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Fabrication and characterization of electrodeposited $Co_{1-x}Cr_x$ nanowires

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Abstract

 $Co_{1-x}Cr_x$ alloy nanowires with 0.01 < x < 0.93 were fabricated by electrodeposition in a porous alumina membrane from an electrolyte containing Co and Cr ions. The composition, structure and magnetic properties of the nanowires have been characterized. Cobalt-rich nanowires were electrodeposited at a potential of -1.0 V relative to Ag/AgCl and chromium-rich nanowires were deposited beyond -3.5 V. The optimized processing conditions include hydrogen annealing to give hysteresis loops for the $Co_{80}Cr_{20}$ nanowires with coercivity of up to 200 mT and squareness of up to 0.95. Magnetization of the $Co_{80}Cr_{20}$ nanowire is 77 A m² kg⁻¹ and the energy product of the arrays is 35 kJ m⁻³.

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1. Introduction

Porous alumina membranes are ideal templates in which ordered arrays of magnetic nanowires of more or less uniform lengths and diameters are deposited. In recent years, electrodeposition of nanostructured arrays of pure metal nanowires [1,2], multilayered nanowires [3,4] and alloy nanowires [5,6] have been reported. Magnetic nanowire arrays are of potential interest for applications, such as high-density perpendicular magnetic recording, nanosensors, and magnetic MEMS [7–10]. For such applications, materials with perpendicular magnetic anisotropy and adequate coercivity are usually required [11–14].

Here we report the synthesis of $\text{Co}_{1-x}\text{Cr}_x$ nanowires in porous alumina membranes and the effect of annealing on their structural and magnetic properties. Co–Cr-based alloys are extensively used for hard disc magnetic recording [15], but there are no previous reports of electrodeposited ferromagnetic Co–Cr.

2. Experimental details

The Co-Cr alloys were electrodeposited from an aqueous bath containing CrCl₃, 6H₂O; CoCl₂, 6H₂O; H₃BO₃; HCOONH₄; and H₂NCH₂COOH. Ammonium formate (HCOONH₄) was used as complexing agent and glycine (H₂NCH₂COOH) as a brightening agent. The concentrations of the reagents are listed in Table 1. The composition of the $Co_{1-x}Cr_x$ alloy was adjusted by varying the cathodic growth potential from -1.0 to -4.0 V, where the potential is relative to the Ag/AgCl reference. Ammonium hydroxide (NH₃OH) solution was added to adjust the pH to between 5 and 6. Electrodeposition was carried out at constant potential in a conventional threeelectrode geometry consisting of a platinum counter electrode and an Ag/AgCl reference electrode. Porous alumina membranes, with pore diameter $d_{\rm p} \cong 200 \,\rm nm$ and thickness $t \simeq 60 \,\mu\text{m}$ (Whatman anodisc), were used as the working electrode. Prior to electrodeposition of the wires, a 150-200 nm layer of Pt was sputtered one side of the alumina membrane. The bath temperature was maintained at 25 °C during the deposition. After electrodeposition the

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filled alumina membrane was annealed at temperatures ranging from 550 to 800 °C for 40 min, either in a vacuum of 10^{-6} bar or in a hydrogen atmosphere. First, the furnace was heated to the desired temperature and the sample was then pushed into the furnace. After annealing, the samples

Table 1 The composition of the plating bath

Reagent	Concentration (M)
CrCl ₃ , 6H ₂ O (chromium chloride)	0.4
CoCl ₂ , 6H ₂ O (cobalt chloride)	0.2
H ₃ BO ₃ (boric acid)	0.7
HCOONH ₄ (ammonium formate)	1.8
H ₂ NCH ₂ COOH (glycine)	1.0
NH ₃ OH (ammonium hydroxide)	1.0



Fig. 1. Chemical compositions determined on single separated nanowires. Almost pure cobalt is deposited at -1.0 V while beyond -3.5 V the deposits are alloys with $\sim 93\%$ Cr and 7% Co.

were quenched in ice. Nanowires were extracted from the alumina template by dissolving it in an aqueous solution of chromic acid and phosphoric acid in a ratio 1:2. The nanowires were investigated using X-ray diffraction (XRD) with CuK_{α} radiation. Scanning electron microscopy (SEM) was used to examine single nanowires and the cross section of the filled alumina template. The atomic percentage of Co and Cr in the nanowires was determined by energy-dispersive X-ray spectroscopy (EDS). Magnetic properties of the nanowire arrays were measured at room temperature using a permanent-magnet vibrating-sample magnetometer (VSM) [16], and a 5T SQUID magnetometer.

3. Results and discussion

The arrays of the $\text{Co}_{1-x}\text{Cr}_x$ nanowires were prepared with composition ranging from x = 0.0-0.93 by varying the deposition potential from -1.0 to -4.0 V. The relation between composition and deposition potential is shown in Fig. 1. We focus on the samples with composition x = 0.20. Compositions far from 80:20 are magnetically soft even after annealing or less coercive field.

Fig. 2 shows a typical SEM micrograph of the cross section of a $Co_{80}Cr_{20}$ nanowire array prepared by electrodeposition for 2 h, after dissolution of the membrane. The wires have an average length of 15 µm and the pore diameter d_p is 200 nm; the center-to-center pore distance is 250 ± 30 nm. It can be clearly seen that the nanowires are parallel to each other through the entire pores. The length of the nanowires is very uniform, and it can be controlled in the range from several nanometers to a few tens of micrometers by varying the deposition time. A single wire separated from the alumina membrane is shown in Fig. 2(b). Straight, single nanowires more than 10 µm in length were used for chemical compositional analysis.



Fig. 2. (a) Cross-sectional SEM image of 200 nm diameter $Co_{80}Cr_{20}$ nanowires electrodeposited in the alumina template. (b) SEM image of a 200 nm $Co_{80}Cr_{20}$ alloy nanowire removed from the alumina template.

The XRD patterns for Co₈₀Cr₂₀ nanowires deposited at -2.8 V and annealed in hydrogen atmosphere at various temperatures are shown in Fig. 3. The pattern of the asdeposited wires shows the presence of an hexagonal-closepacked (HCP) cobalt phase with (002) texture. The peaks appearing close to $2\theta = 52^{\circ}$ and 77° are associated with the (430) and (602) reflections of the tetragonal CoCr phase. As can be seen in Fig. 3(b), the HCP (100) peak of cobalt is visible for samples annealed at temperature of 550 °C and it remains visible as the annealing temperature is raised from 600 to 800 °C. The samples annealed at high temperature (>650 $^{\circ}$ C) not only show the broadening of the cobalt HCP (002), peak but the (430) peak corresponding to CoCr tetragonal phase disappears and the (200) reflection of metallic chromium appears. The CoCr and metallic Cr peaks are marked as (\bullet) and (\bigcirc) , respectively, in Fig. 3. A similar appearance of the Cr (200) peak is reported by Schoenmaker et al. [17] on



Fig. 3. X-ray diffraction patterns for $Co_{80}Cr_{20}$ nanowires deposited at -2.8 V, after removal from the alumina template, (a) as-deposited and annealed in hydrogen atmosphere at (b) 550 °C, (c) 600 °C, (d) 650 °C, (e) 700 °C and (f) 800 °C for 40 min. (•) denotes tetragonal CoCr and (\odot) denotes Cr reflections.

 $Co_{76}Cr_{24}$ thin films deposited by magnetron sputtering. The broadening of HCP (002) cobalt peak could be due to the formation a mixture of cubic and hexagonal phases of cobalt [18].

Magnetic measurements of the nanowire arrays were performed at room temperature using the VSM. Fig. 4 shows the hysteresis loops of $\text{Co}_{80}\text{Cr}_{20}$ nanowire arrays of length ~10 µm annealed at 650 °C in vacuum (a) and in hydrogen atmosphere (b) for 40 min. The external field was applied parallel (||) and perpendicular (\perp) to the long axes of the nanowires, which were not removed from the membrane. The hysteresis curves are corrected by the effective demagnetising factor N_{eff} of the filled membrane is given by the expression [19]

$$N_{\rm eff} = N + f(N' - N),\tag{1}$$

where N is the demagnetizing factor of the individual wire, N' is the overall demagnetizing factor for the membrane



Fig. 4. Room temperature magnetization measurements of arrays of $Co_{80}Cr_{20}$ nanowires in an alumina template annealed at 650 °C for 40 min in (a) vacuum and (b) hydrogen atmosphere. Hysteresis loops were measured, with the magnetic field applied along (•) and perpendicular ($^{\bigcirc}$) to the nanowire.

and f is the fill factor (0.7). Hence, when the field is perpendicular to the membrane we find $N_{\text{eff}}^{\perp} = 0.7$, and in the parallel direction is $N_{\text{eff}}^{\parallel} = 0.15$. The coercivities measured along the wire for vacuum and hydrogen annealed samples (Fig. 4a, b) are 91 and 135 mT and the squareness is 0.82 and 0.95, respectively. Much smaller values of coercivity and squareness are measured perpendicular to the wire axis. Other samples have coercivity of up to 200 mT but lower squareness (0.83). The anisotropy is associated with the distribution of easy axis, which has a tendency to lie along the wire axis. The magnetization of the Co₈₀Cr₂₀ alloys is determined from SQUID measurements to be 77 Am² kg⁻¹. The remanent polarization of the filled alumina membrane is estimated as 0.32 T, and the maximum energy product is 35 kJ m⁻³.

Fig. 5(a) and (b) shows the dependence of coercive field and squareness as a function of the annealing temperature for $Co_{80}Cr_{20}$ nanowires annealed for 40 min in vacuum and



Fig. 5. Comparison of (a) coercive field $(\mu_o H_c)$ and (b) squareness (M_r/M_s) of vacuum and hydrogen-annealed $Co_{80}Cr_{20}$ nanowires annealed for 40 min at different temperatures. All measurements were performed at room temperature with the field applied along the nanowires.



Fig. 6. Variation of coercive field as a function of deposition potential after annealing at $650 \,^{\circ}$ C for 40 min in vacuum or hydrogen atmosphere. All measurements were performed at room temperature with the field applied along the nanowires.

in hydrogen atmosphere, when the external magnetic field is applied along the wires. For both, vacuum and hydrogen annealing the coercive field increases rapidly from 20 mT and reaches a maximum for the samples annealed at $650 \,^{\circ}$ C. As seen in Fig. 5(a) the coercive field drops by almost half for higher (>650 $^{\circ}$ C) annealing temperatures. The enhancement in coercive field and squareness could be due to a better alignment between the easy axis and the nanowire axis or a better distribution of secondary phases. The degradation in magnetic properties noticed for higher (> 650 $^{\circ}$ C) annealing temperature seems to be associated with the appearance of free chromium, disappearance of the CoCr phase as well as broadening of HCP Co (002) peak.

Fig. 6 shows the variation in coercive field after annealing in vacuum and hydrogen atmosphere for 40 min as a function of deposition potential. The magnetic field was applied along the nanowires during the measurements. The as-deposited samples were magnetically soft. The improvement in the coercive field is obvious for the samples annealed in hydrogen atmosphere. It is also observed that the wire deposited close to -2.8 V deposition potential the coercivity increases up to 135 and 91 mT for hydrogen and vacuum annealing, respectively. The coercive field systematically decreases as the deposition potential changes on either side of -2.8 V.

4. Conclusions

We have developed a method for producing $Co_{80}Cr_{20}$ nanowire arrays, and single $Co_{80}Cr_{20}$ nanowires, which show useful coercivity and reasonably square hysteresis loops after annealing in vacuum or hydrogen atmosphere. It is expected that the magnetic properties could be further improved with additives, as for magnetic recording media. The system, as it stands, is suitable for producing nanowire array of hard and soft magnetic materials or segmented magnetic nanowires by depositing at different potentials from the same bath.

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