. As a result, an annealed Ni-P hollow microfiber showed a different saturated magnetization value of 14 emu g⁻¹ in the former and 9 emu g⁻¹ in the latter. To understand the phenomena, we investigated the two kinds of annealed Ni-P microfibers by transmission electron microscopy (TEM), inductively coupled plasma atomic emission spectrometry (ICP-AES), and X-ray diffractometry (XRD). Although the powder conductivity and chemical composition were hardly affected, formation of an f.c.c. nickel phase related to the magnetic property was significantly suppressed in the latter case of annealing without template removal. It was suggested that carbonization of the supramolecular template upon annealing suppressed the formation of an f.c.c. nickel crystalline phase.

Key words: nickel-phosphorus, hollow microfiber, electroless deposition, magnetic property, carbonization

1. INTRODUCTION

Single, double, and multi-wall carbon nanotubes are promising for a new type of conductive fillers in polymer matrix. Although powder of the carbon nanotubes has been fabricated on an industrial scale, it is difficult to make a polymer composite in which the carbon nanotubes are aligned in a conventional easy way. We hit upon an idea that if a magnetic property is given to such nanotubes, magnetic nanotubes will be aligned by a magnetic field available easily.

We have studied self-assembly of amphoteric azopyridine carboxylic acids in water [1-3]. The amphoteric molecules, having a hydrogen-acceptor pyridyl group at a molecular terminal and a hydrogen-donor carboxyl group at another molecular terminal, spontaneously form hydrogen-bonded fibrous molecular aggregates. The organized morphology is easily tunable by choice of chemical structure of the amphoteric molecules [4]. The hydrogen-bonded molecular aggregates are available as an advanced supramolecular template to make nickel-phosphorus (Ni-P) hollow microfibers by Pd-promoted electroless deposition [4-6]. The advantages as a template are recyclable in water media and morphology-tunable. However, there are disadvantages of low electron conductivity and magnetic property as a filler material, because the Ni-P hollow microfibers are composed of amorphous Ni-P alloy [6].

To improve conductivity and magnetic property of the Ni-P hollow microfibers, we carried out thermal annealing according to previous papers [7-8], in which a

thin film of an amorphous Ni-P alloy prepared by electroless deposition is crystallized at high temperature, and an f.c.c. nickel phase contributable to conductivity and magnetic property is formed. In this study, we carried out thermal annealing of the amorphous Ni-P hollow microfiber. An annealed Ni-P hollow microfiber was investigated in terms of chemical composition, powder conductivity, magnetic property, and crystallinity. Interestingly, we found that a NaOH treatment to remove the supramolecular template during microfiber preparation significantly influenced the magnetic property. We report the effect of the NaOH treatment on the magnetic property and crystallinity of the annealed Ni-P microfiber.

2. EXPERIMENT

2-1. Materials

An amphoteric azopyridine carboxylic acid of 6-[2-propyl-4-(4-pyridylazo)phenoxy]hexanoic acid was used in this study, and a fibrous supramolecular template with an average diameter of 500 nm was prepared in a similar manner to our previous paper [4]. Other chemicals were the same as those in our previous paper [4]. The fibrous supramolecular template was coated with amorphous Ni-P alloy by electroless deposition at 30 °C for 24 h as described in our previous paper [6]. After multiple rinses with deionized water and freeze-dry, the coated template was separated into two in order to be subject to different preparation routes (I) and (II) in Figure 1. In the route (I), the coated template

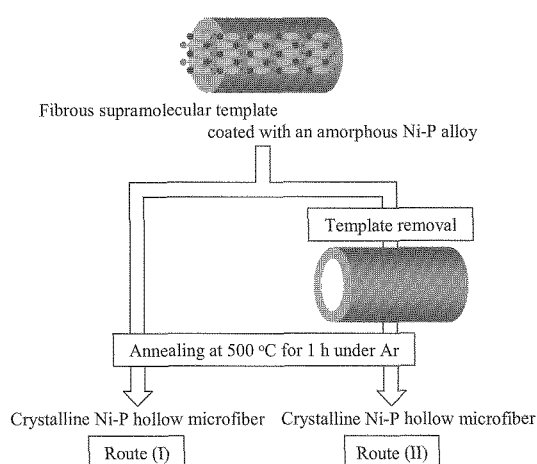


Figure 1. Schematic representation of preparation of crystalline Ni-P hollow microfibers by two ways of route (I) and route (II). The route (I) contains direct annealing of Ni-P-coated template without template removal. The route (II) contains annealing after template removal with a NaOH aqueous solution. In the both cases, annealing was carried out at 500 °C for 1 h under an argon atmosphere.

was annealed in direct at 500 °C for 1 h under an argon atmosphere without template removal. In the route (II), annealing at 500 °C for 1 h under an argon atmosphere was carried out after template removal with a 1 mol dm⁻³ NaOH aqueous solution, multiple rinses with deionized water, and freeze-dry. In the former route (I), we intended to reduce procedure steps to make a crystalline Ni-P hollow microfiber, because the supramolecular template can be pyrolyzed at 500 °C [9]. In this article, the annealed Ni-P hollow microfiber prepared in the former route (I) is abbreviated as a crystalline Ni-P microfiber (I), and the microfiber prepared in the latter route (II) is abbreviated as a crystalline Ni-P microfiber (II).

2-2. Characterization

Crystalline Ni-P microfibers (I, II) were observed by a Hitachi H-7100 transmission electron microscope (TEM). The magnetic property was investigated at room temperature with a Toei Industry VSM-C7 vibrating sample magnetometer (VSM). The volume resistivity in a pressed pellet state was measured in a two-probe method with a Keithley 2400 source meter. The chemical composition was determined by a Shimadzu ICP-8100 inductively coupled plasma atomic emission spectrometer. (ICP-AES). The X-ray diffraction (XRD) pattern was measured with a Rigaku Rint-Ultima diffractometer.

3. RESULTS AND DISCUSSION

3-1. Formation of an f.c.c. nickel phase by annealing

As we described in a previous paper [4, 6], the hydrogen-bonded fibrous supramolecular aggregate formed from the amphoteric azopyridine carboxylic acid

could be available for a template to prepare an amorphous Ni-P hollow microfiber by Pd-promoted electroless deposition. The fibrous supramolecular template after Ni-P electroless deposition was immersed in a 1 mol dm⁻³ NaOH aqueous solution, and the amorphous Ni-P hollow microfiber could be obtained by multiple rinses with deionized water and freeze-dry. Unfortunately, the amorphous Ni-P hollow microfiber exhibited low electron conductivity and poor magnetic property. In addition, the microfiber was brittle. Therefore, it was difficult for us to use the amorphous Ni-P microfiber as a filler material.

Bai et al. report that a thin film of amorphous Ni-P alloy prepared by electroless deposition is altered from paramagnet to ferromagnet by thermal annealing at 500 °C [7]. Accordingly to their report, we carried out the thermal annealing of the amorphous Ni-P hollow

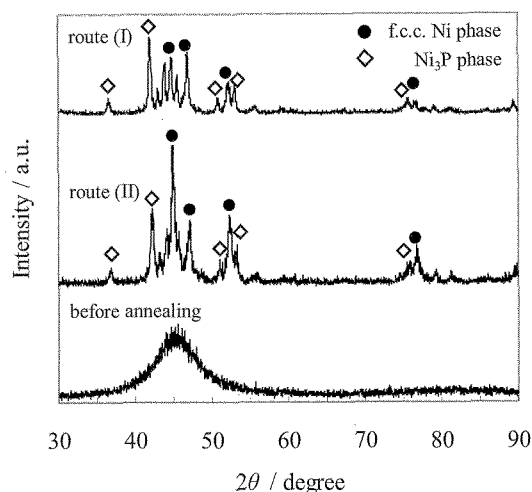


Figure 2. XRD patterns of crystalline Ni-P hollow microfibers (I, II) (upper, middle) and amorphous Ni-P hollow microfiber before annealing (bottom). The microfibers (I) and (II) were prepared by the route (I) (upper) and the route (II) (middle) with template removal, respectively.

microfiber at 500 °C. When the annealing was carried out under an ambient air atmosphere, the annealed Ni-P hollow microfiber exhibited no f.c.c. Ni phase in its XRD pattern. It is anticipated that the amorphous Ni-P alloy was oxidized to nickel oxide. In order to prevent the amorphous Ni-P alloy composing the hollow microfiber from oxidation, we carried out annealing of the amorphous Ni-P hollow microfiber at 500 °C for 1 h under an inert argon atmosphere. The upper and middle of Figure 2 indicate an XRD pattern of the Ni-P hollow microfiber after the annealing under an argon atmosphere. It was found that a broad diffraction pattern at $2\theta = 45^\circ$ [4] corresponding to an amorphous Ni-P phase as shown in the bottom of Figure 2 completely disappeared after the annealing. Instead, sharp diffraction peaks were observed in a 2θ range of 30 – 90°. 4 diffraction peaks observed at $2\theta = 45.0, 47.1, 52.4,$ and 76.6° were attributed to an f.c.c. nickel phase. 5 peaks at $2\theta = 36.9, 42.3, 51.8, 53.2,$ and 76.0°

were corresponding to a Ni_3P phase. The annealing under the inert argon atmosphere suppressed oxide formation and promoted an f.c.c. nickel phase related to conductivity and magnetic property.

Thermogravimetry reveals that pyrolysis of the fibrous molecular aggregate began at about 160 °C and most of the fibrous molecular aggregate is thermally decomposed even under an inert nitrogen atmosphere over 450 °C [9]. Taking a note of thermal decomposition of the supramolecular template, we intended to reduce preparation steps to obtain the crystalline Ni-P hollow microfibers as indicated in the route (I) of Figure 1. The annealing to form an f.c.c. nickel phase was carried out concomitantly with template pyrolysis at 500 °C. The crystalline Ni-P hollow Ni-P microfiber (I) exhibited a XRD pattern in the upper of Figure 2. A feature to note that a diffraction peak at $2\theta = 45.0^\circ$, attributed to an f.c.c. nickel, measured for the crystalline Ni-P microfiber (I) without template removal was significantly smaller than the crystalline Ni-P microfiber (II) prepared by the route

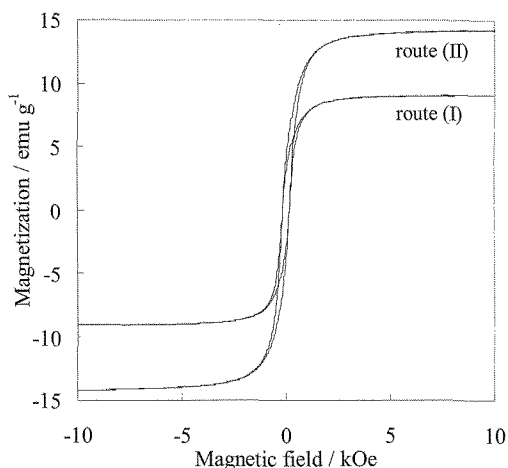


Figure 3. Magnetic field – magnetization hysteresis curves of crystalline Ni-P hollow microfibers (I) and (II) prepared by the route (I) and the route (II), respectively.

(II) involving template removal with a 1 mol dm^{-3} NaOH aqueous solution. In the case of the crystalline microfiber (I), intensities corresponding to a Ni_3P phase were obviously bigger than those to an f.c.c. nickel phase.

Magnetic properties of the crystalline Ni-P microfibers (I) and (II) were measured with a vibrating sample magnetometer (VSM) at room temperature about 20 °C. Figure 3 shows magnetization hysteresis curves against magnetic field measured for the crystalline microfibers. The crystalline Ni-P microfiber (I) showed a saturated magnetization (M_s) of 9.0 emu g^{-1} with a coercive force (H_c) of 0.15 kOe. The crystalline Ni-P microfiber (II) showed $M_s = 14 \text{ emu g}^{-1}$ and $H_c = 0.15 \text{ kOe}$. Formation of an f.c.c. nickel phase exhibiting ferromagnetism in the case of the route (I) was expected to be approximately 2/3 as same as that in

the case of the route (II) under the assumption that the saturated magnetization came from only the f.c.c. nickel phase. The VSM measurement as well as the XRD measurement revealed that formation of the f.c.c. nickel phase in the route (I) without template removal was suppressed. We wondered why formation of an f.c.c. nickel phase was suppressed in the crystalline Ni-P microfiber (I) prepared by the route (I).

3-2. Volume resistivity and chemical composition

It was anticipated that volume resistivity of the crystalline Ni-P hollow microfiber in a pressed pellet state would become large if the formation of the f.c.c. nickel phase contributed to electron conductivity was suppressed. 200 mg of the crystalline Ni-P hollow microfiber prepared by respective methods of the route (I) and the route (II) was pressed at a pressure of 0.2 MPa with a pellet maker for FTIR. Both large surfaces of the pellet of 1.3 cm in diameter and 0.30 mm in thickness were coated with a gold thin film by physical vapor deposition, and gold wires were connected by a silver-epoxy resin. Voltages were measured against currents in a two-probe method. Figure 4 shows correlations of current with voltage measured for the crystalline Ni-P microfibers (I) and (II) in a pellet state. The volume resistivity of the crystalline Ni-P microfiber (I) was $4.4 \times 10^{-1} \Omega \text{ cm}$. The volume resistivity of the

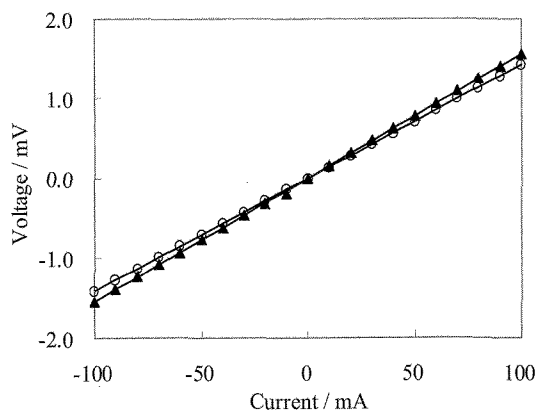


Figure 4. Current – voltage relationships of crystalline Ni-P hollow microfibers prepared by the route (I) without template removal (open circle) and the route (II) with template removal with a NaOH aqueous solution (closed triangle).

crystalline Ni-P microfiber (II) was $6.5 \times 10^{-1} \Omega \text{ cm}$. These values of volume resistivity were almost identical.

To confirm chemical composition of the crystalline Ni-P microfibers (I) and (II), we carried out analysis with inductively coupled plasma atomic emission spectrometry (ICP-AES). Table 1 summarized nickel (Ni), phosphorus (P), and palladium (Pd) on weight detected for the crystalline Ni-P microfibers (I) and (II). Ni of 86.7 %, P of 12.9 %, and Pd of 0.4 % were detected for the crystalline Ni-P microfiber (I). Ni of 84.7 %, P of 12.1 %, Pd of 0.5 % were detected for the crystalline Ni-P microfiber (II). There was no significant difference between them.

Table 1. Chemical compositions of crystalline Ni-P microfibers (I) and (II) prepared by the route (I) and the route (II), respectively.

crystalline Ni-P microfiber	Ni [%]	P [%]	Pd [%]
(I)	86.7	12.9	0.4
(II)	87.4	12.1	0.5

3-3. TEM observation

Figure 5 shows transmission electron microscope (TEM) images of a crystalline Ni-P microfiber, with results for the microfiber (I) and the microfiber (II) shown in parts (a) and (b) of Figure 5, respectively. Most of the crystalline microfiber (II) prepared by the route (II) with template removal were observed in the part (b) of Figure 5. The center of the microfiber was transparent for electron in TEM observation. This means that the template was completely removed by immersion in a 1 mol dm⁻³ NaOH aqueous solution, and that hollow structure was maintained even after annealing at 500 °C. In our previous report [6], an amorphous Ni-P hollow microfiber before annealing is composed of Ni-P spherical grains of 10-20 nm in diameter. Rectangular grains of about 100 nm were observed after annealing at 500 °C. Apparently, crystallization took place during annealing.

In the case of the crystalline Ni-P microfiber (I) prepared without template removal, darkened center of the microfiber was observed sometimes as shown in the part (a) of Figure 5. The others were observed similar to the part (b) of Figure 5. These TEM observations tell us that there were some residues in the crystalline Ni-P microfiber (I) prepared without template removal. The crystalline Ni-P microfiber (I) was immersed in a 10 wt% HNO₃ aqueous solution, to dissolve and remove the crystalline Ni-P alloy. Insoluble species was collected by filtration, multiple rinses with deionized water, and freeze-dry. The insoluble species was black color, which was found to be composed of carbon mainly by elemental analysis. It was found that the carbonized material of 1.4 % on weight was left in the crystalline Ni-P microfiber (I). There was no significant difference in volume resistivity between the crystalline Ni-P microfibers (I) and (II). Taking a note of suppressive formation of an f.c.c. nickel phase in the case of the crystalline Ni-P microfiber (I), we expected that the volume resistivity of the crystalline microfiber (I) was significantly lower than that of the crystalline Ni-P microfiber (II). The carbonized material might improve the volume resistivity in the case of the crystalline microfiber (I). It seemed that the carbonization by pyrolysis of the supramolecular template suppressed the crystallization of an f.c.c. nickel phase. In addition, we should consider a possibility for a grain size of the f.c.c. nickel phase in the crystalline microfiber (I) to be different from the crystalline Ni-P microfiber (II).

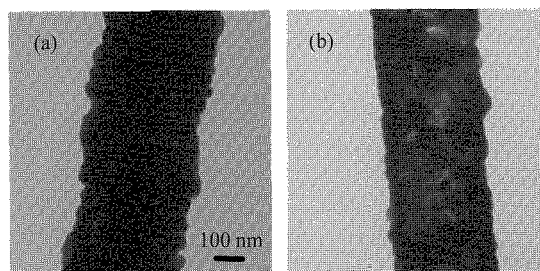


Figure 5. TEM images of (a) a crystalline Ni-P microfiber (I) and (b) a crystalline Ni-P microfiber (II).

4. CONCLUSION

In this report, we described that the magnetic property and crystallinity of the crystalline Ni-P hollow microfiber were significantly affected by its preparation procedures with or without template removal with a 1 mol dm⁻³ NaOH aqueous solution. The saturated magnetization of 9.0 emu g⁻¹ measured for the crystalline Ni-P hollow microfiber (I) prepared without template removal was approximately 2/3 as same as that of the crystalline Ni-P hollow microfiber (II) prepared with template removal. It was anticipated that carbonization by pyrolysis of the fibrous supramolecular template suppressed crystallization of an f.c.c. nickel phase from an amorphous Ni-P alloy at 500 °C under an argon atmosphere. High-resolution TEM observation of the crystalline Ni-P microfiber after micro-processing by FIB will be required to confirm an effect of the carbonized material to the f.c.c. nickel phase.

5. REFERENCES

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