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Effects of additives on magnetic properties of electroplated CoNiFe films

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EFFECTS OF ADDITIVES ON MAGNETIC PROPERTIES OF ELECTROPLATED
CONIFE FILMS

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Tiffany Yun Wen Jiang

August 2008

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ABSTRACT

EFFECTS OF ADDITIVES ON MAGNETIC PROPERTIES OF ELECTROPLATED CONIFE FILMS

by Tiffany Yun Wen Jiang

To meet the high demand for write head to be used in magnetic recording, soft magnetic material with high saturation magnetic flux density, B_{sat} , was prepared by electrodeposition. A wide range of high X_{Fe} ternary alloys has been achieved with selected organic additives sulfolene and methane sulfinic acid. Experiments were carried out in a RDE to examine a wide range of film composition electrodeposite with two different concentration of sulfolene or methane sulfinic acid. The physical and magnetic properties were determined with XRF, KLA-Tencor profilometer, and VSM.

A CoNiFe ternary alloy film with saturation magnetic flux density of up to 2.3 Tesla is exhibited at composition range of approximately 40 - 62 wt. %Fe and 3 – 4 wt. %Ni for samples deposition with 0.10 g/L of sulfolene. These materials present a low H_c values of about 10.5 Oe. The experimental results suggested that the presence of 0.10 g/L sulfolene can be use as an organic addition to manufacture write-head pole materials.

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LIST OF IMPORTANT SYMBOLS

λ_s – magnetostriction
+ λ_s – magnetostriction expands
- λ_s – magnetostriction contracts
 l – length
 Δl – change in length
 χ – amount of electrical charge, in units of ampere second
 A – area, in units of cm^2
 B – magnetic flux density, in units of T
 B_{sat} – saturation magnetic flux density, in units of T
 c – ionic charge
 Eff – plating efficiency
 F – Faraday's constant, 96,500 Coulombs/mol e^-
 H – magnetic field, in units of Oe
 H_c – coercivity, in units of Oe
 $H_{c \text{ easy}}$ – easy axis coercivity, in units of Oe
 $H_{c \text{ hard}}$ – hard axis coercivity, in units of Oe
 H_k – anisotropy, in units of Oe
 i_w – applied current, in units of amps
 J – current density, in units of mA/cm^2
 M – magnetization
 m – mass of plated metal, in units of g
 $M_{s, \text{film}}$ – total magnetic moment of the plated film, in units of emu
 M_{seed} – magnetic moment of the seed layer, in units of emu
 N – average moles of alloy
 n – oxidation number
 t – plating time, in units of minutes
 t_f – total thickness of the plated film, in units of cm
 t_s – total thickness of the seed layer, in units of cm
 X_{Fe} – iron content in films, in units of wt. %

LIST OF ACRONYMS

BCC – body centered cubic
DASD – direct access storage devices
DC – direct current
DET – diethylenetriamine
DMS – digital Measurement System
FCC – face centered cubic
GMR – giant Magneto-Resistance
MSA – methane sulfinic acid
N – north magnetic poles
RDE – rotating disk electrode
S – south magnetic poles
VSM – vibrating sample magnetometer
XRF – x-ray fluorescence

1. Introduction

1.1 Background

Thin film magnetic recording heads have been used in high performance direct access storage devices (DASD) and data processing systems since 1980 [1]. It is the most important component within storage systems such as computer hard disk drives.

Modern magnetic recording heads are microscopic devices that can record and retrieve information from storage media with densities of up to 80×10^9 bits per square inch. This capacity is enough to store more than thirteen thousand 300-page books in a single square inch of recording media [2].

Illustrated in Figure 1 is a simple schematic of today's longitudinal magnetic recording head that consists of a reader and inductive writer structures [2]. The read head consists of a Giant Magneto-Resistance (GMR) element with sensing leads and magnetic shielding on both sides [2]. In the case of the write element, the key component resembles a horseshoe magnet or yoke is which comprised of two layers of soft magnetic material wrapped around with spiral copper coil with a very small non-magnetic gap (approximately 1000 Å). The yoke is used for collecting magnetic flux from the magnetic storage media (i.e., floppy disk, magnetic tape, or hard disk). When current passes through the spiral coil, it generates a magnetic field. The two magnetic layers become North (N) and South (S) magnetic poles of a magnet. The miniature electromagnet records bits of information onto a spinning magnetic disk based on the magnetic induction phenomenon [2,3]. When a moving storage media is placed closely to the write element, the media surface is thus magnetized in the direction of flux in the

gap. If the direction of the current flow is reversed then the magnetic polarity at the gap will also reverse. Each domain of magnetic polarization on the recording media is related to binary numbers “1” or “0” [2]. In simple form, “1” corresponds to the transition of polarity (magnetic polarity from N going S or S going N) and “0” corresponds to no change in current polarity (constant N or constant S magnetic polarity). An illustration of this principle is shown in Figure 1.

Figure 1. Schematic of a longitudinal magnetic recording head consisting of the two magnetic poles of a magnet.

Read/write heads are complex devices whose design and manufacturing require leading edge technological processes. These include high vacuum thin-film deposition, photolithography and etching. In recording head development, innovative head designs, adequate selection of the material properties, and other contributors such as flying height, coding, and disk H_c are significant factors that have allowed the storage capacity of computer hard drives to nearly double every year during the last two decades. Narrow write poles in the sub-micron level are needed for modern recording heads in order to obtain higher areal density recording. Ferromagnetic write pole materials with adequate magnetic, electrical, and mechanical properties are required to achieve this goal.

1.2 Concept of Magnetism

In general, to understand the magnetic recording process, knowledge of the relationship between magnetic flux density (B), magnetic field (H), and magnetic induction or magnetization (M) is essential. Magnetism is a force that attracts and repels. Magnets have two poles called the “north seeking” and “south seeking” poles. Some magnets are made of iron, cobalt, nickel, or alloys of these materials. When a magnet is placed into an iron mesh, the mesh will cling around it by its magnetic field. Illustrated in Figure 2 is a diagram of typical magnetic field lines. As shown, the magnetic field is directional and it always points from north to south. The total number of field lines crossing a given area is the flux density, or magnetic flux density, and is represented by the symbol B . The magnetic flux density can be described by the relationship:

$$B = H + 4\pi M \quad \text{Equation 1}$$

where H is the field strength and M represents as the magnetization intensity. The factor 4π is the area of the sphere field lines that are enclosing the two poles.

Figure 2. Magnetic field lines passing through a magnet from N to S.

1.3 Magnetic Materials: Diamagnetic, Paramagnetic, and Ferromagnetic

A diamagnetic material will align the field lines in the opposite direction when an external field is applied [5]. A paramagnetic material also partially aligns the field lines when subjected to an external field but it will demagnetize if the field is removed [5]. Materials that exhibit magnetic properties like iron such as cobalt, nickel, and some rare earth elements are called ferromagnetic [5]. They tend to stay magnetized after being subjected to an external magnetic field. These materials are mostly used for electronic, motors, solenoids, recording applications, etc. Their magnetic properties are generally described by parameters such as saturation magnetic flux density (B_{sat}), coercivity (H_c), anisotropy (H_k), and magnetostriction (λ_s) [1]. Transition metals such as cobalt, iron, and

nickel are ferromagnetic above room temperature [8]. Rare earth elements like gadolinium, terbium, and erbium are ferromagnetic when below room temperature [5].

1.4 Magnetic Properties for Write Head Materials

The material for the write head element must be magnetically soft for easy magnetization, at the same time it must provide strong magnetic flux at the gap in order to magnetize the media. Magnetically soft or hard materials are classified by the magnitude of the applied field required to move the domain wall through the material against various microstructure obstacles. In general, magnetically soft materials are magnetic materials that have coercivity of less than 1 Oe. Figure 3 shows a hysteresis loop of both, soft and hard magnetic materials [6]. Typical soft magnetic materials that are widely used are permalloy, ferrites, and various amorphous alloys [1].

Figure 3. Hysteresis loops for (a) soft magnetic and (b) hard magnetic materials.

1.4.1 Saturation Magnetic Flux Density (B_{sat}) and Coercive Force (H_c)

Figure 4 is a schematic representation of the hysteresis curves for a ferromagnetic material, where the magnetization (M) is presented in terms of the applied field (H).

When the applied field is increased high enough to direct the magnetization parallel to the field, then it will reach the saturation state. The quantity, $B = H + 4\pi M_s$, known as the saturation magnetic flux density, is designated B_{sat} , and it is measured in units of Gauss (G), or alternatively, in Tesla (T), $1 \text{ T} = 10^4 \text{ G}$ [5]. On the curve, the value of H when $M = 0$ is called the coercive force or coercivity, and it is represented by $-H_{ci}$ or H_c . M_r is known as the remanent magnetization when the applied field is zero which can be decreased to zero applying a reverse coercive field.

Figure 4. Hysteresis curve with important defined parameters for recording head materials.

1.4.2 Magnetic Anisotropy

In many materials, the magnetic properties depend on the direction in which they are measured. Amorphous magnetic metals have no crystal structure, therefore, possess

no magneto-crystalline anisotropy energy that consequently leads to low coercivity [4, 7-14]. Although some ferromagnetic materials have isotropic properties, they become magnetically anisotropic when a magnetic field is applied [8, 10-12]. When these materials are subjected to an external magnetic field, the magnetization depends on the crystal orientation along the applied field.

1.4.3 Magnetostriction

When a material is magnetized, its dimensions can change. It can elongate or shrink along the direction of the applied field and contracts or expands in the transverse directions. Such change is defined as magnetostriction. The change in length (Δl) is measured parallel to the direction of magnetization [5]. Usually, the magnetostriction constant is a measure of relative change in length ($\Delta l/l$), and it is denoted by $+\lambda_s$ and $-\lambda_s$ [1, 5].

1.5 Properties of Write Pole Materials

The pole material for the writer structure must be magnetically soft so that its magnetization can follow the current input easily. Soft magnetic materials require lower magnetic field intensities to magnetize and demagnetize as compare to hard magnetic materials, therefore, less energy is needed during magnetization. Typical hysteresis loops for both soft and hard magnetic materials are shown in Figure 3 [6]. At the same time, the write pole material requires high saturation magnetic flux density (B_{sat}) to overcome or switch the high coercivity (H_c) of the moving media. In general, hard magnetic materials are used to retain the information written on them after they have passed through the recording head. The pole tip reaches saturation during writing, and if the B_{sat}

is not large enough, the yoke will not have sufficient flux to reach the gap to generate a high enough field to switch the media. In other words, an ideal write pole magnetic material must have low H_c , high B_{sat} , and well-defined anisotropy (H_k), the field strength that is critical for switching from one state to another in a few nano-seconds.

Until recently, the most commonly used write pole soft magnetic material was permalloy ($Ni_{80}Fe_{20}$), which has $B_{sat} = 1.0$ Tesla (T) and $H_c < 0.1$ Oersteds [1]. With the increasing coercivity of the recording media, a soft write pole material with higher B_{sat} is required [1]. Currently, the write heads with B_{sat} greater than 2.0 T and zero magnetoresistance (λ) are necessary to meet demand of increasing areal density recording. The H_k value should be in the order of 10 - 20 Oe and $H_c < 10$ Oe depending on saturation magnetization [1]. Also, resistivity higher than 20 $\mu\Omega$ -cm and internal stress lower than 200 mega-Pascal (MPa) is desirable [1]. These properties are critical for high frequency magnetic recording.

Currently, many researchers are exploring other possible alloys for write pole applications. Among ferromagnetic alloys, ternary alloys of CoNiFe are probably the most promising materials due to their excellent magnetic and physical properties such as superior corrosion resistance, low coercivity, and high resistivity. A high B_{sat} (2.1 T), low H_c (1.2 Oe), and high ρ (21 $\mu\Omega$ -cm) can be obtained for plated CoNiFe film according to Osaka T. [8]

1.6 Ferromagnetic Alloy Electrodeposition

There are several methods to deposit soft ferromagnetic thin film alloys such as high vacuum sputtering, chemical vapor deposition, evaporation, electroless deposition,

and electroplating deposition. In the recording head industry, soft thin magnetic films are fabricated through electroplating because it offers several advantages over other deposition processes. First, electroplating is inexpensive and higher deposition rates can be obtained as compared to dry processes in a manufacturing base [1]. Also, it allows deposition through mask where smaller features with high aspect ratio such as the pole tips in the read/write heads are easy to create [1]. Lastly, through mask electroplating methods eliminate the complicated lift-off patterning processes that are required in dry deposition techniques.

A basic electroplating process requires an electrochemical cell that consists of two electrodes, cathode, and anode, connected to a power supply and immersed in a conductive electrolyte. The metal ions in the electrolyte are electrochemically reduced and deposit as a metallic film on the surface of the cathode (Figure 5). The major factors that may affect the film properties in an electroplating process are: bath temperature, pH of the bath, current density used during deposition, bath composition, and electrolyte mixing conditions [15].

Figure 5. Schematic of electroplating process.

In typical head manufacturing processes, the write pole material is electroplated onto 1000Å - 2000Å of a sputtered NiFe or CoNiFe seed layer [1]. The electroplated material must be deposited onto the wafer surface with tight controlled thickness and composition uniformity to maintain their adequate magnetic properties [1, 18, 19]. It is well known that the magnetic properties of binary and ternary alloys of cobalt, nickel, and iron are strongly dependent on their composition [7, 8].

A phenomenon known as “anomalous codeposition,” where the more noble element becomes harder to electrodeposit, makes the electroplating process of these elements harder to understand [1]. According to several researchers, this behavior is closely related to the hydrogen evolution reaction on the cathode [1, 19, 21, 26]. Such reaction promotes the formation of ferrous hydroxide on the cathode surface, inhibits the nickel deposit, and at the same time allows the deposition of iron.

In general, the kinetics of deposition is sensitive to the presence of organic additives in the plating bath. Studies on the electrodeposition of binary and ternary alloys of Co, Ni, and Fe systems have been conducted in the presence of organic additives to better understand their role on the structure and properties of the electroplated materials [1, 8]. Results so far have yielded materials whose magnetic and electrical properties are superior to the traditional permalloy. Thus, exploring the effect of different additives on the structure and properties of electroplated CoNiFe films will help develop write pole material for new high density recording heads.

2.0 Literature Review

The literature recognizes various aspects of the electrodeposition of ferromagnetic materials such as bath compositions, electrodeposition conditions, and organic additives. It also includes the effects on the physical and magnetic properties of the electrodeposited thin films under the various aspects. In this part of the review, experimental results obtained from various researchers with the iron, nickel, and/or cobalt plating systems are to be described.

2.1 Aspects of Electrochemical Deposition of Ferromagnetic Materials

Soft magnetic materials with higher magnetic flux density B_{sat} are essential for the write poles with respect to the traditional permalloy ($B_{\text{sat}} = 1.0 \text{ T}$) [1]. For decades, many researchers have been largely studied in binary and ternary Co, Ni, and Fe systems and have shown drastic improvements in the properties of the electroplated materials [1]. Despite these new improvements, more research is still required to meet the challenges of the magnetic head industry.

The mechanical, the electrical, and the magnetic properties of electroplated ferromagnetic alloys depend on the deposition conditions, the alloy composition, the presence of impurities, and the alloy elements [1]. Understanding the exact composition the film structure and how they relate to their properties on the one hand, and to the bath composition and depositing conditions on the other hand is necessary for proper control and use of these materials in manufacturing. Ultimately, this understanding can have a strong effect on the fabrication of magnetic thin film heads to meet the increasing demand in recording density. Provided in Table 1 is a summary of plating bath

compositions and conditions used by several of these researchers [8-14, 16]. This part of the review will describe the effect on magnetic properties and physical properties that are encountered in nickel-iron and cobalt nickel iron electrodeposition.

Table 1. Bath composition and operating condition for electroplated CoNiFe film from various researchers.

Operating Condition		Bath No.	1	2	3	4
		Researchers (Ref. NO.)	Osaka <i>et al.</i> (8)	Liu <i>et al.</i> (12-14)	Okada <i>et al.</i> (16)	Tabakovic <i>et al.</i> (9,10)
		Agitation	Rotating disk electrode			Rotating disk electrode (225 rpm)
		Current Density (mA/cm ²)	3 - 20	5 – 50	6 - 50	3 - 20
		Bath Temperature	Room Temperature	25°C	30°C	23°C
		Bath pH	2.8	2.8 - 3.5	3 - 4	2.8
Bath Composition	Concentration	Saccharine (g/L)	2		0.4	
		Na Lauryl Sulfate (g/L)	0.01			
		NaCl (g/L)			25	
		NH ₄ Cl (g/L)	15			16
		H ₃ BO ₃ (g/L)	24.7	24.7	25	24.7
		FeSO ₄ 7H ₂ O (g/L)	1.4 - 12.5	5.6 - 11.1	7.0 - 33.3	1.4 - 19.5
		NiCl ₂ 6H ₂ O (g/L)			10 - 16.9	
		NiSO ₄ 6H ₂ O (g/L)	52.6	52.6	10 - 16.9	52.6
		CoSO ₄ 7H ₂ O (g/L)	8.4 - 24.6	14.0 - 28.0	16 - 43	16.9

2.1.1 Bath Composition

The bath composition can strongly influence the alloy composition, the structure, and the properties of electroplated CoNiFe alloys. The concentration of metal ions can have significant effects on the electroplated film composition. Small variation of Fe^{+2} in the plating solution will result in a large variation of Fe content in the plated film [17]. Castellani *et al.* reported that with a Ni:Fe ratio of 40:1 in the plating solution will generate a Ni:Fe ratio of 4:1 in the film [17]. Also, a high concentration of Fe^{+2} in the plating bath will favor the formation of Fe^{+3} on the anode surface which may lead to the formation and incorporation of $\text{Fe}(\text{OH})_3$ into the plated film [1, 16, 18-20]. The incorporation of ferric hydroxide is known to degrade the soft magnetic properties of electroplated CoNiFe films [16]. This finding was supported by the results that a higher B_{sat} value was obtain at a low pH than at higher pH. In their study, they show that the use of reducing agents such as ascorbic acid may improve the magnetic properties of electroplated films by suppressing the formation of ferric hydroxide [8, 16, 19, 21]. Other organic additives such as saccharin, ascorbic acid, and dimethyl amine borane, may also affect properties such as the resistivity and the corrosion resistance of electroplated CoNiFe materials [8, 21, 22].

2.1.2 Bath pH

pH is a measure of the acidity or basic in an aqueous solution. When the pH is less than 7.0 in an aqueous solution at 25°C is consider acidic, while those at pH of higher than 7.0 are considered as basic. When the pH is 7.0 at 25°C, it is defined as neutral. The

pH of CoNiFe plating baths is usually maintained between 2.0 – 4.0. At pH of 3.5 or higher, undesirable precipitation of iron hydroxide may occur, and below 2.0, the current efficiency is undesirably low due to hydrogen evolution on the cathode [19]. Hydrogen may evolve according to the reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ [19]. Typically, the pH is tightly controlled in manufacturing process due to its significant effect on current efficiency. Several authors have also demonstrated that the bath pH can also affect the composition of electroplated CoNiFe alloy films. Horkans *et al.* observed that the iron composition (X_{Fe}) of electrodeposited CoNiFe films was lower at a pH of 2.0 than at a pH of 3.0 [27]. In a separate study, Castellain *et al.* and Horkans *et al.* showed that X_{Fe} can reach a minimum value at a pH of 2.0 using a current density of 40 mA/cm² [27, 34].

2.1.3 Effect of Hydrodynamic Conditions

Agitation can have significant effect on the composition and thickness uniformity of electroplated ferromagnetic materials [1]. In most CoNiFe plating solutions, it was observed that both the hydrogen evolution and the deposition of iron can be strongly affected by convective diffusive mass transport. According to Wolf, the iron content X_{Fe} (wt. %) of the film decreases by increasing the agitation rate at low current density and the opposite effect occurs at high current density [26]. Andricacos and co-workers conducted systematic experiments using a rotating disk electrode (RDE) with rotation rates range of 100 – 3600 RPM [24]. They found that the current efficiency was higher at a lower rotation rate. At 3600 RPM, the current efficiency reached a low value of 20% [26]. The RDE is used widely for academic studies and industry research of electrochemical reactions [23, 25]. The RDE is constructed from conductive material

such as stainless steel and platinum imbedded in a rod of insulated material. The electrode is connected to a motor and can rotate at a designated rotation speed. The rotation movement can lead to a well-defined solution flow pattern.

2.1.4 Effect of Current Density

Various investigators have studied the effect of the applied current density on the composition and properties of plated ferromagnetic alloys. As a result, they have developed materials that are adequate for recording head manufacturing. For instance, Horkans et al. attempted to interpret the curve of the X_{Fe} as a function current density (i) [21]. In their study of plating NiFe, they have shown that the X_{Fe} vs. i curve reaches a maximum in both, sulfate based and chloride based plating bath at a pH of 3. For a pH of 2, the curve has a wider interval as shown in Figure 6 [1]. During their investigation, they concluded that X_{Fe} increases as a result of increased plating current density. But it has the opposite effect when after the maximum is reached, thus, demonstrating that the plating current density can be used to control the alloy composition [19, 24].

It is important to note that current density is not the only parameter that affects X_{Fe} . As described previously, the content of Fe^{+2} in the bath and other parameters such as pH and agitation also have significant effect on X_{Fe} . Also, according to Faraday's Law, see Equation 2, the current density can be used to control the plating rate [15].

$$PlatingRate = \frac{m}{t} = \frac{iw \cdot t}{c \cdot F} \quad \text{Equation 2}$$

where iw is the applied current in amps, and t is the plating time in seconds, c is the ionic charge in the solution, and F is the Faraday's constant (96,500 Coulombs/mol e-).

Finally, m is the mass of the plated metal on the cathode surface and has unit of grams

[15]. In general, low plating rate is undesirable because of the increase operating cost due to extended plating time. However, higher plating rate can lead to formation of ferric hydroxide. Additionally, the thickness and uniformity are hard to control for high plating rate process.

Figure 6. Fe composition in film as a function of current density (i) in various solution at A) pH 3; 1: 0.5 M NiSO_4 , 0.01M FeSO_4 ; 2: same as in 1 plus added 0.4 M of boric acid; 3: 0.5M NiCl_2 , 0.01M FeCl_2 ; 4: same as in 3 plus added 0.4M of boric acid. B) pH 2; 5: 0.5 M NiSO_4 , 0.01M FeSO_4 ; 6: same as in 5 plus added 0.4 M of boric acid; 7: 0.5M NiCl_2 , 0.01M FeCl_2 ; 8: same as in 7 plus added 0.4M of boric acid.

2.1.5 Anomalous Codeposition Phenomenon

According to a theory proposed by Dahms *et al.*, for NiFe electroplating, a phenomenon called anomalous codeposition occurs when higher pH is present at the surface of the electrode with respect to the pH of bulk solution [26]. At high pH, hydroxide that forms at the cathode surface codeposits with iron and inhibits the nickel

deposition rate [26]. This phenomenon is called anomalous codeposition. Other authors disagree with Dahms' theory [26]. For instance, surface pH measurements conducted by Deligianni and Romankiw showed that the pH near the cathode surface during the electrodeposition process is below the value where metal hydroxides are expected to precipitate [27].

2.2 Effect of Additives

The electroplating solutions for plating magnetically soft electrodeposited films usually contain organic additives to enhance the properties of the electroplated and make them suitable for write pole materials in magnetic recording heads. Many authors have studied the effects of addition of organic additives in these plating solutions. The most frequently studied additives were sodium saccharin, thiourea, boric acid, and sodium lauryl sulfate [1, 9-14, 16, 21]. It is essential to understand the nature and quantity of these organic additives since they affect the structure, electrical, and magnetic properties of the plated films.

2.2.1 Effect of Additives on Properties and Structure of Electroplated Ferromagnetic Alloys

To be able to write on media with very high coercive force, write head materials with well-defined anisotropy, near zero magnetostriction, and high saturation magnetic flux density are needed. Developing materials that combines these properties is a very challenging task in the magnetic head industry. Manufacturing simplicity, corrosion resistance, and high resistivity to suppress eddy currents are also as important as the magnetic properties of these materials in thin film head manufacturing [9, 10]. Eddy current is when a conductive metal is moved through an applied magnetic field which

induced current which will create interval magnetic field opposing to the change. The objective of this section of the review is to investigate the effect of different organic additives on the properties of electroplated binary and ternary Co, Ni, and Fe thin films.

Binary and ternary Co, Ni, and Fe electroplated systems have been widely studied for decades [1]. There are several factors including the crystallite size, the crystal orientation, and the alloy composition, that can affect the mechanical, the electrical, and the magnetic properties of these plated films. These properties can be affected by the deposition conditions but also by the addition of organic additives. Sulfur, carbon, and oxygen inclusion in electroplated films are almost inevitable [1]. Although both S and O tend to refine the crystallite size and reduce H_c , they also reduce B_{sat} [1]. Generally, stress relievers, brighteners, and levelers such as saccharin are added to the plating solution. As a result, sulfur is always present in the electroplated films. Oxygen is present due to hydrolysis at the cathode. Typically, boric acid is added to the plating bath to prevent pH increase at the surface of cathode but it has an adverse effect on the magnetic properties when added in with excessive amount [1].

In another study by Osaka and co-workers with added diethylenetriamine (DET) in plating solution, an approximate B_{sat} value of 1.9T was reached for electroplated CoNiFe thin films [20]. They also found that there is a desirable increase of resistivity ρ with an increased concentration of DET, but an undesirable increase in H_c was also observed [20]. This is a result of the co-deposition of carbon in the film. In a systematic analysis of the organic additive DET, it was confirmed that the carbon contents gradually increased with an increased of DET concentration [20]. Figures 7A and 7B shows the

dependence of resistivity and carbon content of the plated film on the DET concentration, respectively.

Figure 7. Relation between resistivity, ρ and carbon content in the plated film as a function of diethylenetriamine (DET) concentration.

The corrosion properties of CoNiFe alloy films are important because even if the material has excellent magnetic properties. If it has poor corrosion resistance, it can be impractical for use in the fabrication of write head, one reason is due to the machining of head from wafer level. Tabakovic *et al.* performed corrosion tests to determine the influence of organic additives using electrochemical polarization techniques [9-10]. It was found that films with high sulfur content had the worst corrosion resistance. A similar study was carried out by Osaka and co-workers, they also demonstrated that CoNiFe alloys with low sulfur content had the best corrosion resistance [8, 20, 26].

2.2.2 Effects of Organic Additives on the Magnetic Properties of Electroplated Ferromagnetic Alloys

In the preparation of soft CoNiFe films, common organic additives such as ascorbic acid, saccharin, and sodium lauryl sulfate, are being used in most electroplating solutions. Ohashi *et al.* studied CoNiFe alloys with Co (65 wt %) and Fe (20-27 wt %) content [17]. Magnetically soft films were found in the entire range of composition range. It was found that plated CoNiFe film with FCC + BCC crystal structure have a higher B_{sat} than films of the same composition but with BCC crystal structure [17]. In a recent study, with sulfur-containing additives, such as saccharin or thiourea, the coercivity of CoNiFe films was found to be less than 2.0 Oe but there was some loss in B_{sat} [8-9, 20]. The work of Osaka *et al.* and Liu *et al.* as well as Tabakovic *et al.* shows that there is a substantial decrease in H_c with the addition of thiourea and saccharin, respectively [8-14, 20]. An increase in concentration from 0.005 g/L to 0.06 g/L of thiourea, can produce a drop in coercivity from 42 Oe to 2 Oe [8-10, 20]. As mentioned already, inclusion of sulfur is closely related to a reduced crystallite size which results in the desirable decrease of H_c . Based on Osaka *et al.*'s and Tabakovic *et al.*'s finding as well as Liu *et al.*'s, the crystallite size in the FCC + BCC phase for electroplated CoNiFe is usually smaller than in the single FCC or BCC phase regions [8-10, 20]. Ternary diagrams for H_c values and the crystal structure of the electroplated CoNiFe films are shown in Figures 8 and 9, respectively [10].

Figure 8. Ternary diagram for coercivity (H_c) values of electroplated CoNiFe films [10]. Reproduced by permission of The Electrochemical Society.

Figure 9. Ternary diagram for crystal structures of electroplated CoNiFe films. The samples indicated by arrows A, B, and C have the crystal structures BCC, FCC+BCC, and FCC, respectively [10]. Reproduced by permission of The Electrochemical Society.

In another study, films with $B_{\text{sat}} > 1.8\text{T}$ were obtained with low or no additives present in the plating solution according to Liu *et al.*, but the resulting high tensile stress makes these materials impractical for thin film heads [9-10]. A study conducted by Tabakovic and co-workers have shown that a gradual increase of the concentration of saccharin, known as the sulfur containing stress-reliever, in the plating solution decreased the stress and coercivity [9-10]. Figure 10 shows the effect of the concentration of saccharin on the stress and H_c values in plated CoNiFe films [9-10]

Figure 10. The effect of saccharin (Sacc) concentration in the plating solution on stress and coercivity of electroplated CoNiFe films [9]. Reproduced by permission of The Electrochemical Society.

Studies related to CoFe plated thin films have also been conducted by several researchers. According to Bozorth, a maximum of 2.4T can be reached with CoFe [5]. See Figure 11. Liao and co-workers patented an electrodeposition process to form $\text{Co}_{90}\text{Fe}_{10}$ thin films [35]. The plating solution included the stress reliever saccharin and the surfactant agent sodium lauryl sulfate. An H_c value of 4 Oe was obtained but B_{sat} only reached 1.9T [17, 22, 28-29]. In a separate study conducted by Liao *et al.*, the

magnetic properties of CoFeB electroplated in the presence of dimethyl amine borane (DMAB) and sodium citrate were investigated. In their study, H_c was decreased to 1.0 Oe while other properties remained the same as in previously studied CoFe films [28].

Figure 11. Saturation magnetization flux density B_{sat} of CoNiFe alloys. The optimum region for maximum B_{sat} is approximately between 52 – 72% Fe composition. [5]. (© [2008] IEEE).

Electrodeposited magnetically soft CoNiFe films with B_{sat} 2.2 T have been developed from a sulfate based plating solution with ascorbic acid [19]. The results obtained in this study show that the high saturation material can be fabricated with minimum Fe^{3+} formation [19]. Undesirable Fe^{3+} formation and the local increase in the pH at the cathode surface may result in ferric hydroxide formation which is likely to lower B_{sat} in the electroplated film [19]. The presence of reducing agents such as

ascorbic acid has shown significant contribution in reducing Fe^{3+} formation. Although, the use of ascorbic acid can improve the magnetic properties of CoNiFe films, unfortunately, its presence may results in an unstable plating bath that is not suitable for practical manufacturing use [19].

These examples show that understanding the role of organic additives on the structure and properties of electroplated CoNiFe films will help to develop write pole materials for new high-density recording heads. Among the organic additives investigated, sulfur containing additive sodium saccharin seems to be one of the most promising and is being used universally in the fabrication of magnetic write heads. In this case, researchers have found that the excellent magnetic properties in the plated film are due to the inclusion of sulfur impurities that reduce the crystallite size and dramatically lower the coercivity. Electroplating of high magnetic flux density CoNiFe materials in the presence of organic additives is currently active and promising research area.

3.0 Research Hypothesis/Objective/Justification

3.1 Objective

Literature has indicated that select organic plating additives can be improved the physical and magnetic properties of the plated CoNiFe films. Electrodeposition of cobalt, nickel, and iron alloys with addition of sulfur containing organic additives can lower the coercivity but can also undesirably lower the B_{sat} value. Harbulak and Park patented an electrodeposition process to improve the properties of cobalt, nickel, and iron alloy systems [29]. In their patent, addition of unsaturated cyclosulfone overcame the side effects of ferromagnetic electrodeposition.

The aim of this thesis project is to understand the effect of two plating organic additives, sulfolene and methane sulfinic acid (MSA), on the magnetic and physical properties of the plated CoNiFe films for use as magnetic write head pole material. The plated CoNiFe film composition and thickness were measured by X-ray fluorescence (XRF) and profilometer, respectively. Vibrating sample magnetometer (VSM) was used to characterize the magnetic properties of the films.

3.2 Justification

According to the literature reviewed, sulfur containing additives can help lower the crystallite size of plated CoNiFe films, resulting in improved soft magnetic properties. For instance, Osaka et al. observed that the addition of thiourea and saccharin, both sulfur containing additives, lower the coercivity of CoNiFe plated films [8, 17, 20].

This thesis presents the electrofabrication and characterization of the magnetic and physical properties of plated CoNiFe alloy films with potential application in

magnetic write heads. This thesis is focused on the use of the organic plating additives sulfolene and methane sulfinic acid. The effects of these additives on the soft magnetic properties of electroplated CoNiFe alloy films have also been studied in this research work for different film compositions.

4.0 Experimental

4.1 Experimental Overview

The experimental studies were performed in four phases. Figure 12 shows a flow chart that briefly describes each of the phases. In Phase I, screening experiments were conducted to determine a plating rate to be used in Phases II - IV to obtain a plated film thickness of $1.0\mu\text{m}$ with $\text{XFe} \leq 70\% \text{ wt.}$

In Phase II, the target film composition of up to 70% Fe was achieved for electroplated CoNiFe films by varying the FeSO_4 content in the plating bath. The amount of iron plated on the film was not factor when adding the FeSO_4 in the plating bath since the depletion amount is less than 0.1%. In other words, the amount of metal plated is negligible compared to the amount of iron in solution. Utilizing the current density and bath chemistry determined in Phases I and II, two different levels of sulfolene additive in the plating bath were studied in Phase III. Similar experiments were carried out using methane sulfinic acid in Phase IV. The effect of different concentrations of the selected organic additives on the plating rate and the magnetic properties of electroplated CoNiFe films was investigated.

Figure 12. Flow chart for the studies on the effect of sulfolene and methane sulfinic acid on the magnetic properties of electroplated CoNiFe films.

4.1.1 Phase I: Plating Rate Determination

Using aqueous sulfate based bath with selected organic additives at different plating condition, a screening experiment without additive was performed. The

compositions and conditions of the baths used for alloy electrodeposition are shown in Table 2 and 3, respectively. As mentioned previously, the pH was controlled in order to stabilize the bath chemistry and to maintain a better control of the plated film composition. The pH of the plating bath had to be within the specified range of 2.80 +/- 0.02. The pH was monitored at the beginning of each plating run. The pH meter was calibrated daily to ensure the accuracy of the pH readings.

Table 2. Plating bath chemistry for electrodeposition of CoNiFe films.

Bath Chemistry	Concentration (g/L)
CoSO ₄ ·7H ₂ O	22.5
FeSO ₄ ·7H ₂ O	0 --> 125
NiSO ₄ ·6H ₂ O	26.3
H ₃ BO ₃	25
NH ₄ Cl	16
Saccharin	0.1
Na Lauryl Sulfate	0.01

Table 3. Plating conditions for electrodeposition of CoNiFe films.

Temperature:	Room Temp. (21°C)
pH:	2.8+/-0.02
Rotation Speed of the RDE	1000RPM

The effect of current density on the plating rate and plating efficiency were determined from this experiment. Duplicate samples were plated to verify reproducibility. Based on the screening experiments shown in Table 4, a current density of 5mA/cm² was selected for Phase II - IV experiments.

Table 4. Design of experiment to determine an adequate plating rate to be used in Phases II, III, and IV experiments.

Current Density (mA/cm²)	FeSO₄ (g/L)	# of Samples
3	10	2
3	60	2
6	10	2
6	60	2

4.1.2 Phase II: Baseline Plating without Organic Additives

The bath chemistry and operating conditions used in this phase were listed in Tables 2 and 3, respectively. To study the film properties at different film composition, the ion sulfate concentration without sulfolene and methane sulfinic acid was varied in the plating bath and duplicate samples were plated to check repeatability. Also, each of the samples was etched in the way described in section 4.3, then the film composition and the magnetic properties were measured. The plating time was adjusted to obtain CoNiFe films with an approximate thickness of 1 μm .

4.1.3 Phase III and IV: Plating Experiments with Sulfolene and Methane Sulfinic Acid

The organic additives were selected based on previous studies of sulfur-containing additives that showed a desirable decreased in H_c . In addition to the bath components described in Table 2, the two selected organic additives (sulfolene and methane sulfinic acid) were separately used in concentrations of 0.05 g/L and 0.1 g/L to study their effect on the magnetic properties of the plated CoNiFe films. Based upon previous researches, the typical organic additive concentration ranged from 0.01 to 0.1 g/L. In these two phases of experiments, the bath components NiSO_4 , CoSO_4 , H_3BO_3 ,

Saccharin, and Na lauryl sulfate, were kept constant with the exception of FeSO_4 . Samples were plated while varying the FeSO_4 concentration in the range with increments of 5 g/L starting with a concentration of 5 g/L FeSO_4 until film compositions of up to 70 wt. % Fe was achieved. Also, the plating conditions such as rotational speed, temperature, pH and current density were kept constant. Saccharin is commonly used in manufacturing, this is the reason why, in this research, saccharin is considered as the baseline. The plating time was also adjusted to achieve film thickness of approximately $1\mu\text{m}$.

Illustrated in Figure 13 are the chemical structures of sulfolene (Su) and methane sulfinic acid (MSA).

Figure 13 Chemical structure of A) sulfolene B) methane sulfinic acid.

4.2 Electrochemical Cell

A rotating disk electrode (RDE) from Pine Instrument, shown schematically in Figure 14 was used for the galvanostatic deposition of CoNiFe films. The RDE was coupled to an AFASR rotor controller and powered by an external power supply. The controller provided consistent unidirectional rotation of the electrode. The electrochemical cell consisted of a 1000 mL capacity glass beaker with a large surface area platinum mesh used as a counter electrode and an Ag/AgCl reference electrode. The

working electrodes consisted of 18 mm diameter removable glass disks with cobalt – nickel-iron sputter deposited seed layer on both sides. The electrical contact to the disk electrodes was made through a stainless steel bar inserted into the working electrode Teflon holder. The experiments were performed with an EG&G Princeton Applied Research (PAR) model 283 Galvanostat/Potentiostat at constant applied current density.

During the plating process, the working electrode was rotated at a designated speed. The electrode rotation in this case provided uniform mixing of electrolyte near the working electrode resulting in uniform and well-defined convective-diffusive mass transport during the plating process. Faster rotation rate increases the convective-diffusive transport to the electrode surface.

Figure 14. Schematic of the Rotating Disk Electrode plating system. The system consists of the working electrode (WE), counter electrode (CE), Ag/AgCl reference electrode (RE), and the Princeton Applied Research Galvanostat/Potentiostat (PAR 283)

4.3 Physical and Magnetic Properties Characterization

Cobalt-nickel-iron films with approximate thickness of 1 μm were electrodeposited onto glass substrates sputter-deposited with 1000 angstroms of $\text{Co}_{40}\text{Ni}_5\text{Fe}_{55}$ seed layer that provided electrical conductivity. The samples were rinsed with deionized water and dried with nitrogen gun immediately after plating. Next, a 3/8 inch diameter protective vinyl tape was adhered at the center of the plated samples. Then, the CoNiFe film surrounding the taped area was etched off using a solution that consisted of 10% HCl with a small amount of nitric acid to get a consistently uniform circular plating area. Immediately after etching, the samples were washed with deionized water and dried with an air gun. Finally, the protective tape was carefully peeled off and the thickness, the composition, and the magnetic properties of the plated films were measured. The schematic description of this process is illustrated in Figure 15.

The thickness of the plated samples was measured with a KLA-Tencor P11 profilometer and the film composition was determined with an Omicron XRF instrument. The saturation magnetization (M_s) and the coercivity (H_c) of each sample were measured with a Digital Measurement System (DMS) model 880 Vibrating Sample Magnetometer (VSM). All the metrology tools were calibrated daily with standards of known composition and dimensions to ensure accuracy.

Figure 15. Schematic of the sample preparation. A) Glass substrate deposited with seed layer. B) 3/8" diameter of protective tape adhere at the center of the plated CoNiFe film. C) The unprotected area of the plated CoNiFe film is etched off leaving a 3/8" diameter of magnetic material. D) The protective tape is peeled off before measuring the thickness and magnetic properties.

4.4 Metrology Equipments

4.4.1 Vibrating Sample Magnetometer (VSM)

Vibrating Sample Magnetometers (VSM) are widely used for measuring the magnetic properties of recording head materials. A Digital Measurement System 880 VSM instrument was used in this work for magnetic properties characterization. The

main components of this instrument include a DC power supply, a pair of pick-up coils, a vibrator, and a PC computer for data acquisition and instrument control.

The DMS model 880 is capable of generating a field strength of up to 15,000 Oersteds, which is adequate to partially saturate any high B_{sat} materials [30]. During measurement, the sample is subjected to vibration using a sinusoidal waveform when the magnetic field is applied along the pick-up coils. Then, the induction (M) is measured from the coil output and output into a X-Y recorder to produce a plot of M vs. H [30].

4.4.2 X-Ray Fluorescence (XRF)

The film compositions were measured on an Omicron X-ray fluorescence (XRF) instrument. X-ray fluorescence is a fast and non-destructive method that is widely used in industry for elemental composition analysis of electroplated materials.

The XRF spectrometry method is based on the detection of emitted X-ray radiation from excited atoms under analysis. This technique is based on a two-step process. First, when a primary X-ray excitation source with sufficiently high energy strikes a sample, electrons will be ejected from the inner shell of an atom, creating vacancies that produce an unstable condition [31]. In the second step electrons are transferred from the outer shells to the inner shells restoring a more stable state [31]. This transition is characterized by emission of an X-ray photon whose energy is the difference between the two energy levels. As a result, the photon energy provides the identification of the element and the intensity of the photon emission provides the amount of the element that is present [31].

4.4.3 KLA-Tencor P-11 Profilometer

The thickness of the plated films was measured on a KLA-Tencor P-11 profilometer. In this technique, the substrate with a plated film step is placed on the stage, then a stylus tip follows the substrate-film contour as it advanced laterally [32]. The stylus tip exerts a force normal to the sample surface by using a light beam as a spring [32]. Figure 16 illustrates the operation of the KLA-Tencor profilometer [20]. The stylus moves with respect to the stage from point A towards point C [32]. The film thickness is measured as the height of the film step.

Figure 16. Schematic of the operation of a KLA-Tencor profilometer.

4.4.4 Collected Data for Characterization of Magnetic Properties

For each of the CoNiFe plated samples, the elemental composition of the film was measured using X-ray Fluorescence (XRF). By using the Digital Measurement Systems (DMS) VSM, the coercivity and saturation magnetization of the plated film were directly obtained. Then the saturation magnetic flux (B_{sat}) was calculated using Equation 3.

$$B_{sat} = 4\pi \left[\frac{m_{s, film} - M_{seed} \times (A \times t_s)}{A(t_f - t_s)} \right] \quad \text{Equation 3}$$

Where $m_{s, film}$ is the total magnetic moment of both the plated film and the seed layer, it has a units of emu. m_{seed} is the saturation magnetization of the seed layer used. A is the area of the film used during the VSM measurement. The value t_s is the thickness of the seed layer and has a units of cm. The quantity $m_{s, film}$ is the total magnetic moment of the plated film from which is subtracted the m_s of the seed layer found by multiplying the known $M_{seed} \times$ seed layer volume. Finally, t_f is the total thickness of the plated film plus seed layer. The total thickness, t_f can be obtained from the step height measurement using a profilometer. Both t_s and t_f have units of cm. Table 5 lists the magnetic and physical properties that were measured for the plated CoNiFe films in Phases I through IV of this work.

Table 5. Magnetic and physical properties that were measured for Phases I through IV of the plated CoNiFe films during the research.

Wt. % Fe	Wt.% Ni	t_f(μm)	H_c (Oe)	$m_{s, film}$ (emu)
XRF	XRF	profilometer	VSM	VSM

5.0 Results and Discussions

5.1 Phase I. Plating Rate Determination

Preliminary screening experiments were designed to determine the cathodic current efficiency and appropriate plating parameters to be used in subsequent CoNiFe electrodeposition studies in the presence of selected organic additives. Table 6 presents the results of composition, magnetic properties, and plating rate from the screening experiment at high and low current densities. As discussed earlier in the Literature Review Section, the plating rate significantly decreases as the concentration of FeSO_4 in the bath increases. A nearly 100% increase in the iron content in the films when FeSO_4 in the plating bath increases by 600% suggests non-anomalous codeposition of CoNiFe for the conditions used in these experiments. Considering for instance that 2% Fe^{+2} in the plating bath, can produce a NiFe alloy with 20% Fe due to anomalous codeposition (Hessami and Tobias, [33]). The CoNiFe films plated at lower current density exhibited white haziness and lower plating rate. In contrast, the films plated at higher current density and higher iron content in the plating bath appeared bright metallic with no haziness due to the reduction in the grain size. Generally, it is preferred to have shiny films with no haziness. In addition, films plated in 60g/L of FeSO_4 solution, at a current density of 6 mA/cm^2 have the desirable roughness on the surface and the plating rate dropped significantly as compared to the samples plated at 3 mA/cm^2 from 1.68 to 0.02 micron per hour. Also, the coercivity is lower by more than twice as the films electroplated at 3 mA/cm^2 as compared to 6 mA/cm^2 . Based on these preliminary results, a current density of 5 mA/cm^2 was selected for Phases II – IV experiments.

Table 6. Coercivity, film composition, and plating rate for the screening experiment.

i (mA/cm ²)	FeSO ₄ in Solution (g/L)	Film Compositio n (% Fe)	Film Compositio n (% Ni)	Plating Rate (μm/hr)	Appearance
3	10	30.23	11.79	1.68	White haziness
3	60	66.92	3.12	0.31	Bright Metallic
6	10	33.52	5.06	4.79	Light white haziness
6	60	69.839	2.83	0.02	Bright Metallic

5.2 Phase II. Baseline Experiment

A series of experiments using different concentrations of iron sulfate in the plating bath were performed with the selected current density of 5 mA/cm². The physical and the magnetic properties of the plated samples were explored as a function of iron content in the film. The CoNiFe films were electroplated in a plating bath using the same bath chemistry and plating conditions shown in Tables 2 and 3, respectively.

Presented in Figure 17 is the iron content in the film (solid circles) and the plating rate (solid diamonds) as a function of the amount of FeSO₄ in the plating bath. As expected, the iron content in the plated film increased as the amount of FeSO₄ in the plating bath increased. As mentioned by Castellani, Fe content variation in the plating bath directly translates to the variation in the Fe content of the plated films [18].

Figure 17. Plating rate (solid diamonds) and X_{Fe} (solid circles) as a function of $FeSO_4$ (g/L) in plating solution for Phase II baseline experiments. The plating rate decreases as the amount of $FeSO_4$ increases in the plating bath.

5.3 Phase III. Plating Experiments using Sulfolene (S)

In Phase III, two different concentrations of sulfolene, 0.05 and 0.10 g/L, were studied. For both sulfolene concentrations, the iron sulfate concentration was varied incrementally in the plating bath gradually until the iron content in the film reached 70 wt. %. The film with an iron content of 70% was compared to the physical and magnetic properties of the CoNiFe films plated without organic additive. According to Bozorth, a maximum B_{sat} of 2.4 Tesla can be reached for bulk system without organic additives when the iron content in the CoFe film ranges from 50 to 70 wt. %Fe. Duplicate samples were run for each condition.

The iron content in the film X_{Fe} (wt.%) as a function of $FeSO_4$ (g/L) for Phase III experiments compared with samples plated in the absence of sulfolene is presented in

Figure 18. For samples plated with 0.10 g/L of sulfolene (.) and without this additive ($\blacktriangle$), X_{Fe} gradually increased as the amount of FeSO_4 increased in the plating solution to the desirable 70%. In contrast, for samples plated with 0.05 g/L of sulfolene ($\square$), X_{Fe} gradually increased and reaches a constant value of about 50%Fe when the FeSO_4 content in the bath reaches approximately 95 g/L. Also, at higher FeSO_4 concentration in the plating bath, precipitation was noticed at the bottom of the solution which is an indication that the undesirable transformation of Fe(II) to Fe(III) is occurring. For the investigation of samples plated with 0.10 g/L of sulfolene, the experiment was stopped at about 115 g/L of FeSO_4 when heavy precipitation occurred at the bottom of the solution. The films electroplated at 115g/L of FeSO_4 have a maximum Fe content of approximately 65%.

Figure 18. Iron content in the electroplated CoNiFe films versus the amount of FeSO₄ in the plating solution as a function of additive amounts.

Figures 19 and 20 present the saturation magnetization (B_{sat}) and the coercivity (H_c) of the electroplated CoNiFe films as a function of the iron content, respectively. The films were plated in solutions with concentrations of 0.05 g/L sulfolene (□), 0.10 g/L sulfolene (◊), and without the selected additives (●).

As shown in Figure 20, B_{sat} for all the electroplated films increased as a function of X_{Fe} . This is in agreement with Bozorth's results for CoNiFe equilibrium alloys in this composition range [5]. However, the CoNiFe films plated with the highest sulfolene concentration appears to have higher B_{sat} value for composition range of 45 to 63 wt. %

Fe. Figure 19 shows that in the composition range of 45 to 63 wt. % Fe and 3 – 4 wt. % Ni B_{sat} reaches a maximum value. Higher concentration of sulfolene appears to enhance B_{sat} in the approximate composition range of 40 to 53 wt.% Fe with B_{sat} values as high as 2.3 Tesla. In contrast, maximum B_{sat} values of about 2.2 Tesla is observed for sulfolene concentration of 0.05 g/L that are similar to those in the absence of this organic additive.

Figure 19. B_{sat} versus X_{Fe} for electroplated CoNiFe films with sulfolene and without additives.

Figure 20 shows that the coercivity of electroplated CoNiFe films increases as a function of iron content in the film. However, a local minimum can be observed in the approximate composition range of 45-50 wt.% Fe for CoNiFe films plated with 0.05g/L of sulfolene. Due to the variation in the data, we cannot clearly establish the effect of the sulfolene concentration on the coercivity. But in general, the H_c value is smaller for

CoNiFe films plated with both concentrations of sulfolene than the films plated without this organic additive. It can be seen from Figure 20 that the H_c values for the electroplated CoNiFe films without sulfolene are constantly higher than the CoNiFe films plated with 0.10 or 0.05g/L of sulfolene. Based on research work taken from Osaka et al. and H. Nam et al., low H_c film form in the FCC-BCC region [8, 20]. In fact, it was concluded that the grain size decrease with inclusion of sulfur and FCC-BCC dual face is formed. In our case, although the decrease in H_c may be related to grain size reduction, it is not related to the creation of combined FCC-BCC phases since these high Fe plated materials have a pure BCC crystal structure. Unlike the films describe by Osaka et al. where sulfur inclusion decreased B_{sat} [8, 20], higher concentration of sulfolene in our case, resulted in higher B_{sat} values. Therefore, sulfur inclusion into the plated film may not occur when sulfolene is used.

Figure 20. H_c versus X_{Fe} for electroplated CoNiFe films with sulfolene and without additives.

For magnetic recording heads soft ferromagnetic alloys with high B_{sat} and low coercivity are desirable. Figures 219 and 20 show that plated CoNiFe alloys with iron content of nearly 50 wt.% and nickel content 3 – 10 wt.% exhibit properties that may be useful for magnetic recording heads. Namely, CoNiFe films with B_{sat} of 2.3 T and H_c in the approximate range of 10 to 25 Oe can be obtained when a concentration of 0.1 g/L sulfolene is used. Table 7 summarizes the best magnetic properties for the electroplated CoNiFe films with and without the sulfolene additive.

Table 7. Results of best magnetic properties for electroplated CoNiFe films with sulfolene and no additives.

Additive		X_{Fe}	X_{Ni}	X_{Co}	B_{sat} (T)	H_{cc}(Oe)
None	Average	50.2	4.3	45.6	2.2	29.7
	Sigma	0.6	0.3	0.4	0.1	3.8
0.05g/L Sulfolene	Average	51.6	5.7	42.8	2.1	18.3
	Sigma	0.6	0.1	0.6	0.1	2.8
0.10 g/L Sulfolene	Average	55.9	4.4	39.7	2.3	16.8
	Sigma	6.1	0.9	5.2	0.1	6.8

5.4 Phase IV. Plating Experiments using Methane Sulfinic Acid (MSA)

In Phase IV, concentrations of 0.05 g/L and 0.10 g/L of methane sulfinic acid (MSA) were used in addition to the baseline bath chemistry to explore the effect of this additive on the magnetic properties of electroplated CoNiFe films. The iron content X_{Fe} (wt.%) for samples plated with MSA and in the absence of this additive are presented as a function of $FeSO_4$ in Figure 21. Similar to the previous experiments, the magnetic properties were studied as a function of the iron content in the electroplated CoNiFe films. Figures 22 and 23 present the B_{sat} and H_c values plotted as a function of iron content in the plated film, respectively.

As shown in Figure 21, the X_{Fe} (wt.%) values for samples plated with 0.05 g/L of MSA and samples plated without this additive increase exponentially as the amount of $FeSO_4$ in the plating solution gradually increases. However, for samples plated with 0.10 g/L of MSA, X_{Fe} gradually increases with the increase of $FeSO_4$ in the plating solution

but it reaches a constant value when the total amount of FeSO_4 reaches about 60 g/L in the plating bath. At this film composition X_{Fe} is not sensitive to the bath composition. Similar to Phase III, the plating solution started to precipitate at high FeSO_4 concentration which indicated undesirable transformation of Fe(II) to Fe(III).

Figure 21. Iron content X_{Fe} in the electroplated CoNiFe films versus the amount of FeSO_4 in the plating solution for Phase IV experiments.

Figure 22 shows that B_{sat} increases as a function of the iron content in the electroplated films. The B_{sat} values in this case are similar to the ones obtained in the presence of sulfolene in the same composition range. In this case however, the maximum iron content in the electroplated films was of approximately 50 wt.% Fe. Figure 22 shows that B_{sat} of the electroplated films plated with 0.10 g/L of MSA can be

as high as 2.20 Tesla in the approximate composition range 45 – 48 wt.% Fe and 5 – 6 wt.% Ni. The results indicated that B_{sat} of these samples are comparable to samples plated in the absence of this additive.

Figure 22. B_{sat} versus X_{Fe} in CoNiFe films plated in the presence of methane sulfinic acid.

Figure 23 shows H_c values as a function of X_{Fe} (wt.%) of the electroplated CoNiFe alloy films plated with two different concentrations of MSA and in the absence of this additive. Figure 23 shows that the H_c values for samples plated with both concentration of MSA are shifted and drop corresponding to samples plated without additives. For both concentrations of MSA, in general, the samples have smaller H_c values compared to the samples plated without additives, which is desirable for magnetic recording heads. It was noticed that the films plated with lower $FeSO_4$ concentration (<60

g/L) exhibited white haziness. As the iron content X_{Fe} increases, the white haziness diminished and H_c reached a local minimum at a film composition of approximately 45 wt.% Fe. In studies done by Osaka and Tabakovic, for ternary CoNiFe films, lower H_c values exhibit along the FCC-BCC phase boundary, indicated by arrow B in Figure 11 which is in the low Fe and low Ni content or high Fe and high Ni content. [8-10, 20] As the composition moves away from the FCC-BCC phase boundary, the value of H_c increases. The H_c values obtained in this study are consistent with that of Osaka *et al.*, at low Ni content and high iron content in the plated film, the coercivity is greater than 5.0 Oe as indicated by Osaka and Tabakovic and their team.

As mentioned earlier, the white haziness is presumably due to the large grain size. Andricacos *et al.* and Osaka *et al.* reported that coercivity is a structure sensitive property. When the grain sizes of the plated samples decreases, it can decrease the coercivity to a certain extent [1, 8, 20]. At a certain concentration level of sulfur containing additives such as thiourea, this phenomenon appears to be closely related to the desirable decrease in coercivity. As shown in Figure 24, lower H_c can be obtained with 0.10 g/L of MSA than with 0.05 g/L of MSA in the CoNiFe plating solution.

The results obtained with methane sulfinic acid show that a high B_{sat} (~ 2.20 Tesla) CoNiFe material with soft magnetic properties ($H_c \sim 12$ Oe) can be obtained for an approximate film composition of 45 wt.% Fe. As mentioned previously, maximum saturation magnetization of 2.4 Tesla can be obtained when the iron content is in the approximately range of 50 – 70 wt. %Fe [5]. However, for both additives, sulfolene and MSA, when the amount of $FeSO_4$ in the plating bath reaches about 80 g/L, the iron

content in the electroplated films reaches a maximum of approximately 50 wt.% and becomes insensitive to further FeSO_4 additions. Table 8 summarized the best magnetic properties for CoNiFe films electroplated in the presence of MSA.

Figure 23. H_c versus X_{Fe} in CoNiFe films plated in the presence of methane sulfinic acid.

Table 8. Summary table of best-resulted magnetic properties for CoNiFe alloy films electroplated with MSA.

Additive		X _{Fe}	X _{Ni}	X _{Co}	B _{sat} (T)	H _{ce} (Oe)
None	Average	50.2	4.3	45.6	2.2	29.7
	Sigma	0.6	0.3	0.4	0.1	3.8
0.05g/L MSA	Average	38.9	6.3	54.9	2.0	16.4
	Sigma	6.8	0.4	6.3	0.1	1.4
0.10 g/L MSA	Average	42.1	6.0	52.0	2.1	20.0
	Sigma	4.2	0.1	4.4	0.1	4.0

5.5 Plating Rate and Cathodic Current Efficiency Comparison

From the manufacturing point of view, another factor that it needs to be taken into account is the deposition rate. Higher plating rate and cathodic current efficiency will result in higher throughput, therefore, less cost. Plating efficiency is the ratio of the amount of charge that results in metal deposition to the total supplied charge. Deviations from 100% efficiency are normally due to undesirable evolution of hydrogen during the plating process. The plating efficiency can be calculated using Faraday's Law. [15]

$$Eff = \frac{nFN}{\chi} \times 100\% \quad \text{Equation 4}$$

where *Eff* is plating efficiency in percent, *n* is the oxidation number, *F* is Faraday's constant which is 96500 coulombs/mol e⁻, *N* is the average moles of alloy, and $\chi = iw \bullet t$ is the amount of electrical charge passed through the cell expressed in coulombs (ampere second).

Presented in Figures 24 and 25 are the plating rate as a function of FeSO_4 for 0.05 g/L and 0.10 g/L of Sulfolene and MSA, respectively. For samples plated in the absence of additives and in the presence of both 0.05 g/L of sulfolene and MSA plotted as a function of iron concentration in the plating solution. For samples plated without additives as compared with samples plated with 0.05 g/L of sulfolene and MSA, the plating rate has a steeper drop. Without additives, the plating rate dropped to about 0.35 $\mu\text{m/hr}$ when the amount of FeSO_4 in the bath reached 50 g/L. On the other hand, the deposition rates for samples plated with 0.05 g/L of sulfolene and MSA were of approximately 1.0 and 2.0 $\mu\text{m/hr}$, respectively, for the same FeSO_4 concentration in the plating bath.

Similar trend is observed in Figures 25 for samples plated with 0.10 g/L of sulfolene and MSA as compared to samples plated without these additives. As discussed previously, optimum magnetic properties can be obtained when the iron content in the film is between 45 – 62 wt. %, however, at this composition the plating rate drops to about 1.4 $\mu\text{m/hr}$.

The results in this work show that the plating rate dramatically decreases as the concentration of FeSO_4 in the bath increases in all cases. This undesirable phenomenon however, is reduced in the presence of sulfolene and MSA. These results suggest a complex plating mechanism where the reduction of H^+ on the working electrode is enhanced at high FeSO_4 concentration in the plating bath resulting in significant drop in the plating rate [1].

Figure 24. Plating rate as a function of FeSO₄ in the plating solution for samples electroplated with the absence of additives (solid circles) and with 0.05 g/L of sulfolene (solid diamonds) and MSA (solid squares).

Figure 25. Plating rate as a function of FeSO_4 in the plating solution for samples electroplated with the absence of additives (solid circles) and with 0.10 g/L of sulfolene (solid diamonds) and MSA (solid squares).

6.0 Conclusion

The effect of additives on the physical and magnetic properties of the two selected additives, sulfolene and methane sulfinic acid, for CoNiFe alloy electrodeposition from a sulfate bath onto a RDE has been analyzed. Several interesting conclusion can be drawn from the data collected in these experiments. It shows that both additives can improve the soft magnetic properties of CoNiFe films. The most significant finding is show that CoNiFe alloy films electroplated in the presence of 0.10 g/L of sulfolene can improve soft magnetic properties. Namely, CoNiFe films in the approximate composition range of 40 – 62 wt. % Fe and 3 – 4 wt. % Ni were produced with B_{sat} of 2.3 Tesla and H_c in the range of 10 - 25 Oe using a concentration of 0.10 g/L of sulfolene in the plating bath. Results for samples plated in the presence of MSA showed a lower B_{sat} than in the presence of sulfolene. A summary of the best resulting magnetic properties is listed in Table 9.

The results obtained in this research work show that sulfolene is a promising plating additive that can be used to improve the soft magnetic properties of electroplated CoNiFe films for applications in magnetic recording heads. Although an increase in B_{sat} from 2.2 to 2.3 Tesla for CoNiFe electroplated in the presence of sulfolene may seem like a modest gain, this achievement is of great significance. Consider for instance that the highest reported value of B_{sat} is of about 2.1 Tesla for CoNiFe and 2.4 Tesla for CoFe alloys [5, 8, 20]. Alloys of CoNiFe however, are more desirable than those of CoFe due to their superior corrosion resistance.

A very important advantage of sulfolene is its ability to reduce the coercivity of electroplated CoNiFe films. This is particularly advantageous for applications that require high frequency switching of the magnetic domains in the material such as write poles of magnetic recording heads. Another advantage of sulfolene is that it can promote a higher plating rate and more efficient electrodepositions process as compared to the case where no additives are present in the bath.

In conclusion, the results in this work show the great importance that plating organic additives can have to engineer the magnetic and other desirable properties of electroplated materials.

Table 9. Best resulting magnetic properties for CoNiFe alloy films electroplated with the two selected organic additions and absence of these additives.

Additives	X_{Fe}	X_{Ni}	X_{Co}	B_{sat} (T)	H_{ce} (Oe)
NONE	50.1	4.1	45.8	2.2	32.5
0.10 g/L Sulfolene	61.3	3.7	35.0	2.3	10.5
0.10 g/L MSA	45.5	6.2	48.3	2.2	20.1

7.0 Future Work

In addition to the magnetic properties studied here (B_{sat} and H_c), other magnetic properties of electroplated magnetic alloys such as $H_{c \text{ easy}}$, $H_{c \text{ hard}}$, anisotropy (H_k), and magnetostriction are also crucial in the performance of magnetic write heads. These properties can be studied when the films are magnetically oriented by applying magnetic field during the plating process and will be of great interest in future studies of organic plating additives. Investigation on the corrosion properties of the electroplated films in this work will be extremely crucial for practical application of these. In addition, to learn more about the characteristic of the two organic additives sulfolene and methane sulfinic acid, it would be important to study the sulfur content in the plated film induced by these two additives in comparison to those reported by Osaka *et al.* Of great interest will also be the characterization of the crystal structure and the grain size of electroplated CoNiFe films and their relationship to their soft magnetic properties and appearance. Lastly, it would be interesting to explore the effect of MSA on the properties of electroplated CoNiFe films with composition in the range of 50 - 65 wt.% Fe.

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