

Contribution of electrolyte pH and deposition potentials to the magnetic anisotropy of electrodeposited nickel films

Hakan Kockar^{a,*}, Mursel Alper^b, Oznur Karaagac^a, Nuri Nakiboglu^c, M. Celalettin Baykul^d

^a Physics Department, Science and Literature Faculty, Balikesir University, 10145, Balikesir, Turkey

^b Physics Department, Science and Literature Faculty, Uludag University, Görükle 16059, Bursa, Turkey

^c Chemistry Department, Science and Literature Faculty, Balikesir University, 10145 Balikesir, Turkey

^d Physics Department, Science and Literature Faculty, Osmangazi University, 26480 Meselik, Eskisehir, Turkey

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ABSTRACT

The influence of electrolyte pH and cathode potential on the magnetic properties of single layer Nickel films electrodeposited on polycrystalline titanium substrates was studied. The films were deposited at the electrolyte pH=3.5 ± 0.1, 2.5 ± 0.1 and 2.1 ± 0.1 by varying the deposition potentials (−1.2, −1.5 and −1.8 V vs saturated calomel electrode, SCE) applied in continuous waveform. The structural analysis by X-ray diffraction revealed that the films have face-centred cubic structure. Results of the magnetic measurements obtained by vibrating sample magnetometer (VSM) indicated that the magnetic properties were affected by the electrolyte pH and the cathode potentials in terms of magnetic anisotropy. At the highest pH the films deposited at the lowest potential had in-plane magnetic anisotropy. As the electrolyte pH decreased from the high (pH=3.5 ± 0.1) to low (pH=2.5 ± 0.1), which is aided by increasing the potentials, resulted in an almost magnetic isotropy in the films. However, isotropic magnetic behaviour was observed for the film deposited at the low pH combined with the high potential (−1.8 V vs SCE). Magnetic thickness profile of the samples obtained by VSM revealed that the isotropic films have a smoother magnetic variation across the film from one edge than the anisotropic ones. This is also verified with a microscopic observation by an optical microscope and the surface of the isotropic films is observed to be smoother than that of the anisotropic ones. Furthermore, all films were found to have planar magnetic anisotropy irrespective of the pH's and the potentials.

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1. Introduction

Nickel (Ni) films are one of the most frequently studied ferromagnetic materials due to their scientific and technological importance [1–3]. In the electrodeposition technique, the film properties are mainly dictated by a number of factors including the deposition potentials and the electrolyte pH. Understanding the magnetic properties of the magnetic films offers a wide potential for the development of new applications especially in sensors and recording media [3,4]. Therefore, the purpose of this study is to deposit the Ni films from an electrolyte containing Ni²⁺ ions at various electrolyte pH by varying the cathode potentials applied in the continuous waveform and then to investigate the magnetic anisotropy of the films as a function of the pH and the potential. The films deposited at the lowest electrolyte pH

displayed a magnetic anisotropy and were observed to have smoother surfaces than the ones obtained at highest pH.

2. Experimental procedure

In this study, single Ni films were grown from an electrolyte containing Ni²⁺ ions under potentiostatic conditions. Electrodeposition was performed in an electrochemical cell with three electrodes using a potentiostat/galvanostat (EGG Model 362). The electrolyte composed of 2.0 M Ni(SO₃HN₂)₂·4H₂O, and 0.5 M H₃BO₃. All chemicals were reagent grade and dissolved in distilled water. A platinum (Pt) sheet with an area of 6 cm² was used as counter electrode. The reference electrode was a saturated calomel electrode (SCE). All potentials are pronounced with respect to the SCE. Titanium sheet was used as the substrate. Prior to deposition, the substrates were mechanically polished, and then washed in 10% H₂SO₄ followed by distilled water.

The pH value of freshly made electrolytes was 3.5 ± 0.1. The electrolyte pH decreased after each deposition. This is because the current leads to a reduction of metal ions at the cathode and their

* Corresponding author. Tel.: +90 266 612 1278; fax: +90 266 612 1215
E-mail addresses: hkockar@balikesir.edu.tr, hakankochar@hotmail.com
(H. Kockar).

replacement by hydrogen ions, lowering the electrolyte pH [5,6]. It is also well known that pH of electrolytes can be adjusted to the desired value by the metal deposition using an inert anode [5]. Continuing in the same way, the desired pH values were obtained by flowing current through the electrolyte. In order to study the pH effect, the electrolyte pH values were varied as 3.5 ± 0.1 , 2.5 ± 0.1 and 2.1 ± 0.1 for each group of specimens. The polarisation curve of the electrolyte (current-potential) was obtained to select the proper potentials for deposition. According to the curve, the films were deposited at room temperature using the cathode potentials of -1.2 , -1.5 and -1.8 V, which were applied in continuous waveform. The nominal thickness of the films was fixed at $4 \mu\text{m}$. The charge amount required for the film thickness was calculated according to Faraday's law by assuming 100% current efficiency for each film deposited at different potential. After the deposition is completed the films were peeled of their substrates.

X-ray diffraction measurements were carried out using a Phillips diffractometer type PW1820 with a beam of $\text{Cu-K}\alpha$ radiation. A commercial vibrating sample magnetometer, VSM (The DMS Model EV9, ADE Technologies) was employed to determine the magnetic anisotropy and thickness distribution. Ni foil was used to calibrate the VSM. Hysteresis loops were measured at arbitrary angles in the film plane and also perpendicular to the film plane. In the film plane, the total angular range of measurement was 180° with 30° intervals, chosen in a way that the 0° and 90° equal the easy and hard axis direction, respectively. Magnetic anisotropy was studied by taking hysteresis loops on 5 mm disk samples. The thickness uniformity of the films was obtained from the saturation magnetisation intensity, by taking measurements on samples cut into strips ($1 \text{ cm long} \times 1 \text{ mm wide}$) across the width of films from one edge. In addition, an optical microscope was used to closely examine the surfaces of the films. All production and measurements were carried out at room temperature.

3. Results and discussion

The crystalline texture of polycrystalline Ni films were examined by X-ray diffraction ranging $40^\circ < 2\theta < 80^\circ$, where θ is the Bragg angle. As an example, the XRD pattern of the film deposited at pH=3.5 with -1.8 V is illustrated in Fig. 1. Bragg reflections were observed at the angles of $2\theta=43.9^\circ$, 51.1° , 75.9° that correspond to the (1 1 1), (2 0 0) and (2 2 0) planes of face-centred cubic (fcc) Ni. Analysis of the XRD patterns revealed that the films have fcc structure irrespective of deposition conditions. An average crystallite size of the films was calculated to be about 20 nm from the Scherrer formula [7].

Magnetisation measurements were preformed to examine in plane and out of plane magnetic anisotropies by taking the hysteresis measurements of Ni films using the VSM. Repeated depositions yielded the maximum film coercivity, H_c ranging from 0.50 to 1.25 kA/m and saturation magnetisation, $M_s=0.40$ kA/m, which is close to the reported values, e.g. 0.48 kA/m of Bulk Ni [8,9]. The average measured coercivities are almost consistent with the published value for bulk nickel of 0.80 kA/m [9].

Hysteresis loops of single Ni film (deposited at pH=3.5 and -1.2 V) measured at 0° and 90° in the film plane and also perpendicular to the film plane are shown in Fig. 2. When the field is applied at 0° , the loop is almost square with a higher H_c of 1.07 kA/m. When the field is applied along 90° in the film plane, the loop exhibits a smaller H_c of 0.78 kA/m than the anisotropy field, $H_k=6.35$ kA/m, but not equal to zero. To obtain the H_k , the extrapolation of the in-plane and perpendicular hysteresis loops back to the saturation magnetisation level were carried out. The

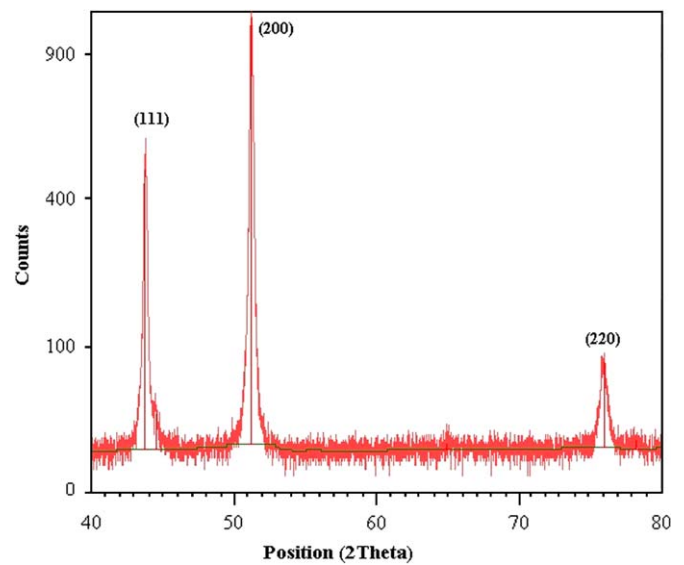


Fig. 1. An example of the XRD patterns for single Ni film deposited at pH=3.5 \pm 0.1 and -1.8 V.

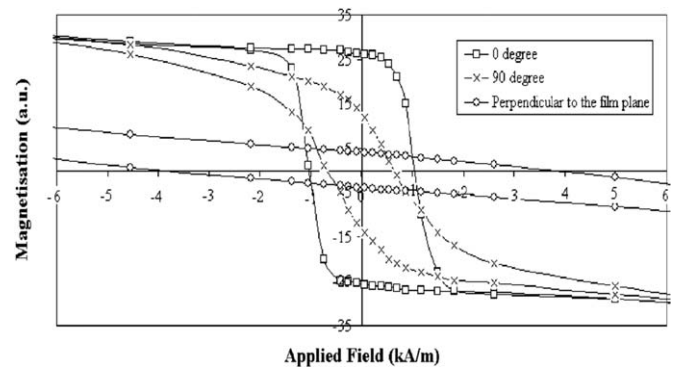


Fig. 2. An example of anisotropic single Ni film deposited at pH=3.5 \pm 0.1 and -1.2 V. Hysteresis loops were measured at 0° and 90° in the film plane and also perpendicular to the film plane.

H_k was taken, as the magnetic field required saturating the film specimen along the hard axis. The H_c decreases when the measurement angle is rotated from 0° to 90° . The H_c is different from the H_k . This means that when the field is applied along the easy axis, the magnetisation does not rotate uniformly but there is a nucleation and propagation of domain walls [10–12]. The H_c reaches 3.80 kA/m, indicating that the film has a planar magnetic anisotropy when the field is applied perpendicular to the film plane.

In-plane magnetisation loops in Fig. 2 closely resemble the behaviour predicted by the Stoner–Wohlfart (SW) model for coherent magnetisation rotation in materials with isolated single domain particles. Single Ni films deposited in this study do not consist of isolated domain particles, however, some success in using this model as a basis deriving hysteresis loops has been reported in the past for various film compositions [10–12]. The ratio of remanent magnetisation to saturation magnetisation, M_r/M_s and the coercivity to anisotropy, H_c/H_k for in-plane directions spanning 180° is shown in Fig. 3. Both the coercivity and remanence ratio have peak values confirming the presence of a uniaxial magnetic anisotropy. The coercivity is maximised in the easy direction and minimised along the hard direction as

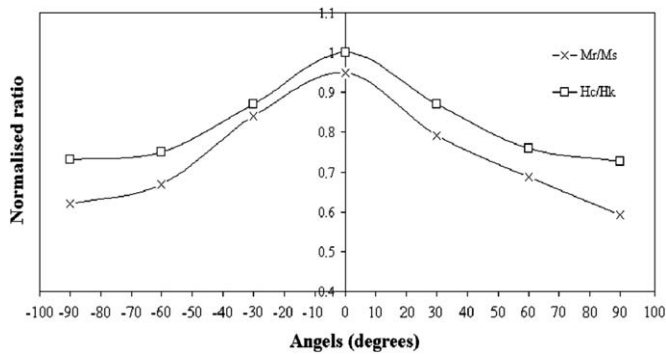


Fig. 3. Normalised remanence and coercivity ratios as a function of arbitrary chosen angles between applied field and magnetisation easy axis in the film plane for single Ni film deposited at $\text{pH}=3.5 \pm 0.1$ and -1.2 V.

predicted in the SW model. In the easy direction the magnetisation reversal switches very quickly, indicating that there is strong magnetostatic and/or exchange coupling forces between crystal grains. However, unlike the SW model, the hard axis in the films was not equal to zero. This probably happens because the magnetisation reversal in these films arises from domain wall motion, domain formation and domain rotation, only the latter is considered in the SW model.

The loops in Figs. 2 and 3 indicate that the film has well-defined uniaxial in-plane anisotropy. To see the effect of the lower electrolyte pH on the deposits, the films were produced at $\text{pH}=2.5 \pm 0.1$ and 2.1 ± 0.1 keeping the potentials constant at -1.2 V. Although the feature characteristics of the in-plane anisotropy for the films produced at $\text{pH}=2.5 \pm 0.1$ were observed, the loops corresponding to the angles are different from the loops in Fig. 2. When the field is applied at 90° , the loop is not as square as in Fig. 2, and when the applied field is at the 0° direction the remanence ratio decreases. Therefore, it should be noted that the lower pH of 2.5 ± 0.1 makes the uniaxial magnetic anisotropy less well-defined. In the case of Ni films deposited at 2.1 ± 0.1 , although there was a slight variation between the loops, this can be expressed as the film shows almost magnetic isotropy. It is indicated that the uniaxial in-plane anisotropy changes towards isotropy as the electrolyte pH decreased.

In order to investigate the magnetic properties of films, further single layer Ni films were deposited at higher cathode potentials of -1.5 and -1.8 V by varying the electrolyte pH. The films produced at $\text{pH}=2.5 \pm 0.1$ had almost an isotropy, and the degree of magnetic isotropy increased with increasing cathode potentials. In the same series of the films, the Ni films deposited at $\text{pH}=2.1 \pm 0.1$ and -1.8 V showed isotropic magnetic behaviour.

Measurements of the magnetic thickness uniformity of the films were also performed. $10 \text{ mm} \times 10 \text{ mm}$ size of the samples was cut from one edge ($1 \text{ mm} \times 10 \text{ mm}$). Magnetic measurement sample were performed on each sample using VSM. The thickness profile of the films was obtained from the saturation magnetisation intensity using the formula $M_{\text{int}}=M_0V$, with M_{int} obtained from the VSM, V is the volume of the sample and M_0 is the saturation magnetisation per unit volume of bulk Ni [9]. It is seen that the films have a smoother magnetic variation than the anisotropic ones across the film. Further verification of magnetic anisotropy study was carried out using an optical microscope. The microscopic investigation at $600\times$ magnification revealed that the smoothness in the film surface increased with the decrease of electrolyte pH at the cathode potential of -1.2 V, and degree of the smoothness on the surface of the films was observed at lowest pH values with the increase of the cathode potential. It can be expressed that the isotropic films have uniform thickness

distributions whereas the anisotropic ones have poor thickness uniformity across the film confirming the findings of the magnetic thickness profile.

In the electrodeposition process of the films, hydrogen evolution may be defined as the ratio of the actual amount of metal deposited to that expected theoretically according to the Faraday law [13,14]. Therefore, the thickness of the films could be lower than the nominal one such as the films deposited at the $\text{pH}=3.5$ and -1.2 V. At this point, the water decomposition reaction leading to hydrogen formation can have a significant contribution to the measured current resulting in retarded current efficiency. Consequently, the roughness of the layer can be expressed to evolve with the thickness as roughness is proportional to the thickness as electrolyte pH decreased. In other words, as it is well known that the low electrolyte pH and the high cathode potential favour the hydrogen evolution. The hydrogen formation is expected to lead to the reduction of metal ions at the cathode and their replacement by hydrogen ions in the electrolyte, and hence the change in the ratio of ions may result in changes in the thickness uniformity across the deposits. However, unlike our expectations, as the pH increased to its lowest value of $\text{pH}=2.1 \pm 0.1$ and the potential increased -1.8 V, the isotropic magnetic behaviour was observed, which was verified by magnetic thickness profile and microscopic observation of the film surface across the film. It should be also noted that although hydrogen evolution leads to a decrease in current efficiency, it may also tend to improve the throwing power of the cell that governs the thickness uniformity across the film [13,14]. The possible explanation for the findings may be found in the latter that probably happens in this study since electrolyte with high throwing power produces only small changes in the thickness uniformity across the film samples whereas solutions with low throwing power can produce large thickness variations in the films, as reported in [13–16].

4. Conclusions

A series of single layer Ni films were grown as a function of the electrolyte pH and cathode potential by electrodeposition. Magnetic measurements showed that the magnetic properties of the films are very sensitive to the pH and the potentials. The higher pH values (< 3.0) combined with lower cathode potentials (> 1.5 V) leads to anisotropic behaviour in the films. Magnetic thickness profile of the samples by VSM and the microscopic observation by an optical microscope indicated that the isotropic films have a smoother variation across the film from one edge than the anisotropic ones. The results obtained in this study have shown that anisotropic and isotropic magnetic materials could be deposited by choosing the proper deposition parameters for their potential applications as sensors and recording media materials.

Acknowledgments

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