Magnetic Properties of Corrosion-Resistant CoW Films

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Abstract

CoW films with different compositions have been prepared by an electrochemical deposition method. The tungsten contents in the CoW films are controlled through adjusting electrolyte concentrations, pH values and applied potentials. The magnetic and corrosion-resistant properties of the CoW films are systematically studied. With the increase of tungsten contents and the annealing temperature, the CoW films transfer from in-plane magnetic anisotropy to magnetic isotropy, which is related to the formation of hexagonal close packed (hcp) Co3W phase confirmed by the morphological and phase evolution. The magnetic properties of CoW films can maintain stable even after having been immersed in a 0.5% NaCl solution for 170 hours. A ultrathin tungsten oxide passivation layer is found on the surface of the films which can protect CoW film from corrosion.

Keywords: CoW alloys, electrochemical deposition, magnetic property, corrosion resistance

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1. Introduction

There are big challenges on materials’ design, development and commercialization to explore multifunctional materials with excellent overall performance and low cost fabrication process. CoW alloys are the kinds of materials combining outstanding magnetic, catalytic and corrosion resistance properties with excellent mechanical performance, attracting great attentions in many fields including recording media, micro-electro-mechanical systems (MEMS) and catalysts for clean hydrogen generation from water decomposition. Typically, CoW alloys are prepared by an electrochemical deposition method, which is a well-developed technology to fabricate films with controllable composition and microstructure in an easy operational way. Compared with physical deposition method such as magnetron sputtering, electrodeposited process is more economic. Furthermore, the composition, morphology and properties of CoW films can be controlled by adjusting electrodeposition parameters. Although tungsten atoms cannot be electrodeposited from aqueous solution by itself due to their low deposition potential, co-deposition of tungsten and cobalt can take place when cobalt salts are also added to electrolyte solutions. In this “induced co-deposition” process, cobalt atoms act as catalysts for the deposition of tungsten. Many theories have been proposed to explain this anomalous co-deposition process, but none of them has been fully proven and accepted. Since there are organic additives in electrolyte solutions, a complex species model is adopted here, which considers the iron-group metal tungstate complexes as precursors to electrodeposit tungsten alloys. Varying the depositional condition, CoW alloys with different compositions, morphologies and thus tailored magnetic properties can be obtained. In particular, the hexagonal close packed (hcp) Co$_3$W films with (001) texture exhibit perpendicular-to-plane magnetic anisotropy, which is promising as next magnetic storage media.
The as-deposited CoW alloys are not well crystallized or even amorphous, which have unsatisfied performance in not only magnetism but also mechanical and corrosion aspects. A post heat treatment process is needed to improve their overall performance for their applications in various conditions. However, effects of compositions and phase structures evolution on the magnetic properties of CoW alloy films have not been systematically studied yet, all of which are worth to be explored in detail to understand the involved mechanism and realize their reliable usage in various conditions. So it is critical to study the magnetic properties of CoW alloy films with different composition, annealing processes and the corrosion environment. In this paper, we dedicate to optimize the electrodeposition and subsequent annealing process to obtain CoW alloy films with better and stable overall performance.

2. Experimental

The CoW films were deposited by using a DC potentiostatic method. The electrochemical deposition was performed in a conventional three-electrode cell with Ag/AgCl electrode, platinum electrode and copper foil as the reference, counter and working electrodes, respectively. Copper substrates were cut into 12×50 mm\(^2\) and annealed at 400 °C in vacuum for 30 min for internal stress relief. Then copper substrates were cleaned with acetone and activated by 1 mol·L\(^{-1}\) H\(_2\)SO\(_4\) solution. The basic electrolyte solution contained 0.1 mol·L\(^{-1}\) of CoSO\(_4\), 0.5 mol·L\(^{-1}\) of Na\(_2\)WO\(_4\), 0.2 mol·L\(^{-1}\) of sodium citrate (Na\(_3\)Cit). Citric acid was chosen to adjust pH values and then sodium citrate/citric acid were also used as buffer solution, which can stabilize the pH value. No inorganic impurity can enter CoW films during electrodeposition process.

The as-prepared CoW alloy films were annealed in vacuum (< 5.0×10\(^{-5}\) Pa) for 30 minutes. The samples were then characterized by a leo-1450 scan electron microscopy with energy
dispersive spectroscopy (SEM-EDS), M21X X-ray diffraction (XRD), physical property measurement system (PPMS), and Kratos AXIS ULTRA DLD X-ray photoelectron spectroscopy (XPS) to determine their compositions, morphologies, crystal structures, magnetic properties and chemical valence of elements at room temperature, respectively.

3. Results and discussion

The properties of CoW films greatly depend on the quality of films, which is decided by electrodeposition parameters including pH values, electrolyte concentrations and applied potentials. Figure 1 shows the cyclic voltammograms for the solutions with different pH values. The pH values are adjusted as 6.0, 6.5, 8.0 through adding citric acid in the basic electrolyte. In order to make the peaks in curves more obvious, current (I) on cyclic voltammograms is converted into log (I). It can be observed that each curve for acid solutions has only one reduction peak, which is between -0.7 V and -0.8 V. Different from acid solutions, two peaks appear during the reduction process when the pH value of 8.0 is adopted. The peak at the potential of -0.7 V corresponds to the reduction of Co\(^{2+}\), and the other one near -0.3 V indicates the formation of metal oxides. In fact, the forms of Co\(^{2+}\) and WO\(_4^{2-}\) are rather complicated, which highly depends on the pH values and the concentration ratio of Co\(^{2+}\) and WO\(_4^{2-}\). In these experiments, the main forms of Co\(^{2+}\) are [(Co)(Cit)]\(^-\) and [(Co)(Cit)]\(^{2-}\), and WO\(_4^{2-}\) ions exist as [(WO\(_4\))(Cit)(H\(_2\))]\(^3+\) and [(WO\(_4\))(Cit)(H)]\(^4+\). The [(Co)(Cit)]\(^-\) can further complex with [(WO\(_4\))(Cit)(H)]\(^4+\) to form [(Co)(WO\(_4\))(Cit)(H)]\(^2+\) which is the only precursor that tungsten can be deposited from. Cobalt itself can also be deposited in a parallel route from [(Co)(Cit)]\(^-\). The main complexes are formed and reduced as below reactions.

\[
\text{Co}^{2+} + \text{Cit}^3\rightarrow [(\text{Co})(\text{Cit})]^-
\]  

(1)
\[ \text{Co}^{2+} + 2\text{Cit}^3 \rightarrow [(\text{Co})(\text{Cit})_2]^4 \] (2)

\[ \text{WO}_4^{2-} + \text{Cit}^3 + \text{H}^+ \rightarrow [(\text{WO}_4)(\text{Cit})(\text{H})]^4 \] (3)

\[ \text{WO}_4^{2-} + \text{Cit}^3 + 2\text{H}^+ \rightarrow [(\text{WO}_4)(\text{Cit})(\text{H})_2]^3^- \] (4)

\[ [(\text{Co})(\text{Cit})]^- + [(\text{WO}_4)(\text{Cit})(\text{H})]^4 \rightarrow [(\text{Co})(\text{WO}_4)(\text{Cit})(\text{H})]^2^- + \text{Cit}^3^- \] (5)

\[ [(\text{Co})(\text{Cit})]^- + 2\text{e}^- \rightarrow \text{Co} + \text{Cit}^3^- \] (6)

\[ [(\text{Co})(\text{WO}_4)(\text{Cit})(\text{H})]^2^- + 8\text{e}^- + 3\text{H}_2\text{O} \rightarrow \text{CoW} + 7\text{OH}^- + \text{Cit}^3^- \] (7)

The exact deposition parameters for CoW films with different W content are shown in Table 1. The tungsten contents in the CoW films increased by increasing the pH values, which are 11, 14, 17 and 19 at.% W for pH 6.0, 6.5, 7.0, 8.0, respectively. This result is reasonable because the cobalt deposition is facilitated by the formation of \([(\text{Co})(\text{Cit})]^-\) species in a near neutral electrolyte. However, with the increasing pH values, more cobalt ions tend to form cobalt hydroxide, which inhibits the deposition of cobalt atoms and increases the tungsten content in films.\textsuperscript{13} For the potential-dependent experiment, the basic electrolyte solution with pH 6.5 is adopted. The tungsten contents in the deposited CoW films are 26, 15 and 9 at.% W when the deposition potentials are -1.0, -1.5 and -2.0 V, respectively. With high current density, which is proportional to the applied potential, the co-deposition exhibits a mass transport control rather than a kinetic one.\textsuperscript{14} Since there is no rotation device to accelerate the diffusion, a lower deposition potential is beneficial to the deposition of small complex with a higher diffusion coefficient, thus the enhancement of the deposition rate of cobalt atoms is more obvious than that of tungsten atoms. The influence of the concentration of Na\textsubscript{2}WO\textsubscript{4} on the compositions of CoW films is also studied. It is observed that the CoW films with 14, 17, 18, 20, 20 at.% W are
produced by 0.05, 0.1, 0.2, 0.3 and 0.4 mol·L⁻¹ Na₂WO₄, respectively. Generally, the tungsten content increases with the concentration of Na₂WO₄ below 0.3 mol·L⁻¹. The increase of the WO₄²⁻ concentration in electrolyte facilitates the formation of cobalt-tungstate complex at the beginning of electrodeposition, causing the tungsten content in CoW films rising. However, when the WO₄²⁻ concentration is further increased to 0.4 mol·L⁻¹, the tungsten content keeps constant, even decrease slightly. Because Cit³⁻ is insufficient to form the [(Co)(Cit)₂]⁺ complex, a simpler complex [(Co)(Cit)]⁺ is preferred from which cobalt can be deposited more readily, resulting in relatively increased cobalt content.

The effect of composition on phase structure of CoW films is studied by XRD, as shown in Fig. 2a. All the CoW films are annealed at 600 °C for 30 min in vacuum. It can be observed that the CoW film with 2 at.% W has a structure similar to pure hcp-Co because tungsten atoms prefer to diffuse into the crystal lattice of hcp-Co and form a solid solution when the tungsten content is very few. However, the solubility of tungsten atoms in cobalt matrix is very limited due to their high difference in atom radius (r₈Co=125 pm, r₈W=141 pm). Further increasing the tungsten content could destroy the solid solution structure and make tungsten atoms segregate, forming a W-rich metallic phase at the Co-rich solid boundaries preferred by surface energy.³ For the CoW film with 18 at.% W, the diffraction peaks of hcp-Co₃W alloy phase begin to appear at 40.56 °, 43.66 ° and 46.29 °, which correspond to (100), (002) and (101) planes, respectively. When the tungsten content in the CoW films gradually rises to 26 at.%, more tungsten atoms incorporate into the lattice causing further expansion of the crystal lattice, and therefore all diffraction peaks shift to lower 2θ angles. All the diffraction peaks can well index to CoW phase without any distinct tungsten oxides peak.
The CoW films with 26 at.% W (expressed as Co$_3$W films in later sections) are annealed at different temperatures and then used to study the crystallization process of hcp-Co$_3$W phase by XRD. As shown in Fig. 2b, the as-prepared and 500 ºC annealed Co$_3$W films have no diffraction peaks. After annealed at 550 ºC, the (100), (002) and (101) peaks of the hcp-Co$_3$W appear. And all diffraction peaks further sharpen and intensify when the annealing temperature rises to 600 ºC and 650 ºC. With increasing the annealing temperature, the (100) peak at 2θ=40.56 º shifts obviously towards a lower 2θ angle. Calculation results show that the $a$-axis lattice constant increases with the increased annealing temperature, while the $c$-axis lattice constant increases from 550 ºC to 600 ºC and slightly decreases for the 650 ºC annealed film.

The morphological evolution of the annealed Co$_3$W films is observed by SEM, as shown in Fig. 3a-e. Fig. 3f is the EDS result of the Co$_3$W films. The as-deposited and 500 ºC annealed Co$_3$W films are almost homogeneous, as in Fig. 3a and b, respectively. This agrees with the reported results that the alloys with high tungsten content have small grain size.$^{15}$ The Co$_3$W films annealed at 550 ºC begin to crystallize. A few tiny surface cracks show up due to the stress between the Co$_3$W film and the copper substrate for their mismatched thermal expansion coefficients. When the annealing temperature increases to 600 ºC, the Co$_3$W grains continue to grow up and the crystalline structure becomes better. Compared with the 600 ºC annealed one, the Co$_3$W film annealed at 650 ºC becomes more compact. The results are consistent with the XRD measurement.

The magnetic properties of the CoW films with different tungsten contents annealed 600 ºC for 30 min in vacuum are measured at room temperature by PPMS, as shown in Fig. 4a-e. The dependence of in-plane magnetic coercivity ($H_C$) on the tungsten content of the CoW films has a
clear transition point at 11 at.% W, as shown in Fig. 4f. When the tungsten content is less than 11 at.%, the $H_C$ of the CoW films decreases with the increased tungsten content. It is due to the random replacement of cobalt atomic positions with nonmagnetic tungsten atoms in lattices, which destroys exchange coupling among cobalt domains and makes magnetic moment be easily reversed. When the tungsten content in the CoW films further increases, $H_C$ increases due to the gradually formed Co$_3$W phase with hard ferromagnetic property. For the in-plane remanence ratio ($M_r/M_S$) curve of the CoW films shown in Fig. 4f, it firstly decreases and then increases when the tungsten content exceeds 11 at. %. $M_r/M_S$ decreases again when the tungsten content is beyond 20 at. %. It is known that the pure Co phase has a larger $M_r/M_S$ value since the magnetic energy level of the pure Co phase is higher than that of Co$_3$W. At the beginning, the nonmagnetic W atoms enter the Co lattice and dilute the magnetic moment of Co atoms, which leads to a reduction of $M_r/M_S$ values. When the tungsten content is beyond 11 at.%, tungsten atoms tend to segregate at the grain boundaries and Co$_3$W phase forms, which results in the mixture of Co and Co$_3$W phases in the films. Dominated by the pure Co phase, $M_r/M_S$ turns to increase with the tungsten content. However, the $hcp$-Co$_3$W phase becomes the main phase when the tungsten content is beyond 20 at.%. Because the $hcp$- Co$_3$W phase is a hard magnetic phase with lower $M_r/M_S$ value than Co, $M_r/M_S$ decreases with increasing tungsten content. Therefore the magnetic properties are contributed to the evolution of composition and crystal structure in the films, which is consistent with the XRD results in Fig. 2. It can also be observed that the CoW films transfer from in-plane magnetic anisotropy to magnetic isotropy with increasing tungsten content. According to the XRD results in Fig. 2a, the transformation of magnetic anisotropy seems to be related to the formation of $hcp$-Co$_3$W phase.
In Fig. 5a-e, with increasing annealing temperature, the Co$_3$W films exhibit a similar transformation of magnetic anisotropy, which is also due to the formation of hcp-Co$_3$W phase according to the XRD result in Fig. 2b. In Fig. 5a and c, the as-deposited, 500 ºC annealed films show in-plane magnetic anisotropy. This is because these films are amorphous and their magnetic anisotropy originates from the surface anisotropy ($\Delta E = K_s V + K_s S$). After annealed at 550 ºC, the film is partially crystallized and the Co$_3$W alloy phase forms gradually. The Co$_3$W phase has a large magnetocrystalline anisotropy that is compatible to the surface anisotropy and leads to a small difference between the in-plane and out-of-plane saturation fields. When the annealing temperatures rise to 600 ºC and 650 ºC, the films have almost identical in-plane and out-of-plane hysteresis loops, which means the magnetocrystalline anisotropy exceeds surface anisotropy and becomes the dominant factor. Because of the random distribution of crystal axis directions, the magnetocrystalline anisotropy axes of the completely crystallographic Co$_3$W films are randomly distributed. As shown in Fig. 5f, for the as-deposited and annealed Co$_3$W films below 600°C, both in-plane and out-of-plane $H_C$ increases with the increasing annealing temperature. The film annealed at 600 ºC has the highest in-plane $H_C$ of 512 Oe and out-of-plane $H_C$ of 388 Oe. However, when the annealing temperature rises to 650 ºC, the in-plane $H_C$ of the film decreases. It may be attributed that the grain boundaries in the Co$_3$W films become ambiguous and the interaction among the grains becomes weak. Actually, different microstructures of the Co$_3$W films annealed at different temperatures have been observed in Fig. 4.

From Fig. 5a, it can also be observed that the saturation magnetization ($M_S$) of the as-deposited Co$_3$W film is very small. For the sample annealed at 500 ºC, $M_S$ reaches 176.5 emu/cm$^3$. However, when the annealing temperature rises from 500 ºC to 650 ºC, $M_S$ almost
reduces linearly, while there is some distinction between the in-plane $M_S$ and out-of-plane $M_S$. $M_S$ is mainly contributed by the mean moment of Co atoms since W has a negligible induced moment. And the magnetic moment of Co atoms is decided by the number of Co first neighbors.\footnote{For the as-deposited film, Co and W atoms are distributed chaotically and Co atoms in the film may have less Co atoms as first neighbors, resulting in a strong reduction on magnetic moment. After the Co$_3$W film is annealed at 500 °C, although it is still amorphous, atomic thermal motion gives rise to the rearrangement of Co and W atoms and thus there are more first neighbors of Co atoms, which can be proved by its large $M_S$. The Slater-Pauling model suggests that a gap in conduction-band density of states tends to conserve the number of conduction electrons in an alloy series leading to a linear variation of $m_{\text{at}}$ (the mean magnetic moment per atom of the alloy) with $Z_M$ (the atomic valence of the metal M. $Z_M = 6$ for W).\footnote{The relationship between $m_{\text{at}}$ and x (at.% W) is then expressed as
\[ m_{\text{at}}(x) = m_{\text{metal}} - x(10 + Z_M - Z_T)\mu_B, \] (8) where $Z_T$ and $m_{\text{metal}}$ represent the atomic valence and magnetic moment in the pure T metal ($Z_T = 9$ and $m_{\text{metal}} = 1.7\mu_B$ for Co). According to equation (8), the magnetic moment of Co atoms in Co$_3$W alloy is nearly zero, which means the $M_S$ of Co$_3$W alloy is very small. Increasing annealing temperature, the film is gradually crystallized to form hcp Co$_3$W alloy, while $M_S$ decreases almost linearly with the crystallization of Co$_3$W alloy.} The addition of tungsten atoms in the CoW alloys not only modifies their magnetic properties significantly, but also greatly enhances their corrosion resistance. The corrosion resistance of the Co$_3$W films is evaluated through measuring their $H_C$ after immersing them in 0.5 % NaCl solution at room temperature. The as-prepared, 550 °C annealed and 600°C annealed Co$_3$W films are
chosen to be studied. Their $H_C$ values with different immersing time have been shown in Fig. 6a. It can be observed that all the Co$_3$W samples only show little changes of $H_C$ even after being immersed in 0.5 % NaCl solution for 170 h. Subsequently, XPS measurements are performed on the CoW films with different tungsten contents. Fig. 6b shows the W 4f$_{7/2}$ peak of all the CoW films annealed at 600 ºC. For the CoW films with 2, 11, 18 and 26 at.% W, the W 4f$_{7/2}$ peak at 31.4 eV and W 4f$_{5/2}$ peak at 33.6 eV belong to tungsten metal, while the W 4f$_{7/2}$ peak at 35.8 eV and W 4f$_{5/2}$ peak at 37.98 eV belong to WO$_3$.\textsuperscript{18} It suggests that some tungsten atoms on the surface of the CoW films have been oxidized although no obvious tungsten oxides can be observed on the XRD patterns of Fig. 2a. However, because of the ultrathin tungsten oxide layer on the surface, the inner Co$_3$W alloy is protected from further oxidation. The formation of the WO$_3$ passivation layer should be attributed to the fact that tungsten atoms are easily oxidized in air because WO$_3$/W has a low standard reduction potential of -0.09 V. Fig. 6c shows the Co 2p$_{3/2}$ peak of the CoW films. For the film with 2 at.% W, the Co 2p$_{3/2}$ peak at 778.3 eV and Co 2p$_{1/2}$ peak at 793 eV of Co metal are very weak, while the Co 2p$_{3/2}$ peak at 780.4 eV and Co 2p$_{1/2}$ peak at 795.6 eV of CoO have relatively strong intensities.\textsuperscript{19} It indicates that the Co atoms on the surface of the films almost have been completely oxidized. However, when the tungsten content in the CoW films increases from 11 at.% to 26 at.%, the intensity of the Co 2p$_{3/2}$ peak of Co metal increases following the reduced intensity of the Co 2p$_{3/2}$ peak of CoO. It can be concluded that the tungsten atoms in the CoW alloys helps to reduce the oxidation of Co atoms and therefore enhance their corrosion-resistance. For the CoW film with 26 at.% W, the W 4f$_{7/2}$ peak occurs at 30.98 eV, shifting to higher binding energy upon forming Co alloys compared to the W 4f$_{7/2}$ peak at 30.89 eV for the CoW film with 11 at.% W. The result is similar with the XPS result of some other
Co-based alloys. The excellent corrosion-resistance properties make the Co$_3$W alloy films very promising in practical applications.

4. Conclusions

A series of CoW films have been fabricated by electrochemical deposition method. Their compositions can be modified by adjusting electrolyte concentrations, pH values and applied potentials. The effects of the composition and annealing temperature on the structural and magnetic properties of the CoW films were studied. When either the tungsten content or annealing temperature is low, the CoW films exhibit in-plane anisotropy because the surface anisotropy is dominated. When the hard ferromagnetic Co$_3$W phase forms completely, the CoW films become isotropic because their magnetocrystalline anisotropy exceeds the surface anisotropy. The corrosion-resistance of the Co$_3$W films is also studied. After being immersed in 0.5% NaCl solution for 170 h, the as-prepared and annealed Co$_3$W films have no dramatic change of the magnetic properties, which means the Co$_3$W films have excellent corrosion-resistance property. Theoretical analysis and XPS measurement suggest that the corrosion-resistance originates from the tungsten oxide passivation layer on the surface of the films.

Acknowledgment

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González-Calbet, F. Petroff, C. Deranlot, S. Pascarelli, P. Bencok, N. B. Brookes, F. Wilhelm and A.


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Figures Captions:

Table 1 The W content and the deposition parameters. There are 0.1 mol·L$^{-1}$ of CoSO$_4$ and 0.2 mol·L$^{-1}$ Na$_3$Cit in every solution.

Fig. 1 Cyclic voltammograms for the solutions with different pH values.

Fig. 2 (a) XRD patterns of the CoW films with different compositions annealed at 600 °C for 30 min in vacuum. (b) XRD patterns of the CoW films with 26 at.% W(Co$_3$W) annealed at different temperatures for 30 min in vacuum.

Fig. 3 SEM micrographs of the 26 at.% W (Co$_3$W) films. (a) as-deposited; (b) 500 °C annealed; (c) 550 °C annealed; (d) 600 °C annealed; (e) 650 °C annealed. (f) EDS of the as-deposited Co$_3$W film.

Fig. 4 Hysteresis loops of the CoW films with different tungsten contents. (a) 2 at.% W, (b) 11 at.% W, (c) 18 at.% W, (d) 20 at.% W, (e) 26 at.% W. (f) Dependence of $H_C$ and $M_r/M_S$ of the CoW films on the tungsten content. All the samples have been annealed at 600 °C for 30 min in vacuum.

Fig. 5 (a)-(e) Hysteresis loops of the Co$_3$W films annealed at different temperatures for 30 min. (f) $H_C$ of the Co$_3$W films as a function of the annealing temperature.

Fig. 6 (a) $H_C$ of the Co$_3$W films with different immersing time in the 0.5% NaCl solution. The XPS spectra for W 4f peaks (b) and Co 2p peaks (c) of the CoW films with different tungsten contents.
Table 1. (Lina Yu et al.):

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<th>Tungsten content (at.% W)</th>
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Fig. 1. (Lina Yu et al.):
Fig. 2. (Lina Yu et al.):

(a) 

(b)
Fig. 3. (Lina Yu et al.):
Fig. 4. (Lina Yu et al.):

(a) 2% W in-plane | 2% W out-of-plane
(b) 11% W in-plane | 11% W out-of-plane
(c) 18% W in-plane | 18% W out-of-plane
(d) 20% W in-plane | 20% W out-of-plane
(e) 26% W in-plane | 26% W out-of-plane
(f) $H_C$ (in-plane) | $M_r/M_S$ (in-plane)

at.% W vs.

$H_C$ (in-plane) | $M_r/M_S$ (in-plane)
Fig. 6. (Lina Yu et al.):

- (a) as-dep. in-plane and as-dep. out-of-plane
- (b) 500°C in-plane and 500°C out-of-plane
- (c) 550°C in-plane and 550°C out-of-plane
- (d) 600°C in-plane and 600°C out-of-plane
- (e) 650°C in-plane and 650°C out-of-plane
- (f) Hc (Oe) vs. T (°C) for as-dep., in-plane, and out-of-plane
Fig. 6. (Lina Yu et al.):

(a) Graph showing magnetic field (H) against time (in hours) for different temperatures and conditions.

(b) Graph showing intensity (a.u.) against binding energy (eV) for different W concentrations.

(c) Graph showing intensity (a.u.) against binding energy (eV) for different W concentrations.
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(a) 

\[ H_C \text{ (Oe)} \]

Time (hour)

(b) 

Intensity (a.u.)

Binding Energy (eV)

(c) 

Intensity (a.u.)

Binding Energy (eV)

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<th>Tungsten content (at.% W)</th>
<th>Na$_2$WO$_4$ (mol·L$^{-1}$)</th>
<th>pH</th>
<th>Potentials (V vs. Ag/AgCl)</th>
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Table 1 The W content and the deposition parameters. There are 0.1 mol·L$^{-1}$ of CoSO$_4$ and 0.2 mol·L$^{-1}$ Na$_3$Cit in every solution.