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Ultrafine Fe–Co nanowires: Fabrication and heat treatment influence on the structure and magnetic properties

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ABSTRACT

Ultrafine nanowires of Fe–Co with a diameter around 15 nm have been fabricated by electrodeposition method using anodic porous alumina as a template. The alloy nanowires were in the form of arrays and consisting of polycrystalline structures. They showed obvious shape anisotropy parallel to the axis of nanowires and the perpendicular coercivity ($Hc_{\perp}$) was found to be 2576.8 Oe which is higher than any coercivity value reported in the literature. The effects of critical factors such as heat treatment and temperature of annealing on the structure and magnetic properties of the ultrafine nanowire arrays were studied and discussed.

1. Introduction

Magnetic nanowire arrays have attracted considerable attention due to their potential applications, in particular, in areas of ultrahigh-density perpendicular magnetic recording media [1–4]. At present, the level recording mode, as the main recording mode, has reached the highest limit theory storage density. Hence, the perpendicular recording plays a vital role in improving the date storage density [5]. High saturation magnetization (Ms), superior perpendicular coercivity ($Hc_{\perp}$) and large squareness (Mr/Ms) are indispensable factors. Fabrication of high Ms and large Mr/Ms magnetic recording media is, therefore, receiving much attention of scientists worldwide [6]. In this regard, one-dimensional magnetic nanowires have high magnetic anisotropy [7] and its easy magnetic axis is parallel to the nano spools. The nanowires also show large squareness (Mr/Ms) when the additional magnetic field is applied parallel to nano spools [8]. Due to these peculiar features, these nanowires are at the forefront of the perpendicular magnetic media.

It is worth mentioning that the properties of nanomaterials in general largely depend on the way they have been synthesized. One promising technique to fabricate such nanomaterials is the electrodeposition within the nanoporous membranes [9]. Porous anodic alumites are considered as particularly attractive template materials for fabrication of a variety of nanowires due to their high pore density, uniform pore distribution and smaller pore diameter [10,11].

Previously, the synthesis of a variety of magnetic nanowire arrays such as Co [12], Ni [13], Fe [14], Fe–Pt [15], Co–Pt [16,17], Fe–Co [18], etc. using the porous anodic alumina oxide (AAO) as template have been reported by us as well as other researchers. However, the diameter of the nanowire was found to be above 20 nm. Interestingly, the density of magnetic recording and the coercivity are increased by the decrease in the size of nanowires [19]. To the best of our knowledge, only few reports could be found in the scientific literature describing the fabrication of ultrafine magnetic nanowire arrays with a diameter ∼15 nm. Wang et al. [20] reported the synthesis of ultrafine Fe and Ni–Co nanowire arrays with a diameter ∼5 nm and their magnetic properties were studied. In this study, ultrafine nanowires of Fe–Co alloy with a diameter around ∼15 nm were fabricated by electrodeposition method with the help of anodic porous alumina as a template. These ultrafine nanowires were found to be in the array form and their diameter was measured to be ∼15 nm. The effects of heat treatment on the microstructure and magnetic property of the nanowires were studied systematically.

2. Experimental section

2.1. Synthesis

Porous anodic alumina oxide substrates which were used as a substrate in this study were fabricated by anodizing pure alu-

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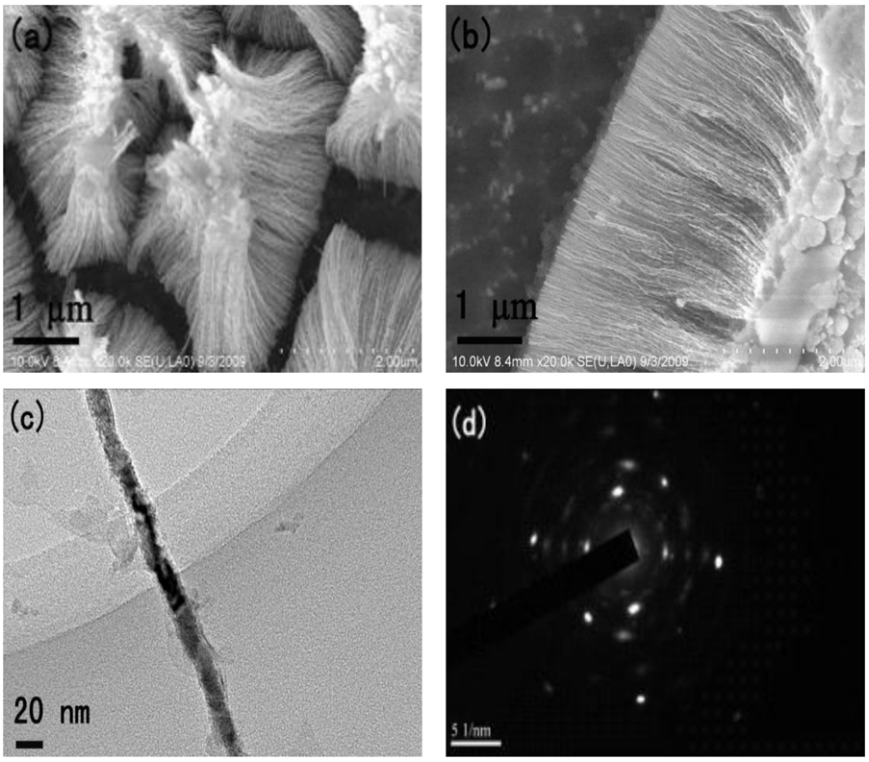

Fig. 1. (a) Top-view and (b) cross section SEM images of the ultrafine nanowire arrays; (c) TEM image of single Fe–Co ultrafine nanowire; (d) selected-area electron diffraction pattern of the nanowire.

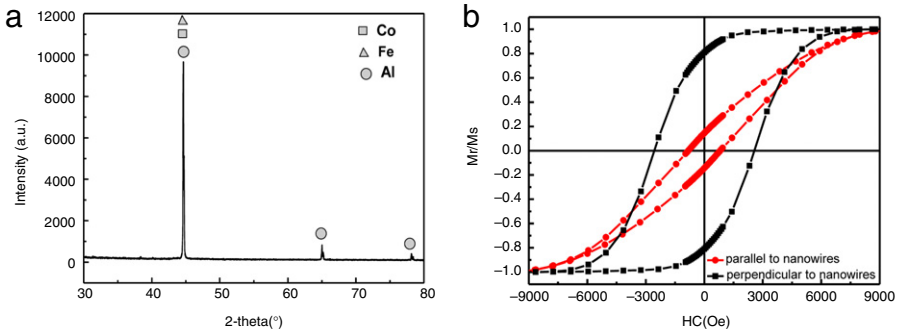

Fig. 2. (a) XRD patterns of the ultrafine Fe–Co nanowire arrays with AAO template; (b) the hysteresis loops of the Fe–Co nanowires at room temperature.

minum foils (99.9%) in a solution of sulfuric acid. Prior to anodizing, the aluminum foils were annealed at 500 °C for 2 h in order to reduce the defects in the foils and improve the crystallization quality of the substrates during the anodizing process. After heat treatment, the foils were polished and anodized by applying DC (15 V) in H_2SO_4 (0.36 mol/L) solution. The temperature was maintained at 0 °C for 20 h. After the anodization, the Anodic Aluminum Oxide (AAO) substrates were disposed by H_3PO_4 (0.3 mol/L) and washed with distilled water. The Fe–Co nanowires were electrodeposited into the pores by AC electrolysis in 100 mL electrolyte consisting of 2.47 g $Co(CH_2COO)_2 \cdot 4H_2O$, 2.78 g $FeSO_4 \cdot 7H_2O$, 1.0 g H_3BO_3, 1.0 g ascorbic acid, respectively, with a pH value of 4 AC electrodeposition was conducted at 50 Hz and 10–15 V.

2.2. Characterization

The obtained nanowires were characterized by field emission scanning electron microscopy (FE-SEM, JEOL S4800) and transmission electron microscopy (TEM, JEOL JEM-2100). The crystal structure and the texture of the nanowire arrays with AAO templates were studied using X-ray diffraction (XRD, Bruker D8 ADVANCE), and the magnetic properties of the samples annealed at different temperatures were measured by a vibrating sample magnetometer (VSM, Lakeshore, Model 7400 series).

3. Results and discussion

The microscopic images of ultrafine Fe–Co nanowire arrays, obtained after partly dissolving the aluminum substrate in NaOH solution, are illustrated in Fig. 1(a) and (b). It can be seen from the figures that the nanowires are ultrafine, uniform and well aligned vertically to the substrate with the same size and length. The features of the nanowires were found to be similar to the nanochannels of the AAO substrates indicating the growth of bimetallic nanowires was well controlled by the substrates. A typical TEM image of an isolated ultrafine Fe–Co nanowire obtained after complete elimination of the aluminum substrate is presented in Fig. 1(c), the diameter of the nanowire was measured to be about 15 nm, and the aspect ratio was found to be above 100. From the TEM images, a structure of slub shape can also be observed in crystal interior which might be caused by the defects existing in the nanowires. Fig. 1(d) presents the corresponding selected-area

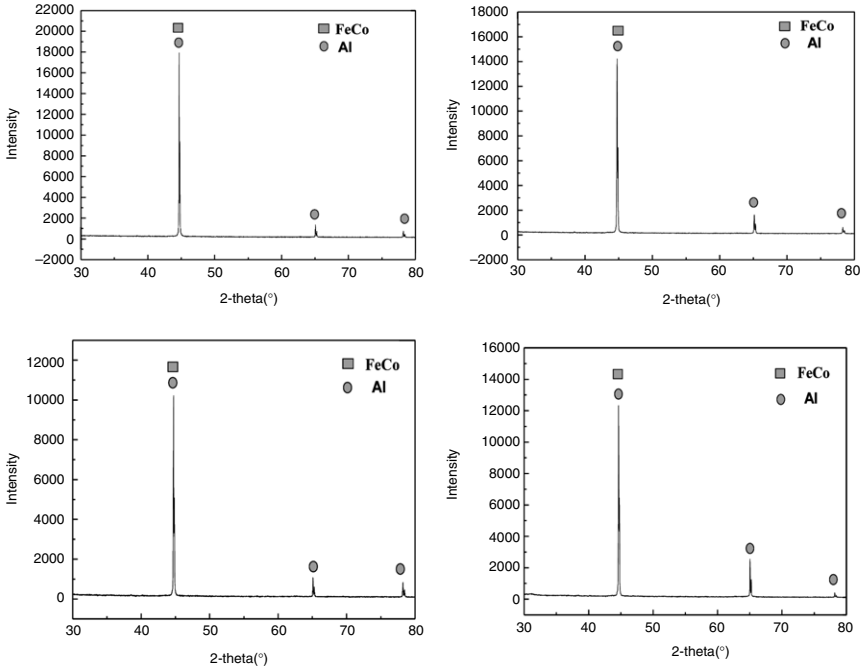

Fig. 3. Change in XRD patterns of the ultrafine Fe–Co nanowires with respect to heat treatment at different temperatures: (a) 300 (b) 400 (c) 500 and (d) 600 °C.

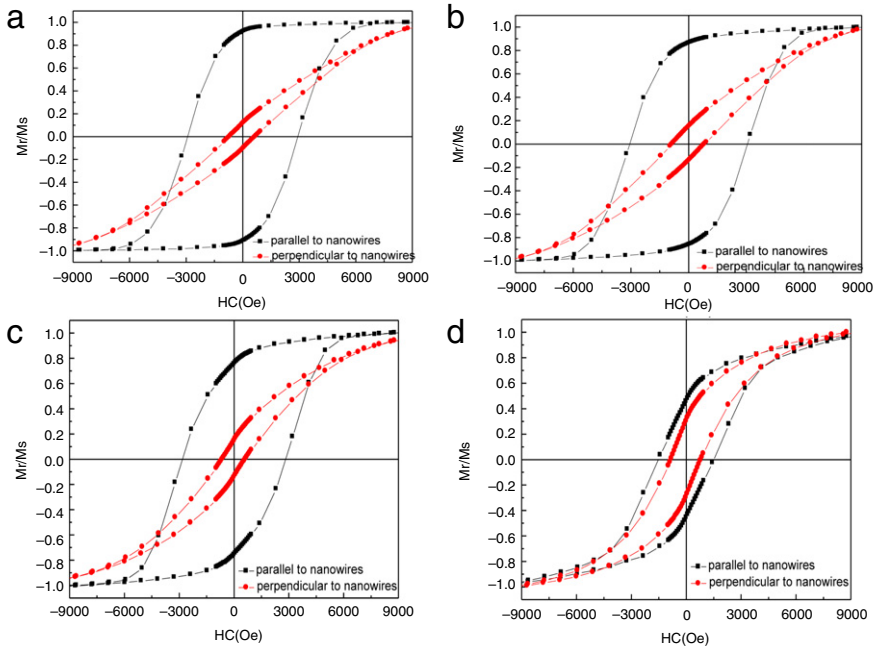

Fig. 4. The hysteresis loops of the Fe–Co nanowires obtained after heat treatment at different temperatures: (a) 300 (b) 400 (c) 500 and (d) 600 °C.

electron diffraction (SAED) patterns of the nanowires which clearly indicated that the nanowire is polycrystalline in nature.

Fig. 2(a) displays the XRD patterns of the ultrafine Fe–Co nanowire arrays obtained along with AAO template. Compared with the diffraction of pure aluminum, we can clearly see the diffraction peak of Fe–Co alloy at 44.6° which present the body-centered cubic (BBC) structure. To investigate the magnetic properties of the ultrafine nanowire arrays, hysteresis loops with the external field perpendicular (⊥) and parallel (//) to the sample plane at room temperature were measured and are shown in Fig. 2(b). It was obvious from the figure that the ultrafine nanowire arrays have an easy magnetic axis parallel to the axis of the nanowires due to the shape anisotropy; the perpendicular coercivity ($Hc_{\perp}$) and squareness (Mr/Ms) of the ultrafine Fe–Co nanowires was found to be 2576.8 Oe and 0.81, respectively. It is worth mentioning that the $Hc_{\perp}$ of Fe–Co ultrafine nanowire is higher than those reported in the literature [21].

The effect of temperatures such as 300, 400, 500 and 600 °C under inert environment on the microstructure and magnetic properties of the Fe–Co nanowires was also investigated and obtained results are presented in Figs. 3 and 4, respectively. In this heat treatment process, nanowires were heated along with the AAO templates. From Fig. 3, it is found that the diffraction peaks of (110) match very well with the BBC Fe–Co nanowire structure and the intensity of the peak was significantly improved after heat treatment.

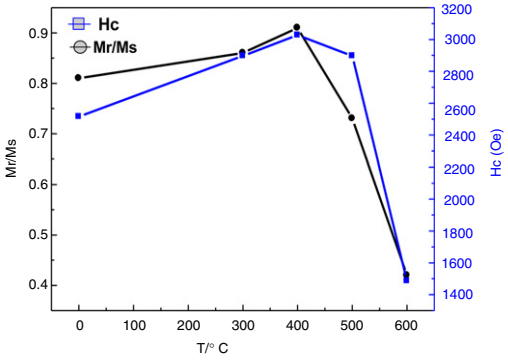

Fig. 5. The perpendicular coercivity ($Hc_{\perp}$) and squareness (Mr/Ms) of the ultrafine Fe–Co nanowires versus annealing temperature.

Fig. 4 shows the influence of different annealing temperatures on the hysteresis loops of the nanowires. It can be seen from the figures that the shape anisotropy and the easy magnetic axis parallel to the axis of the nanowires were maintained even after heat treatment. The higher is the annealing temperature, the more difficult to reach saturation. At the same time, the remanence ratio was found to be decreased, however, $Hc_{\perp}$ expanded. This was presumably caused by oxidization of the arrays under high annealing temperature.

Fig. 5 shows the change in $Hc_{\perp}$ and Mr/Ms of the ultrafine Fe–Co nanowires as a function of annealing temperature. It can be seen from the figure that the $Hc_{\perp}$ and Mr/Ms of the bimetallic ultrafine Fe–Co nanowires was found to be improved with the increase in temperature and a maximum value (3029.35 Oe and 0.92 respectively) was obtained at 400 °C. A further increase in the temperature deteriorated the $Hc_{\perp}$ and Mr/Ms values. At 600 °C, $Hc_{\perp}$ and Mr/Ms were 1008 Oe and 0.53 which were disproportionately lower than before. This phenomenon can be attributed to the following reasons: (1) the as-prepared ultrafine Fe–Co nanowires have a number of defects and high intrinsic stress due to the synthesis method which will reduce the Ms in the samples and the anisotropy induced by stress may compete with the shape anisotropy, which will decrease the coercivity and squareness. Heat treatment relieves the internal stress, so high Hc and Mr/Ms are expected. (2) When the temperature of heat treatment is more than 500 °C, the alumina will distort. The pore of the template will deflect from its original position and the shape anisotropy will drop down. The mechanism of this phenomenon is similar to Ni–Pb nanowires [22] reported previously.

4. Conclusion

A simple fabrication of ultrafine nanowires of Fe–Co with an average diameter ∼15 nm was demonstrated following electrochemical method and porous alumina as a template. Ultrafine nanowires showed a polycrystalline structure. The results indicate that the coercivity and squareness obtained by the fields applied parallel to the axis of nanowire arrays were much larger than those applied perpendicular to the nanowire arrays. The effects of heat treatment on the nanostructures and magnetic properties were investigated.

Acknowledgments

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