Fabrication and Magnetic Properties of Ternary Alloy Co–Ni–Pb Nanowire Arrays

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Ferromagnetic–nonmagnetic heterogeneous ternary alloy Co–Ni–Pb nanowire arrays having composition, Co, 15 atom%; Ni, 45 atom%; Pb, 40 atom%, were successfully fabricated by alternating current (AC) electrodeposition into nanoporous alumina templates. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) observations revealed that the Co–Ni–Pb nanowries were polycrystalline with uniform diameters of around 20 nm and lengths up to several micrometers. Magnetic measurements showed that the coercivity of the samples increased with the annealing temperature up to 550 °C and reached a maximum (1020 Oe).

A great deal of attention has been paid to the fabrication of magnetic nanowires in recent years for their potential application in ultra-high-density magnetic recording media.[1] Many different techniques have been employed to synthesize such materials. Among the various methods used for fabrication nanoarrays, template synthesis, pioneered by Martin,[2] has proved to be a low cost and high yield technique for producing large arrays of nanowires. Examples of nanoporous membranes that have been used include polycarbonate membranes, nanochannel arrays glasses, mesoporous channel hosts, and anodic alumina oxide (AAO) templates. Compared with the other membranes, the pore channels of the AAO template are parallel, perpendicular to the surface and the holes can be readily controlled by properly adjusting the anodizing condition. The AAO template is also stable at high temperature and in organic solvents. The AC electrodepositon into AAO template has proved a simple approach in comparing with direct current (DC) electrodeposition process because it does need to remove the Al substrate and the barrier layer of alumina.[3]

Many arrays of magnetic nanowires including Fe, Co, Ni, and their alloys[4–9] have been prepared based on this method. However, only a few studies on heterogeneous ferromagnetic–nonmagnetic alloy nanowire array systems exist in the literature. Among them, Blythe et al.[10] have fabricated Co–Cu alloy nanowires and presented a preliminary study of their transport property. Fedosyuk et al.[11] reported on the granular deposited Ag/Co in porous anodic aluminium oxide that exhibited a magnetoresistance effect at room temperature. Recently, Wang et al.[12] have fabricated Fe–Ag and Co–Ag nanowire arrays embedded in the AAO template and showed the variation of the coercivities versus annealing temperature. To our best knowledge, fabrication and magnetic properties of ternary alloy Co–Ni–Pb systems have not been reported so for. Here, we report the first successful synthesis of ordered Co–Ni–Pb nanowire arrays by AC electrodeposition into AAO template, and the annealing temperature dependence of their magnetic properties has been studied.

Ordered porous alumina templates were prepared via the anodizing process described in detail previously.[13] The deposition was carried out at room temperature with an AC voltage of 16 V, 50 Hz using graphite as counter-electrode and AAO template with aluminum plate as working electrode. The electrolyte used to electrodeposit the Co–Ni–Pb nanowires had the following composition: $Co(CH_3COO)_2{\cdot}4H_2O$; $Ni(CH_3COO)_2{\cdot}4H_2O$; $Pb(CH_3COO)_2{\cdot}3H_2O$; H_3BO_3. The composition of Co–Ni–Pb nanowires was investigated by induction-coupled plasma spectrometer (ICP). The components of Co, Ni, and Pb are present 15 atom%, 45 atom%, and 40 atom%, respectively. Nanowires were electrodeposited in porous anodic alumina oxide membranes with the length range from 0.5 to 5 µm and the average diameter basically equals to that of pores of the used template. After electrodeposition, the Co–Ni–Pb nanowire arrays were annealed for 20 min at different temperatures (350, 450, 550, and 650 °C).

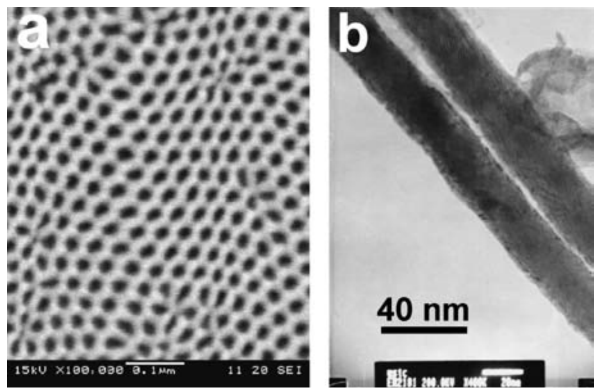

Figure 1. SEM image of AAO template with 20-nm-diameter pores (a); TEM image of the ternary alloy Co–Ni–Pb nanowire arrays detached from AAO template (b).

Figure 1a shows the scanning electron microscopy (SEM) image of ordered nanopores in an anodic aluminum oxide template. The average diameter of the pores is 20 nm and the center-to-center distance is 60 nm. TEM was used to characterize the structure and morphology of the ternary Co–Ni–Pb nanowires. Samples were prepared for TEM by dissolving the AAO matrix in 0.1 M NaOH. The resulting suspension was washed with distilled water and ethanol and resuspended in ethanol by sonication. A representative TEM image of the ternary Co–Ni–Pb nanowires extracted from an AAO is shown in Figure 1b. It can be seen that the Co–Ni–Pb nanowires are of regular size and are continuous with a diameter of about 20 nm and the length up to several micrometers. The selected-area electron diffraction (SAED) pattern reveals that the Co–Ni–Pb nano-

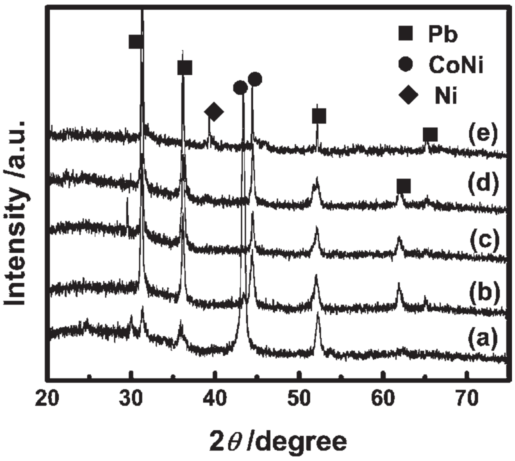

Figure 2. XRD patterns of the ternary alloy Co–Ni–Pb nanowire arrays (a) as-deposited (b) annealed at 350 °C (c) 450 °C (d) 550 °C (e) 650 °C.

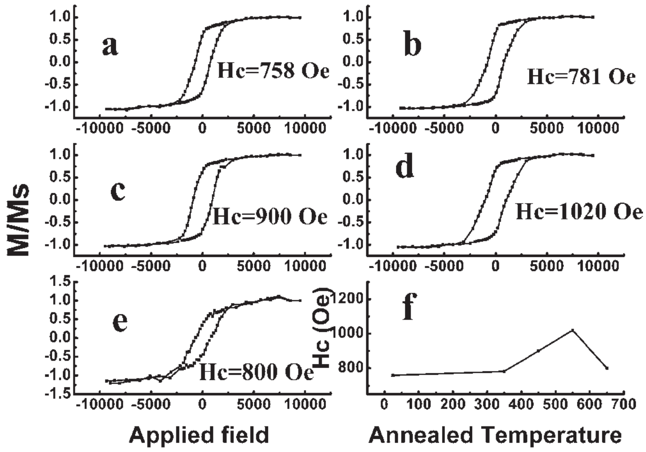

Figure 3. Typical magnetic hysteresis loops for the ternary alloy Co–Ni–Pb nanowire arrays grown in an AAO membrane measured at room temperature with the applied field parallel to the long axis of the nanowires (a) as-deposited (b) annealed at 350 °C (c) 450 °C (d) 550 °C (e) 650 °C. (f) is the perpendicular coercivity as a function of annealed temperature.

wires are composed of polycrystalline structure.

The structural properties of the samples are studied by XRD using Cu Kα radiation. Figure 2 shows the XRD patterns of the ternary alloy Co–Ni–Pb nanowire arrays with different heat-treatment temperature. It can be seen that the as-deposited sample is CoNi and fcc Pb, but the Pb and CoNi diffraction lines are shifted toward higher and lower angles, respectively. We know that the CoNi–Pb represents immiscible materials under equilibrium conditions. However, under nonequilibrium conditions such as the quick AC electrodeposition, the CoNi–Pb system could form miscible phase to a certain extent. Further annealing from 350 to 550 °C, all peaks of our samples are consistent with those of a typical structure of fcc Pb and fcc CoNi, indicating the recrystallization of the as-prepared samples into fcc Pb and fcc CoNi. However, the Ni peak was observed after annealing at 650 °C, indicating the existence of Ni precipitates.

Magnetic properties of the samples were tested by a vibrating sample magnetometer (VSM). Figure 3a–e present the hysteresis loops of the samples at different annealing temperatures with the external magnetic field parallel to the nanowire arrays. The coercivities of the as-deposited sample and the annealed samples at different annealing temperatures are 758, 781, 900, 1020, and 800 Oe, respectively. The variation of perpendicular coercivity with annealing temperature for the Co–Ni–Pb nanowires is shown in Figure 3f. It can be seen that perpendicular coercivity increases with the annealing temperature up to 550 °C and reaches a maximum (1020 Oe). The mechanism of this phenomenon is proposed as follows. The as-deposited samples have a number of defects due to the repaid AC electrodeposition. As the annealing temperature increases from 350 to 550 °C, the perpendicular coercivity increases because of structural relaxation and reduction of defects. However, by further annealing above 550 °C, the coercivity decrease which can be attributed to the precipitation of Ni out of the alloy nanowires was observed (see Figure 3f).

In summary, we have investigated the microstructure and magnetic properties of the ferromagnetic–nonmagnetic heterogeneous ternary alloy Co–Ni–Pb nanowire arrays prepared by AC electrodeposition with AAO as template. Magnetic measurements show that the perpendicular coercivity increases with increased annealing temperature and reaches the maximum (1020 Oe) at 550 °C.

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