Isotropic magnetization response of electrodeposited nanocrystalline Ni-W alloy nanowire arrays

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Abstract

Isotropic magnetization response was demonstrated in electrodeposited nanocrystalline Ni-15%W alloy nanowire arrays, which can be applied to nanoscale magnetic field sensors. The Ni-W alloy nanowire arrays were electrochemically synthesized on a nanochannel template electrode from an aqueous electrolytic solution. X-ray and electron diffraction patterns revealed that Ni-15%W alloy deposits were composed of ultrafine crystal grains with a supersaturated solid solution phase. The magnetization of the Ni-15%W alloy thin films reached saturation at around 2.5 kOe in a perpendicular direction to the film plane, whereas the pure Ni thin films hardly magnetized in the perpendicular direction. On the contrary, Ni-15%W alloy nanowire arrays were easily magnetized, and reach saturation at around 1.0 kOe, even in a perpendicular direction to the array film plane that corresponds to the long axis direction of the alloy nanowires.

Keywords: nanocrystalline, nanowire, nickel, tungsten, electrodeposition, magnetization

1. Introduction

Tungsten (W) has the highest melting point (3,695 K) among all metals in their pure forms, so its alloys exhibit excellent mechanical strength and thermal resistance. Usually, W alloys are produced by a powder metallurgy process at high temperatures. However, Ni-W [1], Fe-W [2], and Ni-Fe-W [3] alloy thin films can be prepared by an electrodeposition process at room temperature. WO_4^{2-} ions cannot be reduced to their metallic state in aqueous solutions containing only WO_4^{2-} ions, but they can be reduced when the aqueous solutions include iron-group metal (M^{iron}) ions, such as Ni^{2+} , Co^{2+} , and Fe^{2+} . Brenner classified this reduction process into the “induced co-deposition mechanism” [4].

Electrodeposited M^{iron} alloy thin films, which contain several tens of a percentage of W, usually consist of a supersaturated solid solution phase with nano-sized crystal grains [5]. Recently, nanocrystalline metallic materials and nanoparticles have received much attention due to their unique physical properties, such as mechanical strength [6], corrosion resistance [7-8], electron transport [9] and magnetic property [10-11]. Nanocrystalline M^{iron} -W alloy thin films are of special value to developers, because they exhibit excellent magnetization response and corrosion resistance [12]. Hence, M^{iron} -W alloy thin films can be applied to magnetic field sensors that are used for monitoring magnetic fields in corrosive environments, such as monitoring the wheel rotation rate in an automobile’s antilock brake system [13]. These magnetic field sensors will be required to sense the field 3-dimensionally. However, the conventional magnetic thin film sensors are hardly magnetized in a perpendicular direction to the film plane due to the large demagnetizing field caused by the inverse magnetic poles generated on the film surfaces [14]. On the other hand, nanoparticle-integrated structures [15-16] with strong shape magnetic anisotropy (K_s), such as electrodeposited M^{iron} magnetic nanowire arrays [17-19], can be magnetized even in a direction that is perpendicular to the array film plane, but the coercive force reaches around several hundreds of Oersted, which is too large to be applied to a conventional magnetic field sensor. To improve the soft magnetic property of the M^{iron} nanowire array, the magneto crystalline anisotropy (K_c) should be decreased. If nanocrystalline M^{iron} -W alloy nanowire arrays are synthesized by the electrodeposition technique, then a 3-dimensional nanoscale magnetic field sensor will be realized.

In this study, the nanocrystalline structure and magnetization behavior of Ni-W alloy nanowire arrays were synthesized from acidic aqueous solutions by using an induced co-deposition technique to develop a corrosion-resistant nanoscale magnetic field sensor with an isotropic magnetization response.

2. Experiment

The bath compositions for the electrodeposition of the Ni-W alloys are shown in Table 1. The electrolytic solutions were synthesized from the following chemicals: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3$ (citric acid). The solution's pH was adjusted to 2.0 by adding H_2SO_4 and NaOH . An ion track-etched polycarbonate membrane filter with numerous nanochannels (pore diameters of 80 and 160 nm, pore length of 6 μm , and pore density of 6×10^8 pores·cm⁻²) was used as a template for growing Ni-W alloy nanowires, while a copper foil was used as a cathode for the electrodeposition of the Ni-W alloy thin films. On the surface of the membrane filter, a gold layer was sputter-deposited to cover the pores and to create a cathode. A gold wire and a Ag/AgCl electrode were used as the anode and reference electrode, respectively. To determine the optimum cathode potential for the electrodeposition of Ni-W alloys, a cathode polarization curve was plotted over the wide potential range from 0 to -2.0 V. According to the cathode polarization curve, the cathode current density (CCD) increased at around -0.7 V due to the beginning of the Ni-W alloys' electrodeposition. In the potential region of less than -2.0 V, the cathode's potential polarized significantly to a less-noble region as the CCD increased. This polarization was caused by the diffusion limit of Ni^{2+} and WO_4^{2-} ions. The surface appearance of the metal electrodeposits changed from an ideal smooth surface to powder-like rough deposits as the CCD increased to the diffusion limit of the metal ions. Therefore, the optimum cathode potential for the electrodeposition of Ni-W alloys was determined to be -1.5 V vs. Ag/AgCl at 313 K.

After growing the Ni-W alloy nanowire arrays, polycarbonate nanochannel templates were dissolved in an organic solvent and the remains, which consisted of electrodeposited Ni-W alloy nanowires, served as the samples for the SEM and TEM observations. To investigate the relationship between the WO_4^{2-} concentration ratio in the solutions ($R_W^{\text{bath}} = 100 \times [\text{WO}_4^{2-}] / ([\text{WO}_4^{2-}] + [\text{Ni}^{2+}])$) and the W content in the deposits ($R_W^{\text{depo}} = 100 \times [\text{W}] / ([\text{W}] + [\text{Ni}])$), the chemical composition of the

alloy deposits was determined using energy dispersive X-ray spectrometry (EDX). The constituent phase and crystallinity of the electrodeposited Ni-W alloy thin films and nanowire arrays were defined by X-ray diffraction (XRD) and electron beam diffraction (EBD). The magnetization behavior of the alloy thin films and nanowire arrays was investigated by VSM with an increasing magnetic field up to 10 kOe. The magnetic field was applied in-plane or in perpendicular directions to the surface of the substrates.

3. Results and Discussion

3.1 Structure of the electrodeposited Ni-W alloy nanowires

Figure 1 shows the relationship between the WO_4^{2-} concentration ratio (R_W^{bath}) and the W content in the alloy deposits (R_W^{depo}). If R_W^{depo} equals R_W^{bath} ($R_W^{depo} = R_W^{bath}$), then the plotted points are on the composition reference line (C.R.L.). As shown in Fig. 1, R_W^{depo} increased with an increase in R_W^{bath} . At each plotted point, R_W^{depo} is smaller than R_W^{bath} , which indicates that Ni preferentially electrodeposits, whereas W does not. For example, a Ni-15at.%W alloy ($R_W^{depo} = 15\%$) was obtained from a solution containing 40% WO_4^{2-} ions as a molar concentration ratio ($R_W^{bath} = 40\%$). In this condition, R_W^{depo} was diluted ca. 0.4 times lower than R_W^{bath} . WO_4^{2-} ions cannot reduce to a metallic state in an aqueous solution that contains only WO_4^{2-} ions. However, they can reduce to a metallic state as an alloy in an aqueous solution containing WO_4^{2-} ions in the presence of iron-group metal ions, such as Ni^{2+} , Co^{2+} , and Fe^{2+} . This reduction process is known as the “induced co-deposition mechanism,”⁴ and the co-deposition behavior, which appears in Fig. 1, can be explained with this mechanism. Metzler *et al.* have estimated that citrate ions will exist as H_2Cit^- in a solution with a pH of 2 and that WO_4^{2-} will exist as $[(\text{WO}_4)(\text{Cit})\text{H}_2]^{3-}$ complex ions at a pH of 2 [20]. In the present work, as shown in Fig. 1, R_W^{depo} was diluted ca. 0.4 times lower than R_W^{bath} . This dilution of W in the alloy deposits results from the existence of stable $[(\text{WO}_4)(\text{Cit})\text{H}_2]^{3-}$ complex ions. Admon *et al.* reported on the electrodeposition process of ferromagnetic Co-W alloys [21], revealing that R_W^{depo} increases with an increase in R_W^{bath} and that Co preferentially electrodeposits rather than W. For their study, they obtained a Co-32at.%W alloy ($R_W^{depo} = 32\%$) from a solution containing 46% WO_4^{2-} ions as a molar concentration ratio ($R_W^{bath} = 46\%$). Hence, they diluted R_W^{depo} ca. 0.7 times lower than R_W^{bath} .

According to the “induced co-deposition mechanism,” the reduction ability of iron-group metals depends on the number of unpaired electrons [22]. The number of unpaired 3d electrons of Ni, Co, and Fe are 0.6, 1.6, and 2.2, respectively, so the reduction ability of Ni is only 0.375 times than that of Co. Therefore, in the present work, the dilution of WO_4^{2-} in the alloy deposits from the solution containing Ni^{2+} ions should have been caused by the small reduction ability of electrodeposited Ni.

Figure 2 shows the X-ray diffraction profiles obtained from electrodeposited pure Ni, Ni-7at.%W, and Ni-15at.%W alloys. In the diffraction profile obtained from electrodeposited pure Ni, it is apparent that Ni (111) is the most closely packed crystal plane, and appears as a main peak. In addition, its diffraction peaks shifted to a lower 2θ region as R_W^{depo} increased. This shift resulted from the formation of a solid solution phase (α phase) in the electrodeposited Ni-W alloys. On the contrary, the intensity of α (111) decreased, and the shape of its peaks broadened as R_W^{depo} increased, which indicates that the electrodeposited Ni-W alloys are composed of an ultrafine-crystalline phase. Weston *et al.* have also reported that an electrodeposited Co-W alloy consists of a nanocrystalline phase with R_W^{depo} that is higher than ca. 20%. The nanocrystalline structure is formed by W atoms segregated from a supersaturated Co-W solid solution phase into grain boundaries at the W content range ($R_W^{\text{depo}} > 20\%$) [23]. However, in the present work, the segregation of W atoms in the grain boundaries of electrodeposited Ni-15at.%W alloys were not observed.

Figure 3 shows the relationship between R_W^{depo} and the crystal lattice constants of α phase ($a_{\text{Ni-W}}$). With an increase in R_W^{depo} up to ca. 15%, $a_{\text{Ni-W}}$ also increased linearly. The lattice constants of fcc-Ni (a_{Ni}) and bcc-W (a_{W}) are 0.352 and 0.316 nm, respectively. Nevertheless, the atomic radii of Ni (r_{Ni}) and W (r_{W}) are 0.124 and 0.139 nm, respectively, so r_{W} is larger than r_{Ni} , and R_W^{depo} is less than ca. 15%. Hence, $a_{\text{Ni-W}}$ will increase with increasing R_W^{depo} when W atoms are substitutionally alloyed in a fcc-Ni matrix lattice. According to the phase diagram of a Ni-W binary alloy system [24], the solubility limit of W in α phase is ca. 12at.%, and a Ni_4W intermetallic compound phase is formed at the composition of Ni-20at.%W. Therefore, in the present work, electrodeposited Ni-15at.%W alloys are composed of a substitutional α' phase.

Figure 4 shows SEM images of the electrodeposited Ni-15%W alloy nanowire arrays that are

separated from polycarbonate membrane filters and have pore diameters of 160 nm (a), (b) and 80 nm (c), (d). The diameters and lengths of the nanowires correspond well to those of the nanochannels. The cylindrical shape of these nanowires was also precisely transferred from that of the nanochannels, and the aspect ratio of the nanowires reached ca. 75. The length of the nanowires were allowed to range up to 6 μm by controlling the deposition time, while the diameter of the nanowires was fixed to around 80 or 160 nm. The array density (number of nanowires per substrate area) is ca. 6 μm^{-2} . The lateral areas of each nanowire are estimated at 1.4 and 2.8 μm^2 . Hence, the surface area of each nanowire array is estimated at 10 and 18 times larger value than that of thin film. Kim *et al.* have reported that a ferromagnetic Ni-Si alloy nanowire array with an extremely large specific surface area can be applied to a T-cell separation device [25]. The dimension of the Ni-Si alloy nanowire array developed by Kim *et al.* was similar to that of the Ni-W alloy nanowire array obtained in the present work. Therefore, ferromagnetic Ni-W alloy nanowire arrays can also be applied to biological cell separation as well as magnetic field sensors. Fig. 5 shows a TEM bright field image (a) and an electron diffraction pattern (b) of an electrodeposited Ni-15%W alloy nanowire that is separated from a polycarbonate membrane filter. As shown in Fig. 5-(a), large crystal grains, each with a diameter that is more than several tens of nanometers, were not observed in the electrodeposited Ni-15%W alloy nanowire. Furthermore, the electron diffraction pattern is composed of broad rings, as shown in Fig. 5-(b), so an electrodeposited Ni-15%W alloy nanowire consists of a nanocrystalline phase.

3.2 Magnetic properties of electrodeposited Ni-W alloy nanowires

Figure 6 shows the magnetization curves of an electrodeposited pure Ni thin film with a thickness of 10 μm (a), a Ni-15%W alloy thin film with a thickness of 3 μm (b), pure Ni nanowires with a length of 6 μm and a diameter of 80 nm (c), and Ni-15%W alloy nanowires with a length of 6 μm and a diameter of 80 nm (d). A magnetic field was applied in-plane (the dashed lines) and in perpendicular (the solid lines) directions to the film plane. Here, the perpendicular direction to the nanowire array film plane corresponds to the parallel direction to the long axis of the nanowires. The pure Ni thin film is easily magnetized in the in-plane direction, and its magnetization reaches

saturation at less than 1 kOe, as shown in Fig. 6(a). The coercive force of this thin film is ca. 100 Oe. On the contrary, the pure Ni thin film hardly magnetized in the perpendicular direction due to the demagnetizing field caused by the inverse magnetic poles generated on the film's surface. The effective magnetic field, H_{eff} , can be expressed by the following equation:

$$H_{eff} = H_a - H_d = H_a - f_d M / \mu_0 \quad (1)$$

Here, H_a , H_d , f_d , M , and μ_0 are the applied magnetic field, demagnetizing field, factor of demagnetizing field, magnetic moment, and permeability constant, respectively. When the magnetic field is applied in a direction that is perpendicular to the film plane, f_d will be the maximum value. In this case, H_d also becomes the maximum value, so H_{eff} will be the minimum value and thus not enough to reach the saturation of magnetization. On the contrary, when the magnetic field is applied in the in-plane direction to the film plane, f_d will be almost zero. Therefore, H_{eff} will be equal to H_a . Zhou *et al.* have also reported that the coercive force depends strongly on the film thickness in electrodeposited NiFeMo alloy thin films [26]. Their experimental results also support H_d depends on f_d that is estimated from the aspect ratio of magnetized samples.

As shown in Fig. 6(b), the magnetization of the Ni-15%W alloy reaches saturation at ca. 2.5 kOe, even in the perpendicular direction. The magnetic moment, M , of the Ni-W alloys will decrease as the non-magnetic W decreases. As shown in equation (1), the demagnetizing field, H_d , is in proportion to the magnetic moment, M , which generates inverse magnetic poles on the surfaces that are perpendicular to the magnetic field. Sulitanu has reported that Ni-W alloy thin films with perpendicular magnetic anisotropy can be obtained due to the binary phase structure with an isolated columnar nanocrystalline phase surrounded by an amorphous-like phase ($4\% < R_w^{depo} < 5\%$) [27]. The present report has also estimated that the perpendicular magnetic anisotropy in the alloy films arises from the magnetoelastic anisotropy associated with in-plane internal stress and positive magnetostriction. Hence, the magnetization behavior in the perpendicular direction observed in the present work resulted from the small demagnetizing field (H_d) and the small magnetocrystalline anisotropy (K_c) that is induced from a nanocrystalline phase in the alloy films. On the other hand, as shown in Fig. 6-(c), (d), pure Ni and Ni-15at.%W alloy nanowire arrays are easily magnetized even in a perpendicular direction because of the extremely small H_d that arises from the low density of the

inverse magnetic poles generated on the edges of nanowires.

The coercive force (H_c) of pure Ni and Ni-15%W alloy thin films are ca. 100 and 20 Oe, respectively, as shown in Fig. 6-(a), (b). On the other hand, as shown in Fig. 6-(c), (d), the H_c of pure Ni and Ni-15%W alloy nanowire arrays are ca. 200 and 80 Oe, respectively. Fig. 7 illustrates the relationship between R_W^{depo} and H_c . With an increase in R_W^{depo} , H_c decreases, and the soft magnetic properties of the Ni-15%W alloy thin films and nanowire arrays improve. As shown in Fig. 2 and Fig. 5, the crystal grain size of the electrodeposited Ni-W alloys decreases with an increase in R_W^{depo} . Herzer *et al.* have reported that the H_c of ferromagnetic nanocrystalline alloys decreases with the decreasing average crystal grain size (D) in the range of less than ca. 50 nm, as shown in the following equation [28].

$$H_c = fD^6 \quad (2)$$

Here, f is a proportional constant. According to equation (2), H_c decreases as D decreases, so the H_c of electrodeposited Ni-W alloys also decreases with an increase in R_W^{depo} due to the decrease in D that the latter change causes. Consequently, the isotropic magnetization behavior of electrodeposited Ni-15%W alloy nanowire arrays results from increasing H_{eff} due to decreasing f_d in the perpendicular direction to the array film plane and from decreasing H_c due to decreasing D .

Electrodeposited Ni-15%W alloy is composed of a substitutional supersaturated solid solution phase (α' phase), as shown in Fig. 2 and Fig. 3. Hence, a certain residual strain seems to exist in an as-deposited alloy. It has been reported that the H_c of Ni alloys increases as the residual strain increases [29]. Therefore, it is predicted that the H_c of electrodeposited Ni-15%W alloys with a supersaturated solid solution phase (α' phase) will decrease as the residual strain decreases via a thermal annealing treatment.

4. Conclusions

R_W^{depo} increased with an increase in R_W^{bath} , and R_W^{depo} was diluted ca. 0.4 times lower than R_W^{bath} . It is estimated that the dilution of W atoms in the alloy deposits, which occurs when the alloy is placed into a solution containing Ni^{2+} ions, will be caused by the small reduction ability of electrodeposited Ni. Electrodeposited Ni-15%W alloys consist of a supersaturated solid solution phase

with a nanocrystalline structure. Pure Ni thin film is hardly magnetized in the perpendicular direction, whereas the magnetization of the Ni-15%W alloy thin film reaches saturation at ca. 2.5 kOe, even in a perpendicular direction, because H_d decreases with decreasing M . The H_c of electrodeposited Ni-W alloy thin films decreases to ca. 20 Oe with an increase in R_W^{depo} to around 15%. On the other hand, the Ni-15%W alloy nanowire array is isotropically magnetized in both directions, and the H_c of the alloy nanowire array is ca. 80 Oe, which is smaller than that of a pure Ni nanowire array. The alloy's coercive force is smaller, because the H_d decreased in response to reductions in f_d and M . Therefore, this study has demonstrated that the electrodeposited Ni-W alloy nanowire arrays can be applied to a nanoscale magnetic field sensor and exhibit isotropic magnetization responses, and the soft magnetic property can be improved by increasing R_W^{depo} up to ca. 15%.

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Table 1. Bath compositions for the electrodeposition of Ni-W alloys.

FIG. 1. Relationship between WO_4^{2-} concentration ratio in baths (R_W^{bath}) and W content in Ni-W alloy deposits (R_W^{depo}).

FIG. 2. X-ray diffraction profiles obtained from electrodeposited pure Ni, Ni-7%W, and Ni-15%W alloys.

FIG. 3. Relationship between W content in Ni-W alloy deposits (R_W^{depo}) and the lattice constants (a_{Ni-w}).

FIG. 4. SEM images of Ni-15%W alloy nanowires electrodeposited into polycarbonate membrane filters with pore diameters of 160 nm (a), (b) and 80 nm (c), (d). Nanowires were separated from the polycarbonate membrane templates.

FIG. 5. TEM bright field image (a) and an electron diffraction pattern (b) of an electrodeposited Ni-15%W alloy nanowire.

FIG. 6. Magnetization curves of an electrodeposited Ni thin film with a thickness of 10 nm (a), a Ni-15%W alloy thin film with a thickness of 3 nm (b), Ni nanowires with lengths of 6 mm and diameters of 80 nm (c), and Ni-15%W alloy nanowires with lengths of 6 mm and diameters of 80 nm (d). A magnetic field was applied in-plane (dashed lines) and perpendicular (solid lines) to the film's plane.

FIG. 7. Effects of W content (R_W^{depo}) in Ni-W alloy thin films and nanowires on coercive force.

Table 1. Bath compositions for the electrodeposition of Ni-W alloys.

Electrolyte (mol/L)			WO ₄ ²⁻ concentration ratio in baths (%)
[WO ₄ ²⁻]	[Ni ²⁺]	[C ₆ H ₅ O ₇ ³⁻]	R_W^{Bath}
0	0.5	0.5	0
0.025	0.475	0.5	5
0.05	0.45	0.5	10
0.1	0.4	0.5	20
0.15	0.35	0.5	30
0.2	0.3	0.5	40
0.25	0.25	0.5	50

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