

Electrodeposition of Superalloy Thin Films: Structural and Magnetic Characterization

G. Nabiyouni^{*1}, Sh. Saeidi¹, I. Kazeminezhad², A. Yousefnejad¹

¹Department of Physics, Faculty of Science, Arak University, Arak 38156-8-8349, Iran

²Department of Physics, Faculty of Science, Shahid Chamran University, Ahvaz, Iran

*g-nabiyouni@araku.ac.ir; saeidi.sh@gmail.com; I.kazeminezhad@scu.ac.ir; asie_you@yahoo.com

Abstract- We have prepared superalloy (Ni-Fe-Mo) thin films using electrodeposition method. In this work electrodeposition of superalloy took place in a single electrolyte containing Ni^{2+} , Fe^{2+} , and Mo^{2+} ions, under potentiostatic control (constant potential). Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) techniques were employed to investigate the morphology and chemical composition of the films. The result indicates that the weight percent (wt. %) of Ni and Mo, decreases by increasing the film thickness while the weight percent of Fe, increases as the film thickness increases. The magnetic properties of the superalloy films have also been studied using alternating gradient force magnetometer (AGFM).

Keywords- Superalloy; Electrodeposition; Magnetic Properties

I. INTRODUCTION

Superalloy is a magnetically soft material composed of nickel, molybdenum, and iron. It has an extremely high magnetic permeability, and a relatively low coercivity. Superalloy is usually used in manufacturing components for telemechanics and telecommunication instruments.

Many different techniques have been used to synthesis alloy and multilayered thin films. The structural and physical properties of the films, nevertheless, are highly dependent on their preparation methods. Thin films are most commonly prepared by vacuum based techniques, such as evaporation, sputtering and molecular beam epitaxy (MBE). In these techniques a material (metal, alloy or semiconductor) is evaporated or sputtered and deposited on a substrate to form a thin film. In MBE, under certain conditions, it is possible to grow one atomic layer after another, forming a nearly perfect single crystal with both a very smooth surface and sharp interface. However, the required equipment is complicated and expensive. Sputtering, which is less complicated and less expensive, has been widely used to produce thin films and multilayers, although the produced materials are not perfect single crystals and do not always have a smooth surface or very sharp interfaces. An alternative method widely used for metallic coatings, is electrodeposition.

Electrodeposition is a simple, flexible and inexpensive technique for fabricating the metallic thin films and does not require complex and expensive vacuum apparatus and the deposition usually takes place at room temperature. By this method, individual layers, multilayer and magnetic alloy layers have been produced in ambient conditions.

Although electrodeposited films first found widespread application as decorative and/or protective coatings, the method is now also widely used in the electronics industry to deposit conducting or magnetic layers. For example, electrodeposited Cu is now the material of choice for interconnects in ultra large scale integrated (ULSI) circuits [1], while electrodeposited soft magnetic alloys are an important component of magnetic recording heads.

Figure 1 illustrates the basic principle of electrodeposition. Two conducting electrodes are placed in an electrolyte containing ions of the metal or metals to be deposited. When the external power supply drives a current through the cell, metal ions are reduced to metal atoms at one of the electrodes, known as the cathode. For example, if the electrolyte contained dissolved Ni^{2+} , Fe^{2+} and Mo^{2+} ions, the cathode reaction would be:

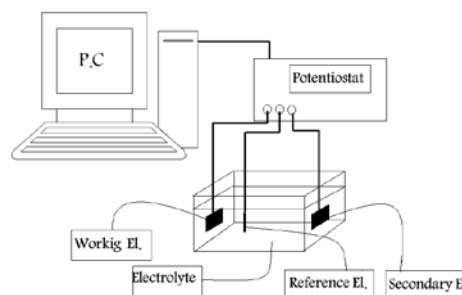
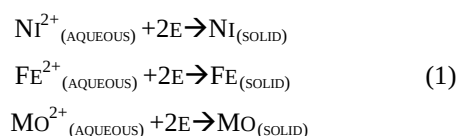


Figure 1 Schematic of a simple electrodeposition cell

Making a thin layer of Ni-Fe-Mo alloy on the cathode (substrate). A problem with electrodeposition is that during the metal deposition hydrogen is also reduced, and the amount could be significant, especially if a relatively high potential is applied between working and reference electrodes. Thus the charge passed between anode and cathode is not only due to metal deposition but also to hydrogen evolution, so the deposited layer thicknesses are less than those calculated assuming all the charge passed reduces metal (the nominal thicknesses). The current efficiency of the Ni-Fe-Mo electrolytes is found to be very low and rarely reaches to 15%. We found the current efficiency of our electrolyte for deposition of Ni-Fe-Mo alloys is only 10%.

Many factors influence the growth of electrodeposited films, including the transport of ions to the cathode, the presence of adsorbed species on the cathode, and the diffusion of adatoms. According to Brenner's explanation: when a less noble metal is professionally codeposited with a more noble metal, anomalous codeposition occurred, i.e., the deposit contains the less noble metal in a higher concentration than expected from the electrolyte composition [2]. Electrodeposition of ferromagnetic alloys consisting of Ni, Fe and Co is an example of anomalous codeposition. The codeposition of Nickel and Molybdenum is also the same [2, 3].

Molybdenum cannot be electroplated from an aqueous solution by itself, but it is possible to co-deposit it with iron group metals; making molybdenum alloy thin films. These alloys have some interesting properties, such as a high corrosion resistance, high wear resistance, and low hydrogen evolution overpotential. Furthermore, metallic alloy films which are composed of these magnetic and nonmagnetic elements have useful applications due to their magnetic properties such as low coercivity, high permeability, and high flux density [4-9]. We have successfully electrodeposited Ni-Fe-Mo alloy from an aqueous solution containing Ni²⁺, Fe²⁺, and Mo²⁺ ions. Structural and magnetic properties of the electrodeposited supermalloy thin films are presented in this paper.

II. EXPERIMENTAL

The deposition took place at room temperature under potentiostatic control in a single electrolyte containing three electrodes at pH of 1.8. The bath compositions for electroplating films are given in Table 1. Copper foil substrates were used as the cathode with a surface area of 1.5×1.5 cm². In order to control the electroplating process, exposing area was chosen as a circle with 10 mm in diameter. Prior to electrodeposition, the substrates were mechanically and electrochemically polished. The electropolishing process was carried out in a 50% H₃PO₄ solution and applied a positive DC potential of 1.8-2V on the substrate. This process removes a very top oxidized layer of Cu from the surface and makes the substrate surface absolutely clean and shiny. The substrate then rinsed with double distilled water and placed into electrolyte immediately to prevent substrate from any oxidation and contamination.

TABLE I. ELECTROPLATING COMPONENTS OF NI-FE-MO ALLOYS

Component	Quantity
NiSO ₄ , 6H ₂ O	60 g l ⁻¹
FeSO ₄ , 7H ₂ O	4 g l ⁻¹
Na ₂ MoO ₄ , 2H ₂ O	2 g l ⁻¹
NaCl	10 g l ⁻¹
C ₆ H ₈ O ₇ (Citric acid)	66 g l ⁻¹
C ₇ H ₅ NO ₃ S (Saccharin)	3 g l ⁻¹

In order to decrease the ohmic resistance and prevent from potential drop in the electrolyte, working electrode is located quite close to the reference electrode, while the working and secondary electrodes are located parallel and far from each other (about 10 cm).

Electrochemical reaction starts by switching on the computer control potentiostat and applying a constant potential. Computer measures the deposition current between cathode and anode and integrate it over the time until the passed charge between cathode and anode reaches to a certain amount corresponds to a desired film thickness. The amount of charge is calculated according to Faraday's equation [10]:

$$q = \frac{n F \rho A h}{M} \quad (2)$$

Where F= 96485 C/mol is Faraday's constant, h is thickness, A is exposed area, n is valence, ρ is atomic density, and M is atomic mass.

The optimum voltage for depositing of Ni-Fe-Mo alloy layers was found to be -1.35 V. After deposition, the supermalloy films were rinsed in ultra pure water and dried with N₂ gas. The films are now ready for characterization and magnetic studies.

III. RESULTS AND DISCUSSIONS

The composition of the alloy films was measured using energy dispersive X-ray (EDX) analysis. The result is presented in Figure 2. Different weight percents of Ni, Fe, and Mo have been achieved by changing the thicknesses from 0.6 μm to 2.1 μm. Scanning electron microscopy (SEM) was employed to study the surface morphology of the samples. SEM images are given in Figure 3. The figures reveal that, by increasing the film thickness, the film surface becomes granular. Ni-Fe-Mo alloy layers with higher amount of molybdenum and nickel (in weight percent) are more suitable for coating the substances in order to make them highly corrosion resistance. For this application, the sample with the thickness of 0.6 μm is a good candidate.

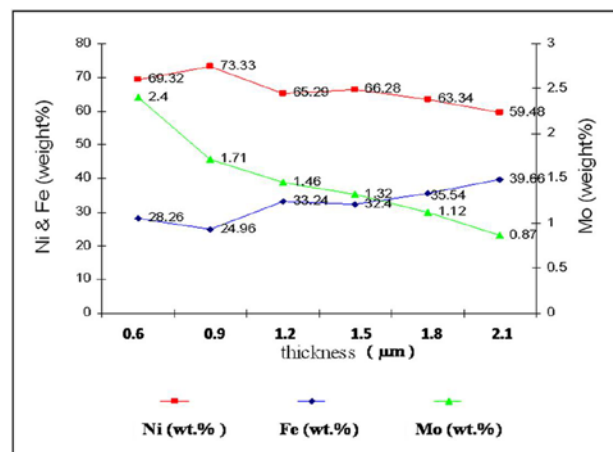


Figure 2 Weight percent of Ni, Fe, and Mo versus thickness

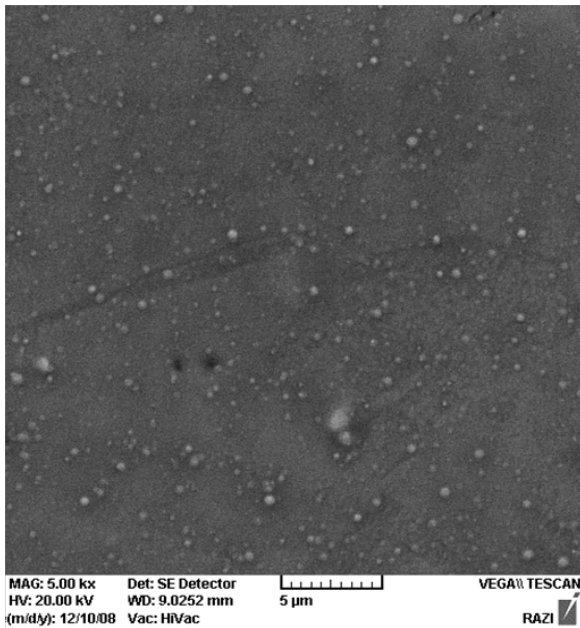


Figure 3 Scanning electron microscopy image of a Ni-Fe-Mo alloy film for the samples with nominal thickness of 1.5µm

The crystalline structure of films prepared by electrodeposition method was verified by X-ray diffraction (XRD). Figure 4 shows a typical XRD pattern for a supermalloy film electrodeposited on a Ti plate substrate. The reason for choosing a Ti plate substrate is that the films can be easily pilled out from its substrate and get rid of the substrate peaks in the XRD patterns. The XRD patterns show four narrow peaks at $2\theta = 38.5^\circ$, 44.7° , 65.1° , and 78.21° respectively, indicating crystalline structure of the electrodeposited supermalloy.

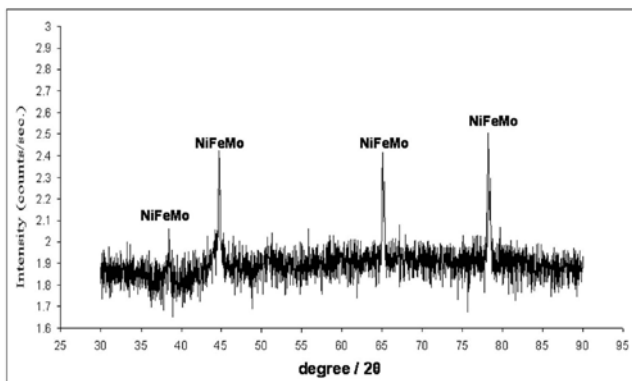


Figure 4 X-ray diffraction pattern of the stripped Ni-Fe-Mo alloy film

In order to assess the suitability of our samples for micromachined magnetic devices, we studied the M-H characteristics, coercivity, saturation magnetic moment and remanence magnetic moment, using an alternative gradient force magnetometer (AGFM). As can be found from the EDX results, the amounts of Ni and Mo decrease and the weight percent of Iron increases with increasing of the film thickness, and consequently affect on the magnetic properties of layers. The results are demonstrated in Figures 5 and 6. The figures represent hysteresis loops of the samples while the applied magnetic field is either parallel or perpendicular to the film surface.

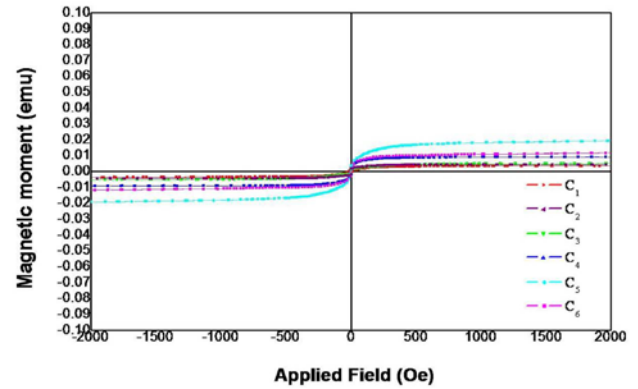


Figure 5 Hysteresis loops for the samples with magnetic field parallel to the film surface. The films' thickness are C1=0.6µm, C2=0.9 µm, C3=1.2µm, C4=1.5µm, C5=1.8µm, and C6=2.1µm

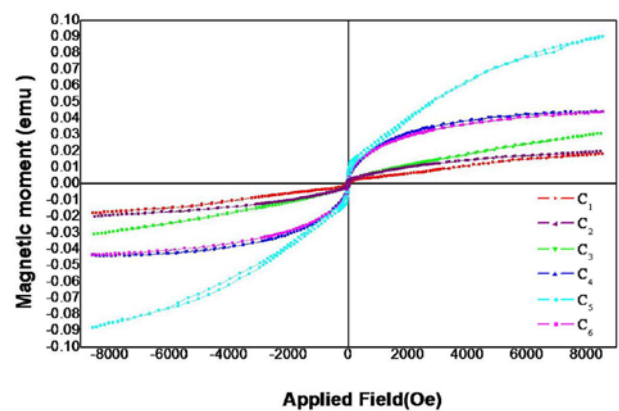


Figure 6 Hysteresis loops for the samples with magnetic field perpendicular to the film plane. The films' thickness are C1=0.6µm, C2=0.9µm, C3=1.2µm, C4=1.5µm, C5=1.8µm, and C6=2.1µm

Increasing the amount of iron in the films, makes the hysteresis loop narrow and leads to increase the saturation magnetic moment and enhancement of soft magnetic properties of layers.

In parallel field all of the samples are saturated in nearly same fields. By adding a few percentage of molybdenum to nickel-iron composition, the domains can be easily aligned with the applied external magnetic field and caused high permeability. In addition, due to the function of molybdenum ions as electron-scattering centers, the electrical resistivity enhances. By increasing electrical resistivity, eddy currents will be reduced. This decrease in eddy currents result in high permeability so that the magnetic field caused by these internal eddy currents acts against the applied magnetic field and has the effect of reducing the internal flux density [4]. In other words, the hysteresis loop reaches saturation sooner when Mo percent increases. The results appear in M-H curves of the thinner films in Figures 5 and 6. Comparing these figures, one can see that the hysteresis loops saturate in the higher field when the field is perpendicular to the film surface than when it is parallel, suggesting an existence of magnetic anisotropy, with an easy axis parallel and a hard axis perpendicular to the film plane.

Tables 2 and 3 respectively give a comparison among magnetic characteristics of Ni-Fe-Mo alloy films when the applied magnetic field is parallel and perpendicular to the film plane. The figures in the tables also indicate that, the remanence magnetic moment in perpendicular configuration is higher than those in the parallel configuration. In addition, in both parallel and perpendicular configurations, coercivity decreases when the film thickness changes from 0.6 μm to 1.5 μm then rises again by increasing the film thickness from 1.5 to 2.1 μm . The reason of this irregular change can be attributed to the amount of deposited molybdenum in the films and existence of some impurities in the electrolyte.

TABLE II MAGNETIC CHARACTERISTICS OF NI-FE-MO ALLOY FILMS IN PARARELL APPLIED MAGNETIC FIELD

Thickness (μm)	Coercivity (Oe)	Remanence Magnetic Moment (emu.)	Saturation Magnetic Moment (emu.)
0.6 μm	13.13	7.14 E-4	0.00356
0.9 μm	12.12	16.51 E-4	0.00427
1.2 μm	5.05	13.02 E-4	0.00499
1.5 μm	5.05	21.14 E-4	0.00904
1.8 μm	7.79	20.44 E-4	0.01161
2.1 μm	6.06	35.70 E-4	0.01938

TABLE III MAGNETIC CHARACTERISTICS OF NI-FE-MO ALLOY FILMS IN PERPENDICULAR APPLIED MAGNETIC FIELD

Thickn ess (μm)	Coercivity (Oe)	Remanence Magnetic Moment (emu.)	Saturation Magnetic Moment (emu.)
0.6 μm	68.69	15.87 E-4	0.01822
0.9 μm	36.37	22.75 E-4	0.03068
1.2 μm	56.57	21.41 E-4	0.01976
1.5 μm	12.12	45.24 E-4	0.04404
1.8 μm	16.16	40.48 E-4	0.04412
2.1 μm	40.40	103.31 E-4	0.09006

IV. CONCLUSIONS

In summery, Ni-Fe-Mo alloy magnetic films were fabricated on Cu and Ti substrates by electrodeposition technique. The structure and morphology of the layers were characterized using SEM, EDX and XRD analyses. XRD patterns reveal the crystalline structure of the deposited layers. The percentage weight of Ni, Fe and Mo in the deposited alloys varies with the film thickness. The magnetic properties of the Ni-Fe-Mo alloy films have been studied using AGFM with the applied field parallel and perpendicular to the film plane. The results reveal of the existence of a magnetic anisotropy with an easy axis parallel and a hard axis perpendicular to the film plane.

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