JNS 1 (2012) 249-255

Journal of
NANOSTRUCTURES

JNS
NANOSTRUCTURES
JNS.kashanu.ac.ir

The effect of pulsed electrodeposition parameters on the microstructure and magnetic properties of the CoNi nanowires

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Article history:
Received 17/1/2012
Accepted 26/2/2012
Published online 1/3/2012

Keywords:
Pulsed electrodeposition
CoNi nanowires
Porous alumina template

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Abstract

CoNi nanowires were deposited by pulsed electrodeposition technique into porous alumina templates. The effect of off time between pulses (t_{off}) and reductive/oxidative time ($t_{reduc/oxid}$) on the microstructure and magnetic properties of the CoNi nanowires were investigated. Maximum coercivity and squareness were obtained for samples fabricated at $t_{reduc/oxid}$= 0.5 ms and t_{off} =400 ms. The coercivity increases in the range of 930–1990Oe by increasing of off time from 20 to 400 ms. The initially hcp structure of the nanowires was converted to an amorphous structure by increasing of off time between the pulses.

1. Introduction

The fabrication of nanoporous materials has recently attracted more attention due to their potential utilization in magnetic, electronic and optoelectronic structure and devices [1]. Development of two step anodization technique by Masuda and Fukuda [2] has been created possibility for production of ordered nanopores with perfectly hexagonal structure. The self-ordering mechanism during pore growth leads to densely packed andhexagonally ordered pore structures reported under some specific anodization conditions in oxalic, sulfuric and phosphoric acid solutions [3].

Ferromagnetic nanowires such as Fe, Co and Ni are interested because of their potential applications in ultrahigh density magnetic recording media [4-5]. CoNi as a binary ferromagnetic alloy has many applications in mechanical [6], electrocatalytic [7]

and magnetic fields [8, 9]. CoNi alloy is an important material in industrial because of its unique magnetic properties.

In the present work, the effect of pulsed electerodeposition parameters, $t_{reduc/oxid}$ and t_{off}, on the microstructure and magnetic properties of CoNi nanowires prepared by pulsed electrodeposition technique into nanoporous alumina was studied.

2. Experimental

The high-purity aluminum plate (99.999% and thickness of 0.3 mm) was degreased in acetone and de-ionized water. In order to remove oxide layer of the aluminum surface, the samples were etched in a 0.3 M NaOH solution for 3 min. subsequently, the sample was electro-polished by 1:4 volume mixture of $HClO_4$ and C_2H_5OH with current density of 100mAcm^{-2} at ambient temperature. To obtain highly ordered pores, a two-step anodization process was employed. In the first step, anodizing of sample was performed in the 0.3 M oxalicacid solution at 40V and 17°C for about 10 h. Wet chemical etching by mixture solution of 0.5 M phosphoricacid and 0.2 M chromicacid was used for removing of thick oxide layer at 60°C for 10 h.The sample was re-anodized for 60 min using the first step conditions. Following the second anodization, the voltage was systematically reduced to promote thinning of the barrier layer. The voltage was lowered by 4 Vmin^{-1} to 20 V, 2 Vmin^{-1} to 10 V and then, 1 Vmin^{-1} to 8 V. In order to facilitate periodic electrodeposition process, anodization was continued in this voltage for about 3 min which balanced the system and created uniform barrier layer at the pores. The CoNi nanowires were electrodeposited in an aqueous electrolyte consisting of 0.3 M $CoSO_4$, 0.3 M $NiSO_4$, 45 gl^{-1} boric acid at a pH value of about 5 at 30°C. The effects of off-time (50, 100, 200 and 400ms) and reductive/oxidative time (5, 2.5, 1.75, 1 and 0.5ms) on the physical properties of the pulsed electrodeposited nanowires were studied.The morphology of the nanowires was obtained using scanning electron microscope (SEM, model LEO 440i). Room temperature magnetic properties of the nanowire arrays were characterized using a home-made alternating gradient force magnetometer (AGFM). The crystal structure of the samples was determined by X-ray diffraction (XRD) analysis. XRD spectra were recorded in the θ/2θmode, between 2θ=35°and 80°with a step of 0.05° using monochromatic CuKα Radiation (XRD, PW1800, Philips). The individual layers of Co and Ni were identified by Energy Dispersive X-ray Spectroscopy (EDS, model LEO 440i).

3. Results and discussion

A top view of porous Alumina template and a cross-section of CoNi nanowires are shown in Fig.1. An arranged hexagonal cell configuration is observed with acell and pore sizes ofapproximately 104 and 30 nm, respectively. The cross-sectional view indicates non-intercrossing and parallel pores with high aspect ratio.

Coercivity variations with off-time were identified with applied field parallel to nanowires axis at

room temperature. Pulsed electrodepositionwas performed using sine waveform at t_{off}= 50, 100, 200, 400 ms and $t_{reduc/oxid}$= 0.5, 1, 1.75, 2.5, 5 ms.Figure 2 shows coercivity of the nanowires as a function of off time between pulses which differ in $t_{reduc/oxid}$value in the range of 0.5-5 ms.

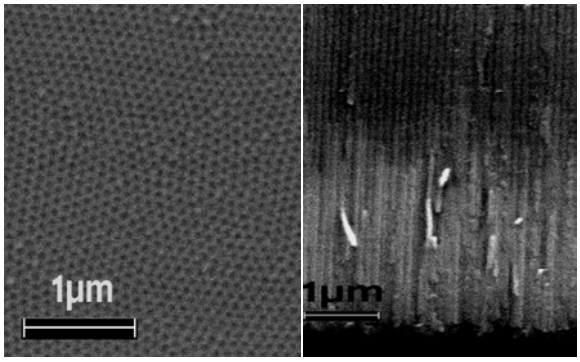

Fig. 1.(a) Top view SEM micrograph of porous Alumina template and (b) cross-section view SEM micrograph of CoNi-filled alumina template.

It is seen that the coercivity as a function of off-time with $t_{reduc/oxid}$ in the range of 1.75-5 ms follows the same behavior. By increasing off-time, coercivity increases up to its maximum value then decreases. In contrast, the coercivity of the prepared samples at $t_{reduc/oxid}$= 0.5 and 1 ms follow ascendant behavior by increasing off-time.

The squareness and coercivity of the samples as a function of off-time with $t_{reduc/oxid}$ = 0.5 and 1ms also show ascendant behavior. The results show coercivity and squareness values increase from 810 Oe and 0.6 for prepared sample at $t_{reduc/oxid}$=1.75 ms and t_{off}=20 ms to optimum values of 1990 Oe and 0.9 at $t_{reduc/oxid}$=0.5 ms and t_{off}= 400 ms. These results illustrate the extraordinary effect of fabrication conditions on the magnetic properties of the CoNi nanowires.

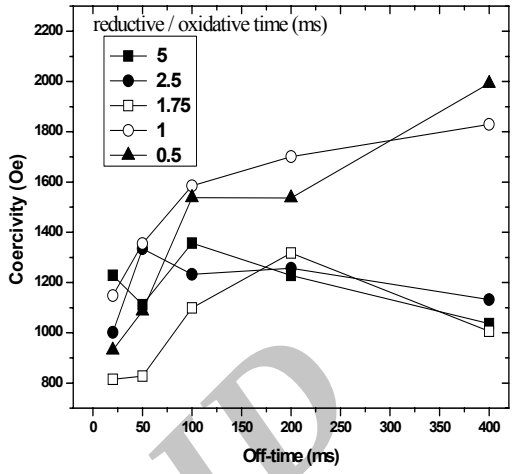

Fig. 2. Coercivity as a function of the off-time in various reductive/oxidative times.

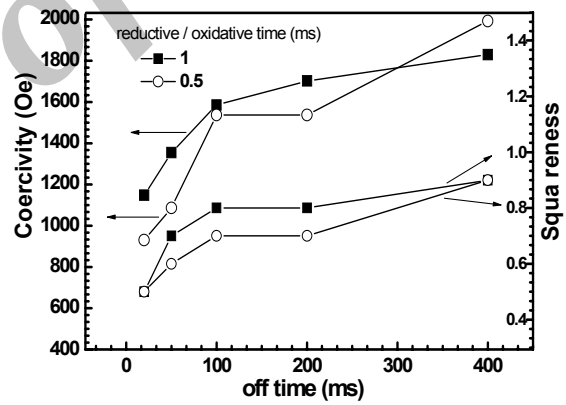

Fig. 3. Coercivity and squarenessas afunction of the off-time with reductive/oxidative times of 0.5 and 1 ms.

The saturation magnetization per unit area (M_s/A) as a function of off-time using $t_{reduc/oxid}$=0.5 and 1ms was measured and is plotted in Fig. 4. As seen in this Figure the M_s/A of the sample prepared by $t_{reduc/oxid}$=0.5msinitially increases with off-time reaches its maximum and the reduces while

M_s/A of the samples fabricated with $t_{reduc/oxid}$= 1 ms are almost independent of the off time.

Magnetic properties of the alloys are related to their composition and crystallinity. However, to analyze magnetic results, the elemental analyses were performed with X-ray diffraction (XRD) and the energy dispersive spectrum (EDS) analyzers. In order to remove Aluminum substrate from samples backward which weakens Co and Ni peaks in the EDS spectrum, a mixture of HCl and saturated $CuSO_4$ solutions was used.

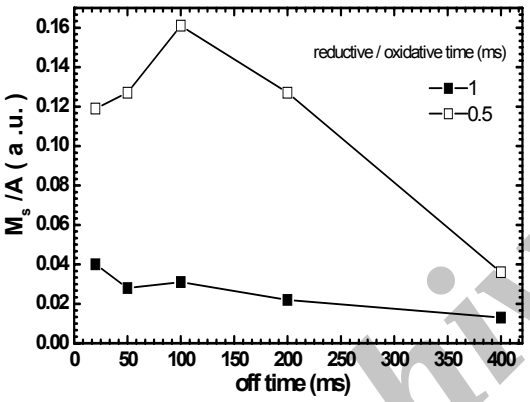

Fig. 4. Saturation magnetization per unit area as a function of the off-time using reductive/oxidative times of 0.5 and 1 ms.

The results of EDS spectrum show that variation of off-time has not any influence on composition of the alloys.However,small variations reported in table.1 are considered as analysis error. As a result, we used XRD to analyze relation of the magnetic properties and structure of nanowires.

Figure 5 shows the XRD patterns of the samples which were prepared at t_{off}=20, 400ms and $t_{reduc/oxid}$=1ms (Fig. 5a) and at t_{off}=100, 400ms and $t_{reduc/oxid}$=5ms (Fig. 5b).

Table 1. The results of composition analysis (EDS) of the CoNi nanowires with the reductive/oxidative times of 1,5ms and off-times of20,100 and 400ms.

$t_{reduc/oxid}$ (ms)	t_{off} (ms)	Co (%)	Ni (%)
5	100	88	12
5	400	91	9
1	20	92	8
1	400	92	8

The X-ray diffraction pattern of the prepared sample at off-time of 20ms and reductive/oxidative time of 1ms (Fig. 5a) exhibit the polycrystalline structure with several peaks in the (100), (002), (101) and (110) directions at 2θ=41.7, 44.6, 47.4 and 76.1° positions, respectively. According to Scherrer formula [10], the peak width indicates growth of small crystallites. The quantitative analysis shows that peak intensity of (100) and (110) directions together are larger than (002) direction. This implies a preferential orientation in the hcp structure of Co with easy axis perpendicular to the nanowire axis. With increasing off-time to 400ms, the crystal structure is converted to quasi-amorphous structure. Therefore increasing of coercivity of the prepared sample in 20–400ms off-time interval and at $t_{reduc/oxid}$=1ms is related to reduction of crystal anisotropy perpendicular to the nanowires axis.In the prepared sample at $t_{reduc/oxid}$=5ms and t_{off}=100ms, the easy-axis has components in the plane and axis

directions of the nanowire. Therefore, growth in perpendicular and parallel directions respect to nanowire axis has an average behavior. The existing peak in (100) direction in curve (b) indicates crystallinity perpendicular to nanowire axismore than parallel direction which causes reduction of the coercivity at t_{off}=400ms.

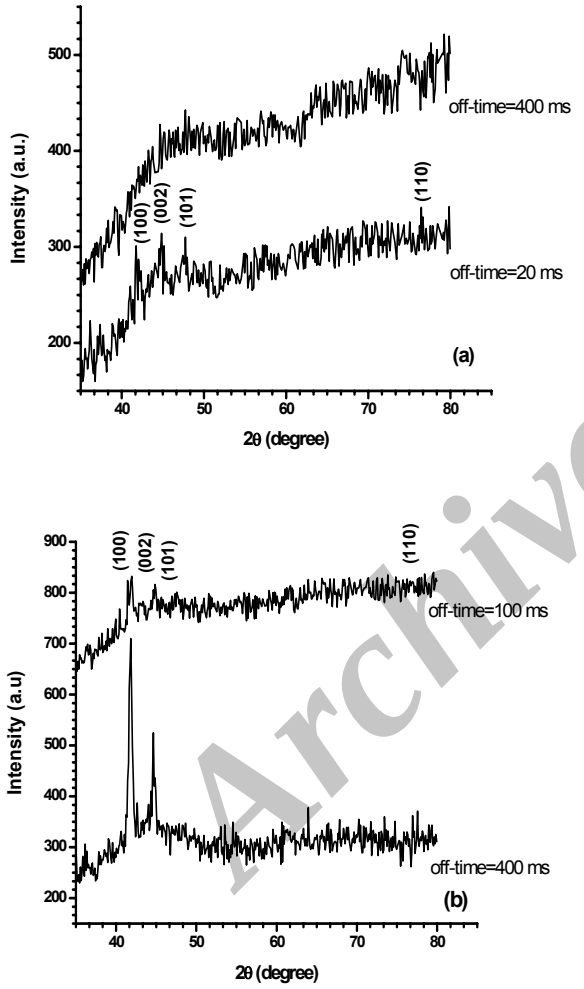

Fig. 5.XRD patterns of prepared CoNi nanowires at (a) reductive/oxidative time of 1 ms and off-time of 20, 400ms, (b) at reductive/oxidative time of 5ms and off-time of 100, 400ms.

Existing peak in (100) direction in Figure 6 ($t_{reduc/oxid}$=1.75ms and t_{off}=20ms) shows that preferential orientation of hexagonal axis is perpendicular to the nanowire.Coercivity increases at t_{off}=200 ms due to the existence of (101) and (002) peaks in XRD pattern which demonstrates preferential growth along the nanowire axis. With increasing off-time to 400 ms nanowire structure is converted to a quasi-amorphous structure or a crystal with very small grains which causes reduction of the coercivity.

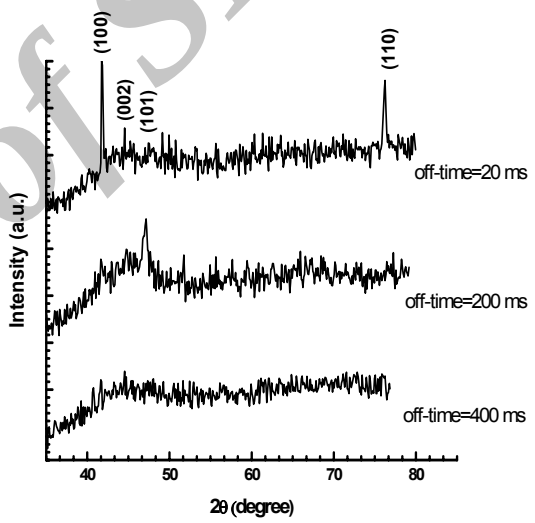

Fig. 6.XRD patterns of CoNi nanowire with reductive/oxidative time of 1.75ms.

The hysteresis loops of the prepared samples with t_{off}=20, 50, 100, 200 and 400ms and $t_{reduc/oxid}$=1ms are illustrated in Figure 7. As can be seen, with increasing off-time from 20 to 400ms and reductive/oxidative time of 1ms, the coercivity increases and the deposition amount decreases.

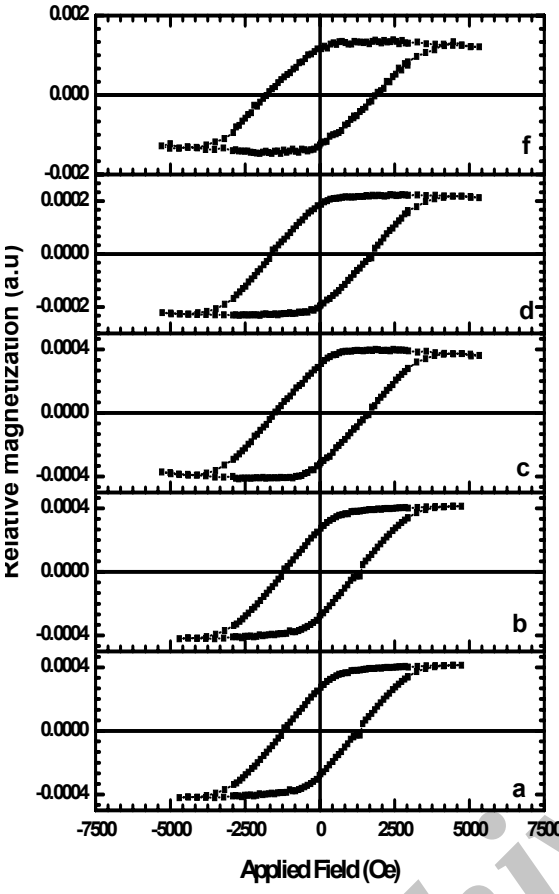

Fig. 7. The hysteresis loops of CoNi nanowire arrays with applied field parallel to the nanowire with the reductive oxidative time of 1ms and off-times of (a) 20ms, (b) 50ms, (c)100ms, (d) 200ms and (f) 400ms.

4. Conclusion

The effect of off-time and reductive/oxidative time on the structural and magnetic properties of the pulsed electrodeposited CoNi nanowires into porous alumina template were investigated. The off time between pulses and the reductive/oxidative timevaried in the range of 20–400 ms and 0.5–5 ms, respectively. The obtained results listed as follows:

The coercivity curves as a function of off-time in the reductive/oxidative times of 1.75, 2.5, and 5ms have similar behavior. With increasing off-time, the coercivity increases up to its optimum value, then decreases.

- The significant difference between the maximum and the minimum values of coercivity occurs in the sample with the reductive/oxidative time of 1.75ms. In addition the coercivity curve versus off-time of the sample with $t_{reduc/oxid}$=0.5 and 1ms has an ascending behavior.
- According to observations the optimum values of coercivity and squareness is related to the reductive/oxidative time and off-time of 0.5 and 400ms, respectively. However, with increasing off-time from 20 to 400ms, the coercivity increases from 930 to 1990Oe.
- The results of XRD analysis showed that with increasing off time between pulses, initially hcp crystal structure with c-axis perpendicular to the nanowires was converted to amorphous structure which causes reduction of crystalline anisotropy perpendicular to the nanowire and increasing of the coercivity.

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