Crystallization and Magnetization of Ni-P Nanotubes by Annealing Treatment

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The metal nanotubes have attracted attention in recent years because of their potential applications. We have reported that the amorphous nickel-phosphorus (Ni-P) nanotubes are successfully obtained through electroless plating on fibrous hydrogen-bonded molecular assemblages formed from amphoteric azopyridine carboxylic acids as template fibers.[1, 2] It is well known that an amorphous Ni-P phase formed by electroless deposition is transformed by annealing treatment to a crystalline phase exhibiting magnetic and conductive properties.[3] In this study, we aimed at preparing novel magnetic Ni-P nanotubes by annealing the amorphous Ni-P nanotubes. The effects of annealing treatment at several different temperatures on physicochemical properties including morphology, crystallization, and magnetism were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis, thermal analysis, and magnetic measurement.

Amorphous Ni-P nanotubes with an inner pore diameter of 500 nm were prepared using fibrous molecular assemblages formed from 6-(2-propyl-4-(4-pyridylazo)-phenoxy)hexanoic acid as templates in a similar manner described in our previous paper.[2] In this study, we used the Ni-P nanotubes with a phosphorus content of 10 wt.% determined by inductively coupled plasma atomic emission spectroscopy. Five kinds of the Ni-P nanotubes annealed at 300, 400, 500, 600, and 700 ^{o}C for 1 h under a N_2 atmosphere were prepared to investigate crystallization behavior of the amorphous Ni-P nanotubes by XRD. An amorphous phase of Ni-P exhibiting a broad peak at 2θ = 45^{o} was maintained up to 300 ^{o}C. At higher temperatures than 400 ^{o}C, characteristic diffraction peaks at 2θ = 43.5^{o} and 46.3^{o} attributable to (112) and (141) of Ni_3P phase as well as a characteristic diffraction peak at 2θ = 44.1^{o} attributable to (111) of f.c.c. nickel phase appeared[3]. The diffraction peak of nickel phase relatively increased at 600 ^{o}C. It was found that crystallization of the amorphous Ni-P nanotubes started at higher 400 ^{o}C and the annealed Ni-P nanotubes mainly consisted of Ni_3P and f.c.c. nickel phases. To confirm that tubular morphology was retained even after the annealing treatment, SEM and TEM observation was carried out. As shown in Figure 1a and Figure 1b indicating the SEM and TEM images of Ni-P nanotubes after annealing at 400 ^{o}C, their original tubular shapes were maintained up to 500 ^{o}C. It was revealed from the TEM image that the Ni-P nanotube was composed of nanoparticles with a diameter of 10 – 20 nm. A wall thickness of the tubular materials was 40 – 60 nm.

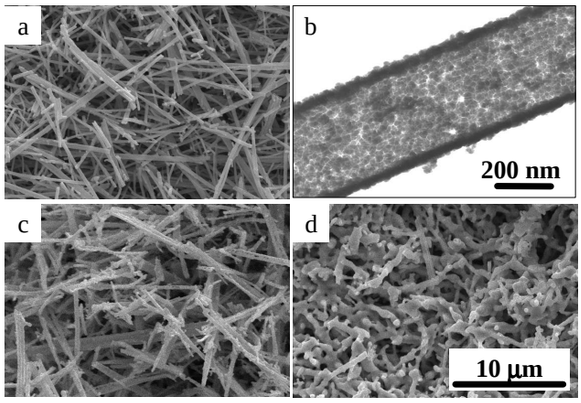

Figure 1. SEM (a, c, d) and TEM (b) images of Ni-P nanotubes annealed at (a, b) 400, (c) 600, and (d) 700 ^{o}C for 1 h under a N_2 atmosphere.

Coalescence among surfaces of the Ni-P nanotubes began from 600 ^{o}C as shown in Figure 1c. The Ni-P nanotubes were fused eventually at 700 ^{o}C, as shown in Figure 1d. Taking account of the fact that Ni-P films with a low-phosphorus content prepared by electroless plating generally show an eutectic melting point above 880 ^{o}C, melting point depression of the Ni-P nanotubes is interesting.[4]

The Ni-P nanotubes after heating at higher 400 ^{o}C were picked up by a ferrite magnet. We could successfully fabricate novel magnetic Ni-P nanotubes by the annealing treatment. Dependences of annealing temperatures and phosphorus contents in Ni-P nanotubes on *H-M* diagrams for magnetic Ni-P nanotubes will be discussed.

Reference

1) Nakagawa, M. et al. *JP03533402*, registered in **2004**
2) Ishii, D. et al. *Trans. Mater. Res. Soc. Jpn.* **2002**, *27*, 517
3) Keong, K. G. et al. *J. Alloys Comp.* **2002**, *192*, 334
4) Ito, H. et al. *Nippon Tungsten Review* **1977**, *10*, 94