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A study on electrochemical growth behavior of the Co–Ni alloy nanowires in anodic aluminum oxide template

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ABSTRACT

This study shows the growth behavior of Co–Ni alloy nanowires in AAO template. Growth of nanowires consists of four different stages namely electronucleation, steady state growth, filling of pores, and coverage of filled nanowires and forming of a film on the template surface. TEM study of nanowires showed that the nanowires possess hemispherical head due to the preferable and more rapid growth phenomenon in central section of nanowires instead of edge sides. Studies on the relations between nanowires composition and ion concentration in solution showed that growth of nanowires is a diffusion-controlled process. The compositional, structural and magnetic properties of nanowires were investigated by means of EDX, TEM and VSM.

1. Introduction

Recently, we have reported on electrodeposition of Co–Ni alloy thin films [1,2] and furthermore, there are some comprehend studies on electrodeposition of Co–Ni alloy films [3] because of their unique properties. This study is about the electrodeposition of Co–Ni alloy nanowires. Arrays of metallic nanowires, especially magnetic nanowires, are attractive for many studies [4–10] because of their potential application in high-density magnetic recording devices, sensors and fundamental scientific studies in nano scale [11–13].

Among the various methods of nanowires fabrication, template synthesis method was proved to be a low cost and high yield technique [4–10,14,15]. Between the possible templates, two-step anodized anodic aluminum oxide (AAO) templates with hexagonally ordered pores are more interesting. Changing the parameters of anodizing process makes it feasible to fabricate templates with different pore geometries [16–22]. Some mechanism studies on metallic nanowires electrodeposition have been done [23–28]. In ac voltage electrodeposition of nanowires in AAO templates [6,8,21], reduction of cations normally occurs in cathodic half cycle of current and in the followed anodic half cycle the current drops to zero and polarization decrease [29]. Accordingly, four different growth sequences have been observed in the growth of nanowires, namely electronucleation, steady state growth, filling of pores, and coverage of filled nanowires and forming of a film on the template surface [23–28].

In the present study, we have investigated the electrochemical growth sequence and growth behavior of the Co–Ni alloy nanowires with emphasis on the TEM observations and electrochemical current transient curves. Moreover, the compositional, structural and magnetic properties of the nanowires were studied by different techniques.

2. Experimental

At first, highly ordered AAO templates were synthesized by two-step anodizing of aluminum in sulfuric acid solution to increase pore ordering [16–19]. High purity aluminum foils (99.99%) were annealed at 400 °C in order to obtain homogeneous condition for pore growth. The Al foils were degreased in acetone, etched, polished and electropolished in a 1:4 volume mixture of $HClO_4$ and C_2H_5OH at temperature 5 °C. The first step of anodizing was carried out under a constant cell voltage of 20 V in a 0.3 M H_2SO_4 solution for 3 h, where temperature was kept constant about 2 °C. Then, the alumina layer was removed in a mixture of phosphoric acid and chromic acid, and the Al sheet was anodized again under the same condition as above for the second step for 1 h. Thickness of the barrier layer of oxide film decreased by reducing the anodizing voltage at the end of the second stage of anodizing and the anodized materials immersed in 5% phosphoric acid for pore opening. The diameter and length of the fabricated AAO templates are around 30 nm and 5 μm, respectively. In practice, special electrical properties of barrier layer in AAOs make ac current a suitable technique for electrodeposition of nanowires. There is Al^{3+} deficit in its lattice at the interface of barrier layer and electrolyte, and O^{2-} deficit at the interface of barrier layer and aluminum. So, it acts like a couple of N and P semiconductor and rectifies the current like a diode [29]. Solutions were prepared by dissolving reagent grade chemicals in triply distilled water and were composed of $CoSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}6H_2O$ and 0.4 M H_3BO_3 with pH 3.6 (Table 1). A three electrode cell was used with anodized template as working electrode (surface area 0.38 cm^2) and platinum plate 10 times larger as anode. Reference electrode was a saturated calomel elec-

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Table 1
Composition of solutions considered in present study.

Solution	$CoSO_4 \cdot 7H_2O$ (M)	$NiSO_4 \cdot 6H_2O$ (M)	H_3BO_3 (M)
1	0.150	–	0.4
2	0.100	0.2	0.4
3	0.125	0.2	0.4
4	0.150	0.2	0.4
5	0.175	0.2	0.4
6	0.200	0.2	0.4

trode (SCE) and the current curves were obtained in 25 °C. Different ac voltages in the range 12–22 V (constant frequency of 50 Hz) were applied for electrodeposition. The chemical composition of the nanowires was determined by energy-dispersed X-ray spectrometry (EDX). The structure of nanowire arrays was investigated by transmission electron microscopy (TEM). The magnetic properties of the nanowire arrays were studied using vibrating sample magnetometry (VSM) technique. The disk samples with diameter 0.7 cm were used for the measurement and the magnetization curves (*M*–*H*) were recorded at 25 °C.

3. Results and discussion

Magnetic nanowires of Co and Co–Ni alloys with diameter of 30 nm and length of 5 μm were fabricated by electrodeposition into the AAO templates. Morphology of the Co–Ni alloy nanowires is illustrated in Fig. 1 by TEM. Templates were immersed in chromic acid to separate the nanowires in solution and preparing them for TEM studies. Fig. 1a shows that nanowires have smooth surface and according to Fig. 1b it is obvious that nanowires have hemispherical head which is not completely packed. In other words, each nanowire has compound of two distinct sections; the first section is the body of the nanowire which is completely packed and retains the pore shape, and the second section is the growing part of the nanowire which is not completely packed and has hemispherical form. Fig. 1c shows the corresponding selected-area electron diffraction patterns (SAED), showing a HCP dominant structure for Co–Ni alloy nanowires (due to high cobalt content of alloy).

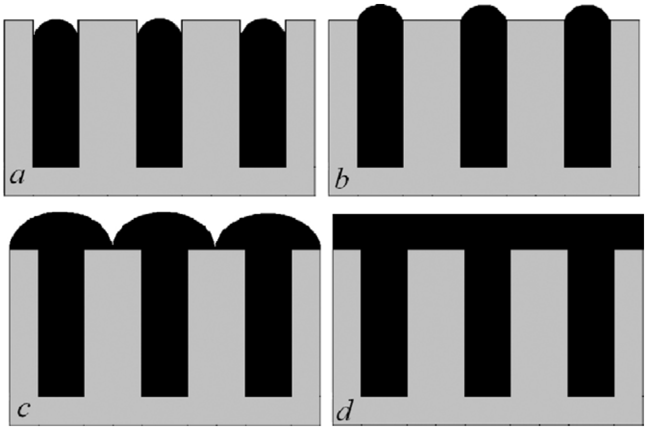

Fig. 2. Schematic illustration of growing nanowires in AAO template.

Fig. 2 illustrates the schematic pictures of growing nanowires in AAO template. Structural differences between Al_2O_3 and Co–Ni alloy cause rapid growth of nanowires in central section with hemispherical head. Furthermore, as shown in Fig. 2, there is a decrease in electroactive surface area during the transfer from stage “c” of the nanowires growth to stage “d”. So, there should be a decrease in electrodeposition current too. Fig. 3 shows the current transient curves for the growth of Co and Co–Ni alloy nanowires that supports the presented growth behavior in Fig. 2. According to Fig. 2 and current transients for the single Co deposition in Fig. 3a, there are four different growth stages: (1) After a current peak at the initial time due to the double layer formation on the template surface, the faradic current starts the nucleation of the nanowires. Progress in nucleation accelerates the current drop due to increase in mass transport limitations. (2) Then steady state growth of nanowires starts with hemispherical head due to easier growth in central section of nanowires (stage “a” in Fig. 2). (3) The pores are filled up

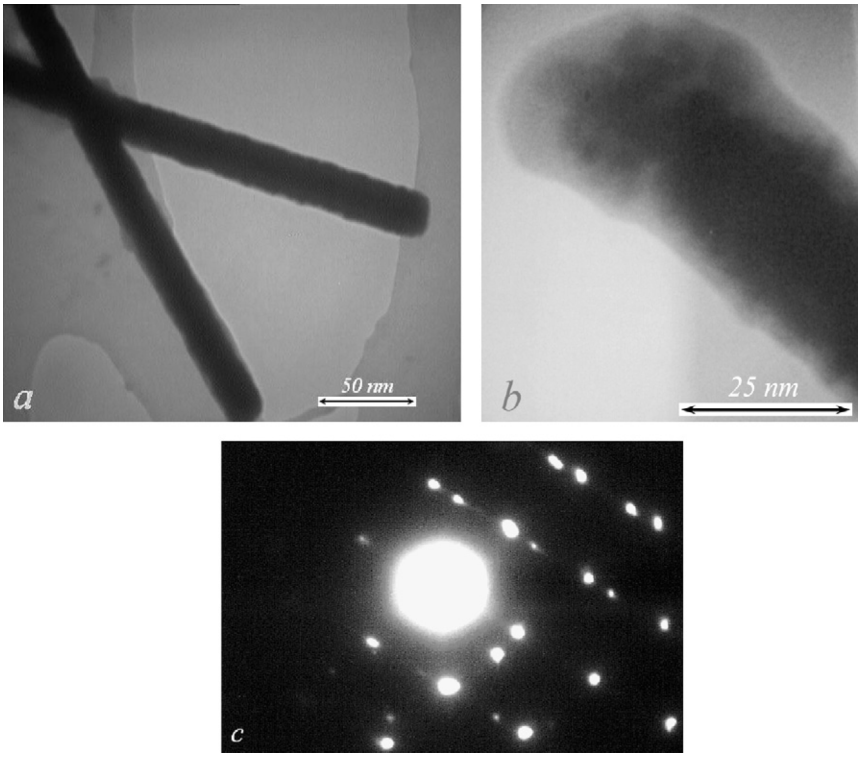

Fig. 1. TEM images of Co–Ni alloy nanowires: (a) solution 3, 19 V ac, (b) solution 5, 19 V ac, (c) selected-area electron diffraction pattern (SAED).

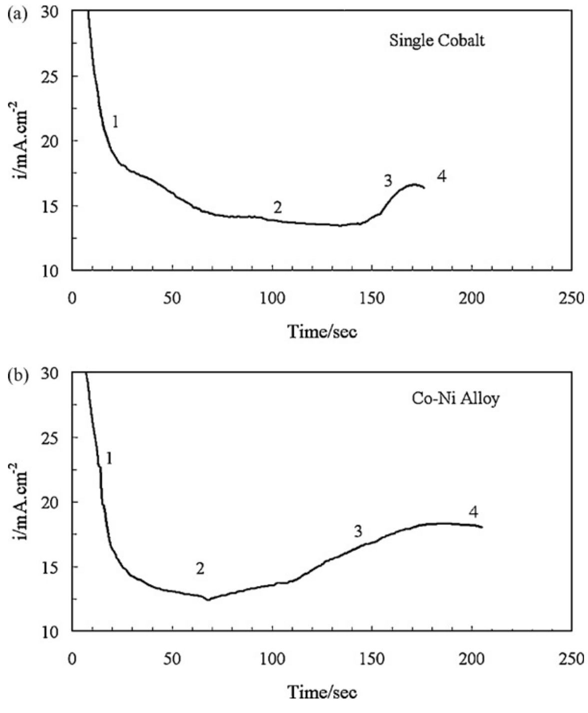

Fig. 3. . *I–t* transients for deposition of: (a) single Co nanowire (solution 1), (b) Co–Ni alloy nanowire (solution 4); pH 3.6, voltage 19 V ac.

and 3D caps form on the raised head of each of nanowires and just a moment before the complete coverage of caps, the current will reach to the maximum amount due to the existence of maximum electroactive surface area (stage "c" in Fig. 2). (4) Afterward, caps reach together and cover the electrode surface (stage "d" in Fig. 2). Consequently the electrodeposition current will decrease due to the decrease in electroactive surface area. In this situation, the total electroactive surface area is equal to the total exposed surface area of template in solution (Fig. 2). This growth mechanism is also adaptable for the Co–Ni alloy nanowires growth as shown in Fig. 3b.

Figs. 4 and 5, respectively show the influence of solution concentration and electrodeposition potential as two important process parameters on the chemical composition of the electrodeposited Co–Ni alloy nanowires. Fig. 4 supports a direct relation between nanowires composition and solution concentration. Interestingly, Fig. 5 shows a relation between applied voltage and solution concentration for low voltages (<17 V), and for higher voltages, this relation disappears and increasing the voltage does not affect the composition of nanowires. As an explanation, in low voltages, the electrochemical reactions are charge transfer controlled and a change in voltage will affect the rate of electrochemical reactions and so the composition of deposited alloys. For the higher voltages, the diffusion-controlled growth condition appears and Co^{2+} and Ni^{2+} ions compete together for reaching to the electrochemically active surface and therefore, the diffusion coefficient of ions (which mainly is a function of temperature) has the most significant affect on the electrochemistry of process or nanowires composition. This kind of behavior in electrodeposition of Co–Ni alloy nanowires is different from the behavior of film deposition. Electrodeposition of Co–Ni alloy film shows anomalous codeposition behavior [1] but in the case of nanowires increasing the concentration of Co^{2+} in solution increases the cobalt content of nanowires (Fig. 4).

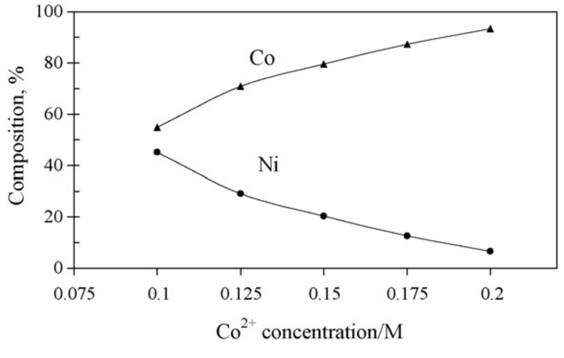

Fig. 4. The composition of the Co–Ni alloy nanowires vs. Co^{2+} concentration, voltage 19 V ac.

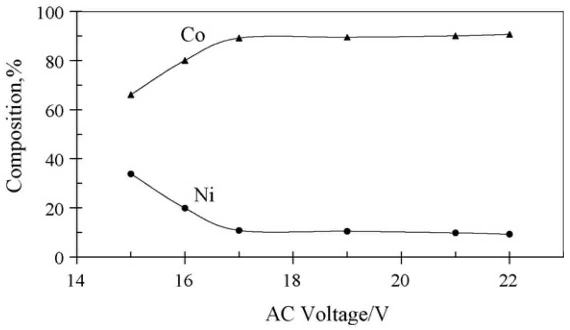

Fig. 5. The composition of the Co–Ni alloy nanowires vs. ac voltage, solution 5.

Table 2
The H_C and M_r/M_S values for the Co–Ni nanowires.

	Solution		
	2	3	4
	55% Co[a]	72% Co[a]	80% Co[a]
H_C (Oe)			
In plan	540	540	640
Out plan	1020	920	1000
M_r/M_S			
In plan	0.15	0.18	0.26
Out plan	0.59	0.45	0.53

[a] Co (%) in nanowire.

It is known that nanowire arrays show an apparent magnetic anisotropy [9], because the shape of a material is a source of magnetic anisotropy. In the case of nanowires, the magnetostatic vector prefers to be along the nanowires axis where the demagnetizing factor is the smallest and so the magnetostatic energy is the lowest. Therefore, the directions perpendicular and parallel to the substrates of arrays are easy and hard axis, respectively. For magnetic studies nanowires were prepared in solutions 2–4 with same voltage (19 V ac) and length of approximately 5 μm. The hysteresis loops of the deposits are measured with external field perpendicular (out-plan) and parallel (in-plan) to the templates plane at 298 K. The H_C and M_r/M_S values for all measurements are gathered in Table 2. In this case, the squareness and coercivity (perpendicular to substrate) are 0.59 and 1020 Oe, respectively, in solution 2 whereas are 0.45 and 920 Oe in solution 3, and 0.53 and 1000 Oe in solution 4. According to other study [30], the nanowire arrays are more applicable for magnetic recording medium that has coercivity between 500 and 1000 Oe, and has a high squareness.

4. Conclusions

The AAO templates were prepared by two-step anodizing process, where pores were arranged in a hexagonal configuration with an almost perfectly round section. The Co and the different Co–Ni alloy nanowire arrays were successfully electrodeposited by ac current. TEM studies showed hemispherical head for nanowires during the growth process. This growth behavior supports the fact that the growth in central section of nanowires is more rapid than the outer layer of nanowires. Furthermore, regarding TEM studies it was concluded that hemispherical head of nanowires is not completely pack. In other words, nanowires consist of two distinct sections out of which the first one is the body of the nanowire with dense structure and the second one is the hemispherical growing head of the nanowire with unpacked structure. It was shown that for the voltages more than 17 V ac, the electrochemical reactions are restricted by mass transport (diffusion-controlled growth). The nanowires composition was changed directly by changing ions concentration in solution. The fabricated nanowires are very dense with smooth wall and possess a HCP dominant structure and high H_c and M_r/M_s values.

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