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Anisotropic Magnetization Behavior of Electrodeposited Nanocrystalline Ni-Mo Alloy Thin Films and Nanowires Array

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Molybdenum (Mo) has a high melting point (Tₘ) of 2896 K and is used as an alloying agent in high strength and high corrosion resistance materials such as stainless steels, tool steels, cast irons and high-temperature superalloys. Mo alloys are also used as a catalyst in electrolysis process to produce hydrogen gas from aqueous solution and hydro-desulfurization process to remove sulfur from refined petroleum products. It is very difficult to obtain the bulk alloys containing Mo using a casting method or a deformation processing because of their high Tₘ and high strength. On the contrary, it is well known that iron-group metal alloy thin films containing Mo such as Ni-Mo, Co-Mo and Ni-Fe-Mo alloys can be electrodeposited from aqueous solution at room temperature and the reduction process is known as induced co-deposition. Sanches et al. reported that the electrodeposited Ni-50at.%Mo alloy thin film with a good electro-catalytic activity for hydrogen evolution reaction and the alloy thin film could be suitable cathode materials for hydrogen production through water electrolysis.

Usually the electrodeposited and electroless-deposited iron-group metal alloy thin films containing Mo consist of small crystals with the diameter of several tens of nanometer. The nanocrystalline iron-group metal alloy thin films are known to show excellent soft magnetic properties, which can be applied to high sensitive magnetic field sensors. Gómez et al. reported that the coercive force of electrodoped Co-10at.%Mo alloy thin film was less than 70 Oe and Co-Mo alloy deposits with Mo content ranging from 5 to 10% showed an excellent soft-magnetic properties. It is also well known that a magnetic thin film is hardly magnetized in perpendicular direction to the film plane due to the demagnetizing field caused by magnetic poles generated on the film surfaces. On the other hand, a magnetic nanowires array which is assembled in a membrane thin film is known to be easily magnetized in a perpendicular direction to the film plane. If an iron-group metal alloy nanowires array containing Mo such as Ni-Mo, Co-Mo and Fe-Mo alloys can be electrodeposited into a membrane filter with numerous nanochannels such as an ion-track etched polycarbonate membrane filter or an anodized aluminum membrane filter, a novel catalytic nanowires array with high corrosion resistance and magnetic moment can be synthesized at room temperature. The catalytic nanowires array can be applied to a novel functional device such as a ferromagnetic and catalytic electrode with extremely large specific surface area. For example, in a water electrolysis process, a ferromagnetic and catalytic nanowires array electrode can be easily recovered under certain magnetic field. In this study, Ni-Mo alloy thin films and nanowires array were synthesized using an induced co-deposition technique and their nanocrystalline structures and magnetic properties were investigated for the application of a novel ferromagnetic and catalytic electrode.

Experimental

Aqueous electrolytic solution was synthesized from nickel sulfate (NiSO₄·6H₂O), sodium molybdate (Na₂MoO₄·2H₂O), sulfuric acid (H₂SO₄), sodium citrate (C₆H₇O₆·H₂O), sodium carbonate (Na₂CO₃), hydrochloric acid (HCl), sodium chloride (NaCl), iron sulfate (FeSO₄·7H₂O) and acid. The solution pH was adjusted to 2.0. The solution compositions are shown in Table I. Copper foils (2 cm × 2 cm) were used as a cathode for electrodoping Ni-Mo alloy films, while iron track-etched polycarbonate membrane filters with pore-diameter of 100 nm, pore-length of 6 μm and pore-density of 6 × 10⁸ pores · cm⁻² were used as a nanochannel template for growing Ni-Mo alloy nanowires array. On a surface of the membrane filter, a gold wire was used as an anode and Ag/AgCl/KCl sat. electrode was used as a reference electrode. According to a cathodic polarization curve obtained in the preliminary experiment, at around −0.7 V (vs. Ag/AgCl/KCl sat.) which was less than the equilibrium potential of Ni⁰/Ni and MoO₂²⁻/Mo, the cathodic current density increased rapidly. Hence, it was estimated that the increase in cathodic current density was mainly caused by the electrodeposition of Ni-Mo alloys. At the potential region less than −2.0 V, with increasing cathodic current density, the potential polarized significantly to be less-noble region due to the diffusion limit of Ni²⁺ and MoO₂²⁻ ions. Consequently, the optimum cathode potential for electrodeposition of Ni-Mo alloys was determined to be from −1.5 V. Ni-Mo alloy thin films and nanowires array were electrodeposited potential- statically at −1.5 V (vs. Ag/AgCl/KCl sat.). Temperature of the electrolytic solution was kept to 313 K. During the electrodeposition of Ni-Mo alloy thin films, the current density was ca. 100 A/m² at the cathode potential of −1.5 V and the electrodeposition time was kept to 60 min. Therefore, charge for the electrodeposition was estimated to 144 C. After growing Ni-Mo alloy nanowires array, the nanochannel templates which were made from ion track-etched polycarbonate membrane filters were dissolved in organic solvent and the remains which were consisted of electrodeposited Ni-Mo alloy nanowires array were served as a sample for SEM observation. To investigate the relationship between MoO₂²⁻ concentration ratio in baths (RₓMoO₂²⁻ = 100 × [MoO₂²⁻] / ([Ni²⁺] + [Fe²⁺])) and Mo content in the alloy deposits (RₓMo = 100 × [Mo] / ([Mo] + [Ni] + [Fe])), the composition of electrodeposits were determined using EDX analysis.

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cross-sectional area of electrodeposited alloy thin films, the samples were cut away and cross-sectionally polished using focused ion beams (FIB). Scanning ion microscope (SIM) was used for observing the cross-sectional structure of nanocrystalline Ni-Mo alloy thin films. Magnetic properties of electrodeposited Ni-Mo alloy thin films and the nanowires array were investigated by using a vibrating sample magnetometer (VSM) with the magnetic field up to 10 kOe.

Results and Discussion

Induced co-deposition process of Ni-Mo alloys.— Figure 1 shows the relationship between MoO$_4^{2-}$ concentration ratio (R$_{Mo-bath}$) and molybdenum (Mo) content in the alloy deposits (R$_{Mo-depo}$). With increase in R$_{Mo-bath}$, R$_{Mo-depo}$ also increases. In this figure, composition reference line (C.R.L) means that R$_{Mo-depo}$ corresponds to R$_{Mo-bath}$. As shown in Fig. 1, in the solution not containing Fe$^{2+}$ ions, Ni was preferentially deposited besides Mo. For example, Ni-23.6%Mo alloy deposit (R$_{Mo-depo}$ = 23.6%) was obtained from the solution containing 5% of MoO$_4^{2-}$ ions (R$_{Mo-bath}$ = 50%). R$_{Mo-depo}$ was diluted ca. 0.5 times lower than R$_{Mo-bath}$. On the contrary, in the solution containing Fe$^{2+}$ ions, Mo was preferentially deposited besides Ni. For example, Ni-16%Mo alloy deposit (R$_{Mo-depo}$ = 16%) was obtained from the solution containing 5% of MoO$_4^{2-}$ (R$_{Mo-bath}$ = 5%). In this condition, R$_{Mo-depo}$ was condensed ca. 3 times higher than R$_{Mo-bath}$. It is well known that MoO$_4^{2-}$ ions cannot be reduced to the metallic Mo from aqueous solution containing only MoO$_4^{2-}$ ions while they can be reduced to the metallic state from the solution containing MoO$_4^{2-}$ ions in the presence of iron-group metal ions such as Ni$^{2+}$, Co$^{2+}$ and Fe$^{2+}$ and ligand such citric acid.\[\text{MoO}_4^{2-}\text{ ions are reduced by hydrogen atoms adsorbed on the electrodeposited iron-group metals. According to the mechanism, the reduction ability of iron-group metals would depend on the number of unpaired electrons. The number of unpaired 3d electrons of Ni, Co and Fe are 0.6, 1.6 and 2.2, respectively. Therefore, the reduction ability of Fe would be 3.7 times higher than that of Ni. In the present work, the condensation phenomenon of Mo from the solution containing Fe$^{2+}$ ions into the deposits would be caused by the unpaired 3d electrons of co-deposited metallic Fe.}

Nanocrystalline structure of electrodeposited Ni-Mo alloys.— Figure 2 shows X-ray diffraction profiles of Ni (111) and α (111) obtained from electrodeposited pure Ni, Ni-7%Mo and Ni-23.6%Mo alloy thin films. The other diffraction peaks such as Ni (200), α (220), Ni (311) and α (311), which are not shown in the profile, are also observed in the experiment. Preferential orientation of Ni (111), which is most close-packed crystal plane of Ni, was observed in the diffraction profile obtained from electrodeposited pure Ni. With increasing R$_{Mo-depo}$, the diffraction peaks shifted to the lower 2θ region due to the formation of α phase that is solid solution of Ni-Mo alloys, while the intensities of diffraction peaks due to α (111) were decreased and the shape of peaks has changed to be broad with increasing R$_{Mo-depo}$. The other diffraction peaks such as α (200), α (220) and α (311) also showed a similar tendency. These results suggest that the electrodeposited Ni-Mo alloys would be composed of nano-size crystals or amorphous phase.\[\text{Nanocrystalline structure of electrodeposited Ni-Mo alloys.}

Figure 3 shows the relationship between Mo contents in the alloy deposits (R$_{Mo-depo}$) and the lattice constants of α phase (α$_{Ni-Mo}$). With increase in R$_{Mo-depo}$, α$_{Ni-Mo}$ also increases linearly up to ca. 12% of R$_{Mo-depo}$. It is well known that Mo forms a stable bcc crystal phase while Ni has an fcc structure. The lattice constants of Ni and Mo are 0.352 nm and 0.315 nm while atomic radii of them are 0.124 nm and 0.130 nm.\[\text{Figure 2. X-ray diffraction profiles of Ni (111) and α (111) obtained from electrodeposited pure Ni, Ni-7%Mo and Ni-23.6%Mo alloy thin films.}

\begin{table}
\centering
\caption{Bath compositions for electrodeposition of Ni-Mo alloys and Ni-Fe-Mo alloys.}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Electrolyte (mol/L) & MoO$_4^{2-}$ & Ni$^{2+}$ & Fe$^{2+}$ & C$_6$H$_5$O$_7^{3-}$ & R$_{Mo-bath}$ \\
\hline
0 & 0.5 & 0 & 0.5 & 0 & 0 \\
0.025 & 0.475 & 0 & 0.5 & 5 & 0 \\
0.05 & 0.45 & 0 & 0.5 & 10 & 0 \\
0.1 & 0.4 & 0 & 0.5 & 20 & 0 \\
0.15 & 0.35 & 0 & 0.5 & 30 & 0 \\
0.2 & 0.3 & 0 & 0.5 & 40 & 0 \\
0.25 & 0.25 & 0 & 0.5 & 50 & 0 \\
0.025 & 0.425 & 0.05 & 0.5 & 5 & 0 \\
0.025 & 0.4 & 0.075 & 0.5 & 5 & 0 \\
0.025 & 0.375 & 0.1 & 0.5 & 5 & 0 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Relationship between MoO$_4^{2-}$ concentration ratio (R$_{Mo-bath}$) and Mo content in Ni-Mo and Ni-Fe-Mo alloy deposits (R$_{Mo-depo}$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2.png}
\caption{X-ray diffraction profiles of Ni (111) and α (111) obtained from electrodeposited pure Ni, Ni-7%Mo and Ni-23.6%Mo alloy thin films.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.png}
\caption{X-ray diffraction profiles of Ni (111) and α (111) obtained from electrodeposited pure Ni, Ni-7%Mo and Ni-23.6%Mo alloy thin films.}
\end{figure}
0.139 nm, respectively. According to the binary phase diagram\textsuperscript{22} of Ni-Mo, the alloy forms an fcc substitutional solid solution α phase ranging up to ca.10% of R$_{\text{Mo}}$\textsuperscript{ depos}. Donten et al.\textsuperscript{23} also reported that the distance of α (111) lattice plane increases linearly in the range of Mo content up to 15 at.%. Such a phenomenon is typical for the formation of a binary solid solution phase which is composed of the matrix metal with small atomic radius and the solute metal with large atomic radius. Therefore, the results obtained in this work suggest that Mo in the electrodeposits exist as metallic solute in the fcc substitutional solid solution phase of Ni-Mo alloy.

SEM images of electrodeposited Ni (a), Ni-4.5%Mo alloy (b), Ni-6%Mo alloy (c), Ni-19%Mo alloy (d) and Ni-23.6%Mo alloy (e) are shown in Fig. 4. The average crystal grains size of electrodeposited Ni-19%Mo alloy (Fig. 4d) is apparently smaller than that of pure Ni (Fig. 4a). On the other hand, no crystal grains and several cracks have been found in SEM image of Ni-23.6%Mo alloy as shown in Fig. 4e. As shown in Fig. 2, the shape of peaks has changed to be broad with increasing R$_{\text{Mo}}$\textsuperscript{ depos}. According to the binary phase diagram\textsuperscript{22} of Ni-Mo, the alloy forms an intermetallic phase (Ni$_4$Mo) at 20% of R$_{\text{Mo}}$\textsuperscript{ depos}. Donten et al.\textsuperscript{23} reported that the amorphous or nanocrystalline structure appears for the deposits of Mo content higher than ca. 20%. They also suggested that the transformation of the solid solution of Mo in Ni into either the deformed structure of Ni$_4$Mo or a mixture of the saturated Ni-Mo solid solution with nanstructured Ni takes place at the Mo content higher than ca. 20%. Therefore, the cracks seem to be caused by the formation of a hard phase such as amorphous Ni$_4$Mo. Consequently, these results suggest that the electrodeposited Ni-Mo alloys containing less than 19% of Mo consist of nanocristalline phase while the alloys containing more than 20% of Mo consist of amorphous phase.

Figure 5 shows the cross-sectional SIM images of electrodeposited Ni (a), Ni-4.5%Mo alloy (b) and Ni-23.6%Mo alloy (c). Electrodeposited Ni consists of large crystal grains with the diameter of several μm as shown in Fig. 5a, while Ni-4.5%Mo alloy consists of columnar crystals with the diameter of several hundred nm and the long axis of the columnar crystals was arrayed vertically to the film plane as shown in Fig. 5b. On the other hand, no crystal grains have been found in the cross-sectional SIM image of Ni-23.6%Mo alloy as shown in Fig. 5c. With increasing R$_{\text{Mo}}$\textsuperscript{ depos}, the film thickness was decreased. The film thicknesses of electrodeposited Ni, Ni-4.5%Mo alloy and Ni-23.6%Mo alloy were around 10 μm, 5 μm and 2 μm. During the electrodeposition, the current density was ca. 100 A/m$^2$ and the electrodeposition time was kept to 60 min. Therefore, the current efficiency for Ni, Ni-4.5%Mo and Ni-23.6%Mo alloy deposition were estimated to ca. 81.3%, 43.4% and 21.6%. It has been known that the decreasing of current efficiency for induced co-deposition process is also observed in Ni-W binary alloys system as well as Ni-Mo alloys. Gileadi et al.\textsuperscript{24} reported that the induced co-deposition behavior of Ni-W alloys from the electrolytic solution not containing ammonia. In the report, they have found that the current efficiency for the alloy deposition decreases with increasing W content in the alloy. Therefore, it is suggested that the decreasing of current efficiency for electrodeposition of Ni-Mo alloys in the present work would be caused by the catalytic effect\textsuperscript{25} of electrodeposited Ni-Mo alloys for the reduction of hydrogen ions.

Anisotropic magnetization behavior of electrodeposited Ni-Mo alloy thin films—Fig. 6 shows the magnetization curves of electrodeposited Ni thin film (Fig. 6a), Ni-11%Mo alloy thin film (Fig. 6b) and Ni-10%Mo-12%Fe alloy thin film (Fig. 6c) are shown. Magnetic field was applied to in-plane (dashed line) and perpendicular (solid line) direction to the film plane. As shown in Fig. 6a, Ni thin film was barely magnetized in perpendicular direction due to the extremely large demagnetizing field (H$_d$) caused by the inverse magnetic poles generated on the film surfaces. The effective magnetic field (H$_{\text{eff}}$) can be expressed by the following equation.

$$H_{\text{eff}} = H_a - H_d = H_a - f_d \cdot M / \mu_0$$  \[1\]

Here, H$_a$ is the applied magnetic field, f$_d$ is the marerials shape factor in demagnetizing field, M is magnetic moment and $\mu_0$ is permeability constant. When the magnetic field is applied to perpendicular direction to the film plane, f$_d$ will be maximum value, hence H$_{\text{eff}}$ will be minimum value. On the contrary, Ni thin film was easily magnetized in-in plan direction (f$_d$ = 0) and the magnetization reached to saturation at less than 1 kOe. Coercive force (H$_c$) of Ni thin film was ca. 100 Oe. On the other hand, magnetization of Ni-11%Mo alloy thin film reached to saturation at ca. 2.5 kOe even in perpendicular direction as shown in Fig. 6b. This is resulting from decreasing H$_d$ due to increasing the content of non-magnetic Mo component because H$_d$ caused by the inverse magnetic poles depends on M, H$_d$ of Ni-11%Mo alloy thin film was ca. 10 Oe (Fig. 6b), while that of Ni-10%Mo-12%Fe alloy thin film was around 1 Oe (Fig. 6c). This improvement of soft magnetic property in Ni-10%Mo-12%Fe alloy would be introduced.
Figure 6. Magnetization curves of electrodeposited Ni (a), Ni-11%Mo (b) and Ni-10%Mo-12%Fe (c). Magnetic field was applied to in-plane and perpendicular direction to the film plane.

by decreasing the crystal grain size ($D_c$) due to the co-deposition of Mo and decreasing the magneto crystalline anisotropy due to co-deposition of Fe in fcc Ni alloy matrix. Gómez et al.\textsuperscript{25} reported that $H_c$ of electrodeposited Co-23at.%Mo alloy thin film was less than 100 Oe, and Co-Mo alloy deposits with Mo content ranging from 20 to 23% showed an excellent soft-magnetic behavior. Tanase et al.\textsuperscript{26} reported that $H_c$ of electrodeposited Co-Ni-25.4at.%Mo alloy thin film was ca. 350 Oe. It is well known that the anisotropy field of hcp-Co ($H_k = 7400$ Oe) is larger than that of fcc-Ni ($H_k = 184$ Oe) due to the asymmetry of crystal structure. Therefore, $H_c$ of Co alloys would be much larger than that of Ni alloys obtained in the present work. As shown in Fig. 6, with increase in $R_{M_{dep}}$, $H_c$ decreased. By the way, $D_c$ of Ni-Mo alloys decreased with increase in $R_{M_{dep}}$ as shown in Fig. 2, Fig. 4 and Fig. 5. Herzer et al.\textsuperscript{27} reported that $H_c$ decreases with decreasing $D_c$ in the range of $D_c$ than ca. 50 nm. Therefore, it is suggested that $H_c$ of electrodeposited Ni-Mo alloys decreased due to decreasing in $D_c$ of the deposits.

Structure and magnetic properties of electrodeposited Ni-Mo alloy nanowires array.— Figure 7 shows SEM image of electrodeposited Ni-8.4%M alloy nanowires array separated from a polycarbonate membrane filter. Diameter and length of the nanowires corresponds well to that of nanochannels and the cylindrical shape of nanowires was perfectly transferred from that of nanochannels. Aspect ratio of the nanowires can reach to ca. 60. The length of nanowires can be ranged up to 6 $\mu$m by controlling deposition time, while the diameter of nanowires is fixed to around 100 nm. The density of nanowires array was ca. 6 $\mu$m$^{-2}$. Lateral area of a nanowire is estimated to be around 2 $\mu$m$^2$. Therefore, surface area of the nanowires array is estimated to be around 13 times larger than that of thin film.

Figure 8 shows magnetization curves of electrodeposited Ni nanowires array (Fig. 8a) and Ni-8.4%M alloy nanowires array (Fig. 8b). Magnetic field was applied to in-plane (dashed line) and perpendicular (solid line) direction to the membrane film plane. The perpendicular direction to the membrane film plane corresponds to the parallel direction to the long axis of nanowires. As shown in Fig. 8a, Ni nanowires array was easily magnetized even in perpendicular direction due to the extremely small demagnetizing field caused by the small

Figure 7. SEM image of electrodeposited Ni-8.4%M alloy nanowires array separated from a polycarbonate membrane filter.

Figure 8. Magnetization curves of electrodeposited Ni nanowires array (a) and Ni-8.4%M alloy nanowires array (b). Magnetic field was applied to in-plane and perpendicular direction to the membrane film plane.
density of magnetic poles generated on the edge of nanowires.\textsuperscript{28,29} H\textsubscript{c} of Ni nanowires was ca. 0.2 kOe. On the contrary, as shown in Fig. 8b, Ni-8.4\%Mo alloy nanowires array was isotropically magnetized in the both direction. This is resulting from decreasing H\textsubscript{c} due to the small density of magnetic poles generated on the edge of Ni-Mo alloy nanowires and increasing the content of non-magnetic Mo component.

Conclusions

With increase in MoO₄²⁻ concentration ratio in baths (R\textsubscript{Mo\textsuperscript{bath}}) up to 50\%, Mo content in the Ni-Mo alloy deposits (R\textsubscript{Mo\textsuperscript{depo}}) increased up to 23.6\%, while the current efficiency for the alloy deposition decreased down to 21.6\%. It was suggested that the electrodeposited Ni-Mo alloy acted as a catalyst for hydrogen evolution during the induced co-deposition process. The average crystal grain size (D\textsubscript{c}) of electrodeposited Ni-Mo alloys decreased down to several tens of nanometers with increasing R\textsubscript{Mo\textsuperscript{depo}} up to 19\%, while an amorphous phase was observed in the alloy deposits with R\textsubscript{Mo\textsuperscript{depo}} of 23.6\%. It was estimated that Mo in the alloy deposits existed as metallic solute in an fcc substitutional solid solution phase and suppressed the crystal growth of Ni-Mo alloy. Coercive force (H\textsubscript{c}) of electrodeposited Ni-Mo alloys decreased with increase in R\textsubscript{Mo\textsuperscript{depo}} and decrease in D\textsubscript{c}. H\textsubscript{c} of Ni-10\%Mo-12\%Fe alloy thin film was ca. 1 Oe, which is quite smaller than that of Ni-Mo alloys. It was concluded that the improvement of soft magnetic property in Ni-Mo-Fe alloy was caused by decreasing D\textsubscript{c} due to the co-deposition of Mo and decreasing the magneto crystalline anisotropy due to co-deposition of Fe in fcc Ni alloy matrix. Ni-8.4\%Mo alloy nanowires array were isotropically magnetized and the soft magnetic properties were improved with increasing R\textsubscript{Mo\textsuperscript{depo}} and decrease in D\textsubscript{c}. It was found that the Ni-Mo alloy nanowires array synthesized in the present work has a potential capability as a novel ferromagnetic and catalytic electrode with large specific surface area.

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