J Mater Sci (2010) 45:1523–1527
DOI 10.1007/s10853-009-4116-1

Fabrication and magnetic properties of Fe_3Co_7 alloy nanowire arrays

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Received: 20 October 2009 / Accepted: 5 December 2009 / Published online: 22 December 2009

Abstract Fe_3Co_7 alloy nanowire arrays have been fabricated by direct current electrodeposition of Fe^{2+} and Co^{2+} into anodic aluminum oxide (AAO) templates. The phase structure and magnetic properties of the nanowires were studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM). Magnetic measurements show that the coercivity and remanence of the as-deposited Fe_3Co_7 Alloy nanowires increase dramatically after heat-treatment at 773 K for 2 h, and the nanowire arrays exhibit uniaxial magnetic anisotropy with easy magnetization direction along the nanowire axes owing to the large shape anisotropy. The great difference between practical coercivity and ideal coercivity was also discussed in detail.

Introduction

Highly ordered nanostructured material arrays with controlled diameter and composition have attracted much attention [1–6] in recent years due to their unique properties and potential applications in optoelectronics electronics, photonics, and magnetics. Creations of well-ordered metallic nanowire arrays have become important aspects to realize their promise in ultrahigh-density perpendicular magnetic recording media. Since the magnetic properties are related to their element component, morphology, and microstructure [7], alloy nanowires are expected to exhibit the perpendicular anisotropy. Among these materials, Fe–Co alloy nanowires, especially chemically ordered Fe_3Co_7 with body-centered cubic (bcc) structure have been the focus of extensive research activities due to their large uniaxial magnetocrystalline anisotropy and good chemical stability [8]. Many researchers [9–13] have studied the magnetic properties of Fe–Co binary alloy nanowires, and some outstanding work on FexCoy nanowires have been done by Yue et al. and Shao et al. [14, 15]. They have clearly shown that these nanocomposite materials, synthesized by electrochemical deposition methods, have strong magnetic shape anisotropy and the other unique magnetic properties, but complete understanding of these properties awaits more intense investigation.

Although several different templates [16, 17] have been suggested for the preparation of nanowires, still anodic aluminum oxide (AAO) template is attractive not only because of its thermal stability, but also because of its better parallel alignments of perpendicular pores. The most important of which is that this template is cheap and reliable for producing large arrays of nanowires.

In the present work efforts have been made to fabricate Fe_3Co_7 alloy nanowire arrays by direct current electrodeposition method, in which Fe_3Co_7 nanowires are prepared into pores of the nanoporous template. Then, Fe_3Co_7 alloy nanowire arrays were annealed at 773 K in argon

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atmosphere. Their chemical composition, structural characteristics, and magnetic properties were also investigated.

Experimental details

Ordered AAO templates with pore diameter of about 50 nm were prepared by anodic oxidation of 99.99% pure Al foil in oxalic acid solution under two-step anodizing process. Briefly, the anodization was carried out in 0.3 M oxalic acid solution at 40 V DC and 288 K. The duration of the first anodization step and the second step was 4 h and 8 h, respectively. The remaining Al substrate was removed in a saturated $CuCl_2$ solution. Subsequently, the barrier layer was removed in 5 wt% H_3PO_4 at 303 K for 40 min, and then the template was obtained, which exposited almost uniform pores of approximately 50 nm diameter after etching in the phosphoric acid. In order to serve as the cathode during direct current electrodeposition, a thin Au layer was sputtered onto one side of the continuous holes film. In the end, the Fe_3Co_7 alloy nanowires were electrodeposited into the as-prepared template. The electrolyte of DC electrodeposition had the following composition: 35 g/L $CoSO_4{\cdot}7H_2O$, 15 g/L $FeSO_4{\cdot}7H_2O$, 10 g/L H_3BO_3, and 10 g/L ascorbic acid. Deposition was carried out at room temperature with a DC voltage of 8 V, using graphite as counterelectrode. The pH value of electrolyte was maintained at 2.0–3.0. The solution was continuously agitated by a magnetic stirrer. After electrodeposition, the sample was annealed at 773 K for 2 h.

The formation of Fe_3Co_7 alloy nanowires is studied by field emission scanning electron microscope (FESEM) and transmission electron microscopy (TEM) while the crystal structure is analyzed by selected area electron diffraction (SAED), In addition, magnetic and structural behaviors have also been studied using vibrating sample magnetometer (VSM).

Results and discussion

The XRD spectra of the as-prepared Fe_3Co_7 nanowires are showed in Fig. 1a, where the diffraction peaks are found at 45.17°, 65.7°, and 83.25°, corresponding to the (1 1 0), (2 0 0), and (2 1 1) planes of bcc Fe_3Co_7 structure. The XRD image is almost the same as that of bulk or thin film of Fe_3Co_7, which indicates Fe_3Co_7 nanowires grow in polycrystalline structure, and there is no texture created. As no difference can be seen from the XRD in the Fe_3Co_7 nanowire arrays after annealing, the XRD data of Fe_3Co_7 after annealing are not shown here. The deposition of Fe_3Co_7 can be understood based on the following chemical reactions:

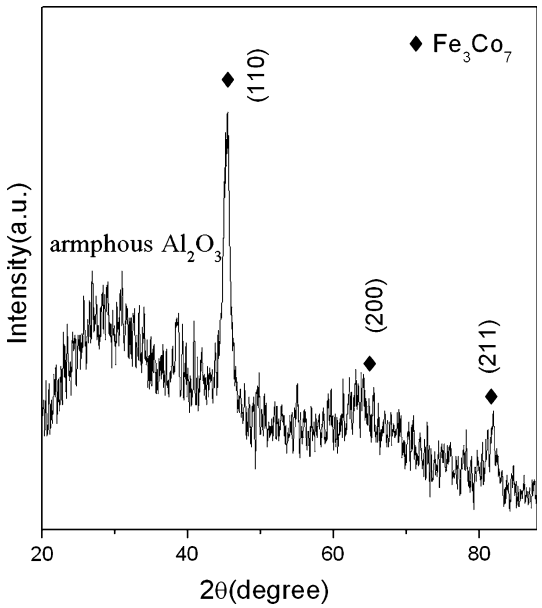

Fig. 1 X-ray diffraction pattern of Fe_3Co_7 nanowires embedded inside porous of the AAO template

$$\text{Oxidation} \quad OH^- - e^- \rightarrow 2H_2O + O_2 \uparrow$$

$$\text{Reduction} \quad 3Fe^{2+} + 7Co^{2+} + 20e^- \rightarrow Fe_3Co_7$$

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$

According to the above formulations, Fe_3Co_7 deposition could take place in the pores of the AAO template with the assistance of DC voltage.

Figure 2a shows SEM image of the porous alumina template used in this study. It can be seen that the template exhibits a perfect two-dimensional array with a circular structure. The average diameter of the pores is 50 nm and the center-to-center distance is about 64 nm. The cross-sectional image of the Fe_3Co_7 nanowires within the AAO template is found in Fig. 2b, which indicates that Fe_3Co_7 has been electrodeposited in the nanoholes of the AAO templates, and the length can be controlled in the range from several nanometers to a few tens of micrometers by varying the deposition time.

TEM result of the as-deposited Fe_3Co_7 nanowires are shown in Fig. 3a, b, which are continuous and uniform in diameter along their length. The wire is about 52 nm in diameter which basically equals to that of pores of the AAO template, and the length is more than 6 m, so the aspect ratio (length to diameter) is up to 120. The lattice fringes, shown in Fig. 3c, can be clearly seen from the HRTEM image in which the interplanar distance is determined to be about 0.200 nm, corresponding to the (110) crystalline planes of the Fe_3Co_7, which further proved that the deposited products are Fe_3Co_7 nanowires. Figure 3d displays a select area electron diffraction (SAED) pattern

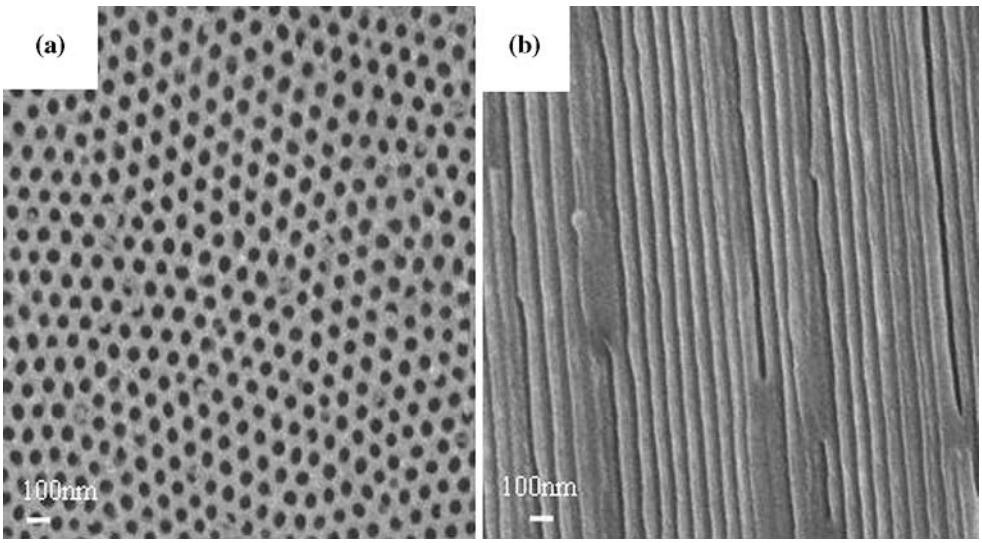

Fig. 2 SEM images of AAO template with 50 nm diameter pores (**a**) and Fe_3Co_7 nanowire arrays embedded in AAO template (**b**)

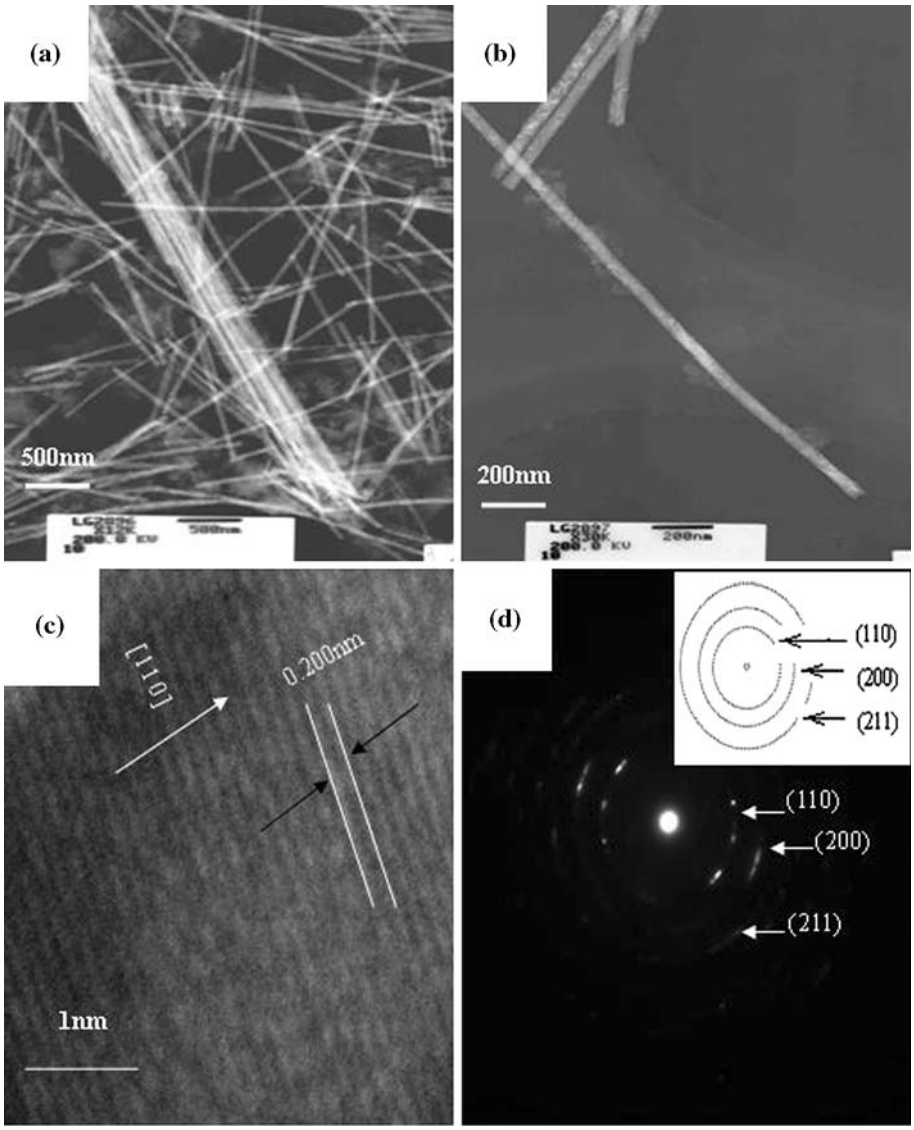

Fig. 3 **a** TEM image of as-deposited Fe_3Co_7 nanowire arrays. **b** TEM image of a single Fe_3Co_7 nanowire with 50 nm in diameter. **c** The corresponding HRTEM image. **d** SAED pattern of a single nanowire

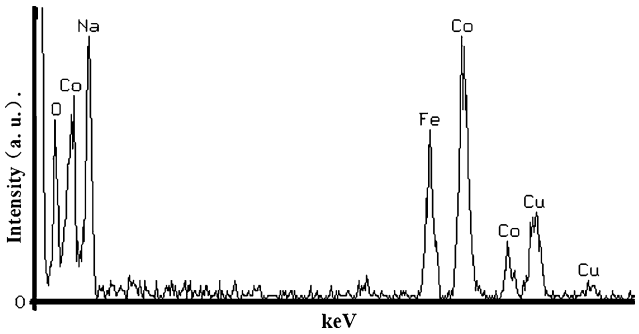

Fig. 4 Representative energy dispersive X-ray (EDX) spectra of Fe_3Co_7 alloy nanowires

of the single nanowire in Fig. 3b. The corresponding electron diffraction pattern exhibits several strong and discontinuous rings with scattered spotty reflections, which are all indexed to (110), (200), and (211) reflections of bcc Fe_3Co_7 phase, indicating that the Fe_3Co_7 alloy nanowires are polycrystalline, which is consistent with the results of XRD analysis (Fig. 1).

Figure 4 shows the representative EDX spectra corresponding to the Fe–Co nanowire arrays in Fig. 3a. Peaks corresponding to Fe, Co, Cu, and O are detected, and the Fe/Co atomic ratio is 30.35/69.65, which is well agreed with the X-ray results. Especially, the peak of element O in Fig. 4 can be ascribed to the oxidation products of Fe_3Co_7 nanowires, while the strong peak of element Na can be attributed to the NaOH residuals.

Magnetic properties of the Fe_3Co_7 nanowires were investigated at room temperature using a vibrating sample magnetometer with an applied field of 15 kOe. Figure 5 shows the magnetic hysteresis loops of Fe_3Co_7 nanowire arrays as-deposited for 2 h and annealed at 773 K with Ar protection for 2 h, where the applied field is parallel (//) or perpendicular ($\perp$) to the nanowire's axis. The nanowires can be regarded as infinite circular columns for their huge aspect ratio (over 120 in this experiment), and the AAO template is seen as thin circular plate, Well then, the hysteresis loops are corrected by the effective demagnetizing factor N_{eff} of the filled membrane is given by the expression [18, 19]

$$N_{\text{eff}} = N + f(N' - N) \quad (1)$$

where N is the demagnetizing factor of the single wire, N' is the overall demagnetizing factor for the whole template and f is the fill factor (0.55). Hence, the N_{eff} along the nanowires is 0.55 and perpendicular to them is 0.22. This suggests that the field required to reach the saturated magnetization, as shown in Fig. 5, is larger in parallel (//) case and may be attributed to the shape anisotropy of the wires.

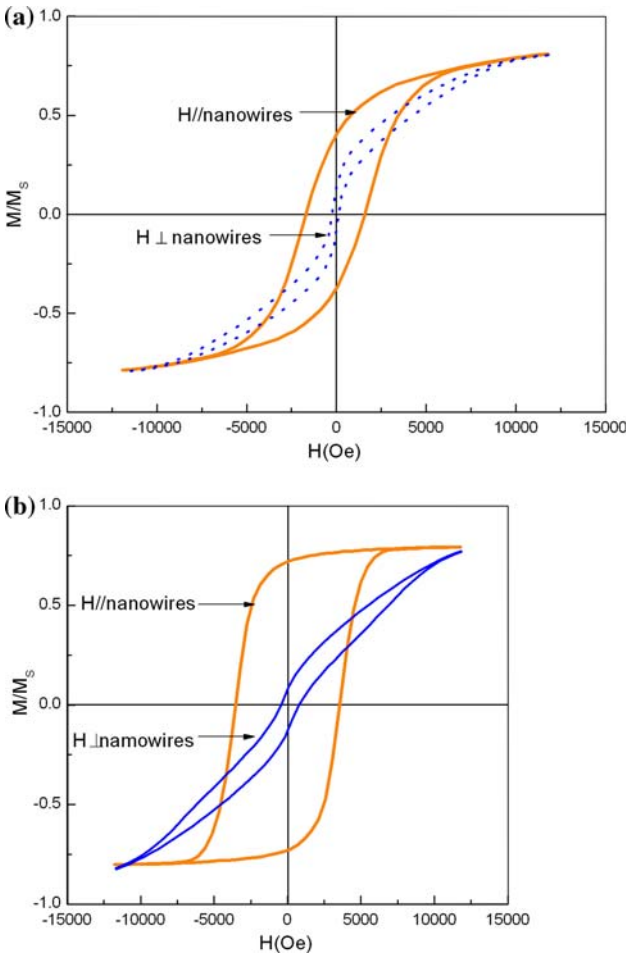

Fig. 5 Typical hysteresis loops of the samples before (**a**) and after (**b**) annealing measured in a magnetic field parallel and perpendicular to the long axes of Fe_3Co_7nanowires, respectively

From Fig. 5, we can see that the magnetic hysteresis loops have different shapes in parallel and perpendicular directions, the coercivities of as-deposited and annealed samples measured along the wire are 1369 and 2952 Oe and the squareness ratios are 0.50 and 0.907, respectively. While the values of coercivity and squareness measured perpendicular to the wire axis are much smaller, which indicate that the arrays exhibit an obvious anisotropy with the easy magnetizing axis along the length of the nanowires, this also means the shape of anisotropy is higher than magnetocrystalline anisotropy [20], hence determines the magnetic behavior of the Fe_3Co_7 nanowires.

The ideal coercivity (along the nanowire) estimated by Stoner–Wohlfarth coherent rotation mechanism is $Hc = 2\pi Ms \approx 15000$ Oe [8, 20]. However, the highest coercivity we obtained is 2952 Oe which is higher than that of most FeCo alloy nanowires reported so far, still much lower than that of ideal sample. The great difference in coercivity can be explained by two factors. First, although internal stress in the as-deposited samples reduced rapidly

and a higher degree of crystallization was obtained with annealing, many crystal defects remained in nanowires, which will decrease the coercivity and squareness in the annealed samples; second, Fe_3Co_7 would react with O_2 existed in AAO template at high temperature, and the presence of Fe_3Co_7 oxide would decrease the Ms (Saturation magnetization) largely in the sample. Therefore, these two factors will prevent the occurrence of coherent rotation in our Fe_3Co_7 nanowire arrays and thus prevent the coercivity from reaching the ideal value. So, the preparation conditions need to be optimized and higher magnetic properties are expected.

Conclusions

To summarize, highly ordered Fe_3Co_7 alloy nanowire arrays were prepared by DC electrodeposition with AAO template. The result of XRD and HRTEM suggests that the nanowires have a body-centered cubic polycrystalline. It is found that the samples (before and after annealing) have superior perpendicular anisotropy with its easy axis parallel to the nanowire arrays. After annealing the Fe_3Co_7 alloy, nanowires present higher coercivity and squareness than that of as-deposited, and the coercivity as high as 2952 Oe was obtained in the case annealing at 773 K, which suggests that Fe_3Co_7/AAO composite is very suitable for perpendicular magnetic recording medium.

Acknowledgements This work is supported by Doctoral Fund of Ministry of Education of China, (Project No. 20060080005). And this work is partly supported by Tianjin Natural Science Foundation of China with No. 09JCZDJC22800.

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