Stress control in electrodeposited CoFe films—Experimental study and analytical model

Stanko R. Brankovic, Burhanuddin Kagajwala, Jinnie George, Goran Majkic, Gery Stafford, Paul Ruchhoeft

A B S T R A C T

Work investigating the effect of saccharin as an additive on growth stress and structure of electrodeposited CoFe films is presented. The saccharin concentrations were in the range between 0.1 g L⁻¹ and 1.5 g L⁻¹. The stress measurements are performed in situ during electrodeposition of CoFe films using cantilever-bending method (curvature measurements). The structure of CoFe films was studied by transmission electron microscopy and X-ray diffraction. Results show that growth stress is a decreasing function of saccharin concentration. No appreciable change in composition, grain size, orientation or texture of CoFe films are observed with increasing saccharin content in solution. The growth stress dependence on saccharin concentration is discussed within the framework of analytical model, which directly links the observed stress decrease with the apparent saccharin coverage of the CoFe film surface during the electrodeposition process.

1. Introduction

Recent trends in magnetic recording and Micro-Electro-Mechanical System (MEMS) technologies indicate that electrodeposited Soft High Magnetic Moment (SHMM) films are a material of choice for fabrication of future magnetic devices and nanostructures [1–3]. Current research in this area is driven by need for ultimately soft magnetic films with high magnetic moment, good corrosion resistance and low stress levels [3–5]. The general approach to electrodeposited SHMM films with good properties is to use different additives in formulation of the plating solutions [3,5–7]. The most frequently used one is saccharin and its derivatives. Their common action is expressed through the leveling and brightening of the deposit [3], refinement of the grains [8] and lowering the stress levels in deposit [4,5,9–12].

The stress in electrodeposited soft magnetic films is dependent on many parameters. Very often, the sign of stress (compressive or tensile) is dependent on the final film thickness, nature of the substrate and the film texture [13]. The electrodeposited SHMM films such as CoNiFe, and CoFe express a tensile stress in an “as deposited” state which can alter their magnetic properties [3]. This is particularly important when CoFe films are considered [4,5]. Their magnetic anisotropy energy is a strong function of their magnetoelectric energy and small alterations in the stress level can produce significant change in magnetic anisotropy [1]. Common practice indicates that sulfur bearing additives are effective as stress relieving agents [1,3–5,9]. It is clear that additives do adsorb on the electrode surface during electrodeposition process [14,15] and as such they can modify the thermodynamics of nucleation process and grain boundary formation [9–11,14]. As a result, the grain structure and level of stress in the deposit could be changed. It is also known that additives incorporate into magnetic films in the form of a low surface energy phase such as sulfur related inclusions, molecular fragments or S- and C-containing intermetallic compounds [5,16,17]. As such, they segregate at the grain boundaries affecting their specific energy, or acting as stress relievers during the grain zipping process [3,13]. In addition to these metallurgical effects, the additive role in stress reduction is through the suppression of hydrogen incorporation into magnetic deposit. During electrodeposition, a small amounts of hydrogen get incorporated into deposit and this effect is known to cause significant post-deposition tensile stress evolution [1,4,5]. Additive adsorption effectively inhibits hydrogen incorporation and contributes to lower post-deposition tensile stress levels (aging stress). For
further progress in fabrication of electrodeposited nanostructures, it is necessary that each of these additive-related stress reduction mechanisms is understood in detail. The phenomenological relationship between additive concentration in the solution and resulting stress reduction has to be established if control over the properties of electrodeposited SHMM films is to be claimed on solid scientific ground.

In this paper, we present work investigating the effect of saccharin on growth stress and structure of electrodeposited CoFe films. The stress measurements are performed in situ during electrodeposition of CoFe films using cantilever bending method [13]. Results show that growth stress is a decreasing function of saccharin concentration. The growth stress dependence on saccharin concentration is discussed within the realm of developed analytical model. The model links the observed stress decrease in electrodeposited CoFe films directly to the apparent saccharin coverage during the electrodeposition process.

2. Experimental

The solution design, additive content and conditions during the CoFe film electrodeposition and in situ stress measurements are summarized in Table 1. All solutions in our experiments were made with high-purity chemicals (99.9%, Alfa Easer, Merck) and 18.2 MΩ-cm ultra-pure water (Millipore Direct Q-UV with Barnstead A1007 pre-distillation unit). The background solution contained H2BO3 and NH4Cl as buffers. The metal ions in the solution were obtained by dissolution of appropriate amounts of CoSO4·7H2O and FeSO4·4H2O. The CoFe films were deposited on 210 × 10−6 m thick, 0.05 m × 0.005 m, glass cantilevers (Precision Glass & Optics) having Young’s modulus E = 72.9 × 1010 Pa and Poisson’s ratio ν = 0.208. The glass cantilevers were coated with 5 × 10−9 m thick layer of titanium (Ti) and 100 × 10−9 m thick layer of gold (Au) on one side using electron-beam evaporation.

Our system for in situ stress measurements [18] is based on the cantilever bending method [13] with optical apparatus developed earlier by Stafford et al. [19]. The whole system resided on a vibration-isolating platform. All optical components were mounted on micrometer-driven rotational and translational supports allowing short-distance fine adjustments of the laser beam optical path. The light source was 1.5 mW JDSU 632.8 nm, He–Ne (Red) laser. The laser beam was collimated (spot size 1 mm) allowing use of only part of the beam with maximum intensity in order to improve the signal to noise ratio. The laser beam reflected from the backside of the cantilevers was directed to a position sensitive photo detector, PSPD, (OSI Optoelectronics). The bending of the glass cantilever due to stress evolution in CoFe films was tracked by laser spot displacement along the vertical axis of the PSPD. The geometry of our system allowed a small angle approximation to estimate the curvature of the glass cantilever directly from the laser spot displacement on the PSPD, δPSPD [18,19]. The curvature of the cantilever was calculated as:

\[
\frac{1}{R} = \frac{n_{air}}{2 \times L \times n_{solution} \times D_{PSPD}} \delta_{PSPD}
\]

In respective order, L, nair, n solution, and DPSPD represent the length of the cantilever from the fixture to the place from which the laser beam is reflected, refractive index of air (n air = 1), refractive index of the plating solution (n solution ≈ 1.33), and distance of the cantilever to the PSPD. Stony’s equation [20] was used to calculate force per width (F/w) acting on the cantilever by the CoFe film directly from measured curvature of the glass cantilever, 1/R. For known thickness of the glass cantilever, δj, Young’s modulus of the glass, E, and Poisson’s ratio of the glass, ν, the force per width acting on the cantilever is calculated as [20]

\[
F = \frac{W}{6} \left( \frac{V_5}{1 - V_5} \right) \frac{E \delta_j}{R}
\]

The temporal thickness of the CoFe films (δj) was estimated using following expression:

\[
\delta_j = \int r \, dt
\]

Here the term r represents the CoFe alloy deposition rate (Table 1), which was estimated from charge stripping measurements of the deposited films. In addition, after each experiment, the thickness of the films was verified using focused ion beam (FIB) cross-sectioning. The FIB data and the final thickness estimate from Eq. (3) were found in very good agreement (±3% error). The final results, i.e. the average stress acting on the cross-section of CoFe films during the growth was calculated by dividing F/w data with the corresponding CoFe film thickness:

\[
\sigma_{AVG} = \frac{F}{w \delta_j}
\]

All signal outputs from the PSPD (stress measurements) and from current/potential measurements (potential) were simultaneously acquired using a National Instruments PC board (NI PCI6143 S-Series) integrated with LabView data acquisition software which provided the real time recording and analysis of the experimental data [18].

The electrochemical cell used for stress/electrodeposition/charge-stripping measurements was made out of quartz with 0.002 m wall thickness. It had rectangular shape and 0.125 L volume. This volume ensured that no compositional or temperature change of electrolyte occurred during the measurements. The working electrode – gold coated glass cantilever, was vertically held in the solution from the top by a special holder made out of titanium to provide a good electrical contact. The cantilever holder was built-in as the integral part of the cell cover ensuring the maximum mechanical stability and integrity of the stress measurements. The reference electrode was saturated calomel (SCE), and all potentials are quoted with respect to SCE. The counter electrode was Ni foil with area approximately 20 times larger than the area of the working electrode.

Electrochemical impedance spectroscopy (EIS) measurements were performed using AutoLab PGSTAT12 with frequency response analyzer module. The electrodeposited CoFe films served as the working electrode. The measurements were performed in background solution (25 g L−1 H2BO3 + 16 g L−1 NH4Cl) with two different concentrations of saccharin: 0.12 g L−1 and 1 g L−1. The EIS data were recorded in frequency range between 30 kHz and 1 Hz, and between the −0.8 V and −1.5 V potential limits with step

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Concentration (g L−1)</th>
<th>Process parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO4·4H2O</td>
<td>28</td>
<td>pH = 2.05</td>
</tr>
<tr>
<td>CoSO4·7H2O</td>
<td>15</td>
<td>Current density, j</td>
</tr>
<tr>
<td>H2BO3</td>
<td>25</td>
<td>4 mA cm−2</td>
</tr>
<tr>
<td>NH4Cl</td>
<td>16</td>
<td>Deposition rate</td>
</tr>
<tr>
<td>Saccharin</td>
<td>0.0–1.5</td>
<td>Galvanostatic deposition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Steady-state potential (vs. SCE)</td>
</tr>
</tbody>
</table>

Table 1
Solution design and parameters of electrodeposition process for CoFe films.
of 0.03 V. The EIS data were modeled using Randles’ circuit [21] and the values of double layer capacitance were extracted from the model fit to impedance data. The standard deviation of the fits is presented as an error bar of the double layer capacitance measurements.

The X-ray diffraction (XRD) measurements were performed on Philips’ X’pert PRO MRD system with automated stage and X-ray beam capabilities. Magnetic properties of the electrodeposited CoFe films were characterized using a vibrating sample magnetometer (VSM), model 7300 from Lakeshore instruments. The composition of CoFe films is measured by Energy Dispersive X-ray spectroscopy (EDX) using Hitachi S-4500 scanning electron microscope with EDX detector from Oxford Instruments.

3. Results and discussion

3.1. Saccharin adsorption on CoFe electrode surface

Saccharin has condensed organic molecule with benzene and heterocyclic rings in its structure. Previous reports suggest that saccharin adsorbs on metal surface during the electrodeposition process forming a certain type of condensed phase [7,14,15]. The saccharin molecule has very small dipole moment and it adsorbs on a metal surface in the region near the potential of zero charge (PZC) [22]. The density and the coverage of adsorbed saccharin phase are dependent on the potential of the electrode surface and saccharin concentration in solution [22,23]. Our EIS measurements of the double layer capacitance for CoFe films are shown in Fig. 1. The measurements are performed in 0.4 M H₂BO₃ (25 g L⁻¹) + 0.3 M NH₄Cl (16 g L⁻¹) solution with 0.12 g L⁻¹ and 1 g L⁻¹ concentrations of saccharin, pH 2.05. Considering the high concentration of the electrolyte, one expects that the double layer capacitance should not have significant dependence on electrode potential [24]. However, a pronounced capacitance minimum, centered at the potential of ∼1.33 V vs. CoFe ≈ 5 × 10⁻⁶ F cm⁻², indicates that a saccharin adsorbed phase is present on the CoFe surface [15,22]. The width of the capacitance well (region with the minimum capacitance) is ≈0.1 V for a solution with 0.12 g L⁻¹ of saccharin and increases to ≈0.4 V in solution with 1 g L⁻¹ saccharin concentration. From CDL vs. E data, Fig. 1A, the corresponding saccharin coverage of CoFe electrode, θ, can be calculated using the Frumkin relation [23]:

$$\theta(E) = \frac{C_{DL}(E)}{C_{DL}^{max} - C_{DL}^{min}}$$

(5)

Here, $C_{DL}^{max}$ and $C_{DL}^{min}$ represent the maximum and minimum double layer capacitance of the CoFe surface for a given potential range. The CDL(E) is the capacity of the double layer at the potential for which the saccharin coverage is calculated. From data in Fig. 1A, the θ vs. E dependence is calculated using Eq. (5) for these two solutions, Fig. 1B.

During our in situ stress measurements, the CoFe films were deposited galvanostatically from solutions containing different saccharin concentrations. The electrode rest potential (steady-state potential) in those experiments was −1.1 ± 0.01 V (Fig. 1B dotted line). At this potential (Fig. 1B), the apparent saccharin coverage of CoFe surface was found to be θ ≈ 80% (Cavs = 0.12 g L⁻¹) and θ = 96% (Cavs = 1 g L⁻¹). The results in Fig. 1A and B suggest that choosing different concentrations of saccharin in the solution, one can effectively control the coverage of this additive during the CoFe electrodeposition [22]. The control of saccharin coverage means a direct control of its action as an additive.

3.2. Composition and structure of CoFe films

The compositions of electrodeposited CoFe films from solutions containing different concentrations of saccharin are presented in Fig. 2A. The composition of the CoFe films does not change to an appreciable extent for a wide range of investigated saccharin concentrations. This trend is slightly different than what has been previously reported by Tabakovic et al. [5]. Considering that our films are produced from stagnant electrolyte and with slightly different bath design and deposition parameters, we do not find this discrepancy concerning. The Fe content in CoFe films was found ≈71 at% and Co = 29 at%. The observed variation in Fe and Co atomic composition of individual CoFe films is within the error bar of the EDX measurements (<±2%). Therefore, the CoFe film composition could be considered constant and independent on saccharin concentration. The XRD measurements revealed that all CoFe films have a body-centered cubic (BCC) structure with predominant (1 1 0) texture [4]. This is not surprising since the Fe is a BCC metal and its content in CoFe films is dominant (>50%). We have used the full width at half maximum (FWHM) of the (1 1 0) peak in 2θ scans to calculate the average grain size of CoFe films [25]. These data are shown in Fig. 2B. The error bars in Fig. 2B represent the standard deviations of the Gaussian function fits to the (1 1 0) peaks in the 2θ scans from which the FWHM are determined. The different saccharin concentrations in the solution have no effect on the grain size of CoFe deposit. The estimated grain size from XRD measurements for all films is in the 20 ± 3 × 10⁻⁵ m range. Fig. 2B. Riemer et al. have already reported the same observation for electrodeposited CoFe films with slightly different composition, solution design and process parameters [5]. Our results are not surprising based on the fact that the steady-state potential for CoFe surface during electrodeposition was the same and deposition current/flux was identical for all samples (E = −1.1 ± 0.01 V, j = −4 mA cm⁻², Table 1). Therefore, the key conditions for nucleation and growth were equal for all CoFe films. Thus, the structure of the films was unaffected by different content and coverage of the saccharin. In order to confirm this result, the CoFe films produced from solutions with 0 g L⁻¹, 0.12 g L⁻¹ and 1.5 g L⁻¹ saccharin concentrations were examined by transmission electron microscopy. Representative TEM images are shown in Fig. 2B for illustration purpose. Our analysis of TEM data revealed qualitatively the same result as the XRD data. The average grain sizes in these samples were found the same (d_c ≈ 15–20 nm).

3.3. In situ stress measurements and analytical model

There are various reports in literature about the effect of additive concentration in solution on the level of growth stress in electrodeposited SHMM films. Most of the data are obtained for saccharin as an additive using ex situ wafer curvature measurements [3–5,9,11,12,26]. The observed stress sign is usually positive (tensile) with a decreasing trend for increasing concentration of saccharin [4,5,9,12].

In Fig. 3A, the in situ growth stress data are presented for electrodeposited CoFe films from solutions containing 9 different saccharin concentrations. The average stress acting on the cross-section of the CoFe films (%) during thickness evolution is tensile, except for the very initial region (δ ≤ 0.03 × 10⁻⁶ m). In this region the compressive stress is observed due to the CoFe films nucleation on Au seed [13]. As expected, the CoFe film electrodeposited from saccharin-free solution shows the largest stress level. For all CoFe films, the shape of the stress–thickness curve is very similar. The main difference is the value of the maximum tensile stress. The maximum stress vs. saccharin concentration dependence is shown in Fig. 3B together with the stress data for 0.3 × 10⁻⁶ m film thickness. The difference for these two sets of data is very small. All CoFe films reach the maximum tensile stress at about the same thickness, (δ = 0.08 ± 0.01 μm). After the maximum tensile stress is developed, a little change in stress value is observed as the film thickness increases. This is evident in both Fig. 3A and B. This type of stress–thickness behavior is characteristic for low
Fig. 1. (A) Double layer capacitance vs. CoFe electrode potential for two different saccharin concentration in solution. (B) Calculated saccharin coverage vs. electrode potential. Data in (B) calculated using Eq. (5) and data in (A). The line indicates potential of CoFe surface during electrodeposition process (steady-state potential).

Fig. 2. (A) at% of Co and Fe in CoFe films as a function of saccharin concentration in solution. (B) The average grain size of CoFe films electrodeposited from solutions with different saccharin concentrations. The data in (B) obtained from FWHM measurements of (1 1 0) peak from 2θ XRD scan. The inset shows representative TEM images of CoFe films electrodeposited from solution containing 0, 0.12 and 1.5 g L⁻¹ of saccharin.

Surface adatom mobility metals (type I) [27] and it is expected for our alloy system. At room temperature both, Fe and Co, have low surface diffusivity [28]. Along with this argument, it should be noted that Fe²⁺ and Co²⁺ are reduced to the metallic state through the formation of intermediate hydroxides (hydroxi-ions) adsorbed on the growing CoFe surface [3]. For relatively large deposition rate in our experiments ((35 ± 2) × 10⁻⁹ m min⁻¹) it is likely that arriving Fe and Co adatoms on the surface immediately nucleate or attach to already existing nuclei or defects rather than continuing to diffuse over the surface and incorporate into the grain boundaries.

For low surface mobility metals [27], the maximum tensile stress is set during the grain coalescence stage as a result of the so called grain zipping process of the grain boundary formation [29–33].

Fig. 3. (A) Stress–thickness curves during in situ CoFe film stress measurements. (B) The maximum of the average stress in CoFe films (circles) and the average stress at 0.3-μm thickness (squares) as function of saccharin concentration in solution. The solid line is the model fit, Eq. (14), to experimental data (circles).
The value of the maximum tensile stress due to grain boundary formation of hemispherical shaped CoFe grains is evaluated as

\[
\sigma_{\text{avr}, \text{CoFe}}^{\text{max}} = 8 \frac{\Delta \gamma_{\text{CoFe}}}{d_c}
\]  

(6)

The \(d_c\) represents the average diameter of the grains while the term \(\Delta \gamma_{\text{CoFe}}\) is the driving force for the grain zipping process. It represents positive difference between the surface energy of impinging CoFe grains, \(\gamma_{\text{CoFe}}^S\), and 1/2 of the energy of newly formed grain boundary, \(\gamma_{\text{CoFe}}^{\text{GB}}\), \((1/2)\gamma_{\text{CoFe}}^{\text{GB}}\). For CoFe film electrodeposited from solution without saccharin, the observed \(\sigma_{\text{avr}, \text{CoFe}}^{\text{max}} = 450 \times 10^6 \text{Pa}\). Fig. 3B. Knowing that \(d_c\) is \(\sim 20 \times 10^{-9} \text{m}\), Fig. 2B, Eq. (6) yields the value for \(\Delta \gamma_{\text{CoFe}}\) to be \(1.125 \text{J} \cdot \text{m}^{-2}\). The literature data (vacuum experiments) suggest that \(\gamma_{\text{CoFe}}^S \approx 2.48 \text{J} \cdot \text{m}^{-2}\) [34]. Considering that our work refers to the CoFe surface in contact with the electrolyte we can take the value of \(2.48 \text{J} \cdot \text{m}^{-2}\) to be an upper limit for the surface energy of CoFe films in contact with electrolyte, \(\gamma_{\text{CoFe}}^S\). The upper limit for \(1/2 \gamma_{\text{CoFe}}^{\text{GB}}\) of CoFe film electrodeposited without saccharin is then calculated as \(1.36 \text{J} \cdot \text{m}^{-2}\). The values, \(\Delta \gamma_{\text{CoFe}}\) and \(1/2 \gamma_{\text{CoFe}}^{\text{GB}}\) from our experimental data and theoretical framework of Eq. (6) are realistic, and they fall within the physically meaningful range. This suggests that our in situ stress measurement system is reliable all approximations in the cantilever curvature evaluation are physically correct.

The saccharin addition to the plating solution significantly lowers the maximum tensile stress in CoFe films, Fig. 3A. The effect is proportional to the amount of saccharin in the solution. For example, the CoFe films electrodeposited from 0.03 g L\(^{-1}\) and 1.5 g L\(^{-1}\) saccharin solutions exhibit a 1.5 and 9 times stress reduction as compared to the CoFe films electrodeposited from saccharin-free solution. The very similar shape of \(\sigma_{\text{avr}}\) vs. \(\delta_f\) dependence for all films indicates no fundamental change in the origin of tensile stress generation with the introduction and increase of the saccharin concentration. The fact that \(d_c\) is measured to be the same for all CoFe films \((\sim 20 \times 10^{-9} \text{m})\) suggests that saccharin’s role in lowering stress in the CoFe films is in reduction of the driving force for grain zipping process, Eq. (6). This can be understood on the premise of saccharin adsorption phenomenon. The saccharin molecules which are adsorbed on the growing CoFe film surface modify its surface energy, and after grain zipping, its grain boundary energy.

Fig. 4A. The value of the maximum tensile stress due to grain boundary formation of hemispherical shaped CoFe grains is evaluated as

\[
\sigma_{\text{avr}, \text{CoFe}}^{\text{max}} = 8 \frac{\Delta \gamma_{\text{CoFe}}}{d_c}
\]  

(6)

Obviously, the extent of this effect is dependent on the coverage of adsorbed saccharin phase, \(\theta\) (Fig. 4B). We can model the surface energy of CoFe grains with adsorbed saccharin phase of an arbitrary coverage, \(\gamma_{\text{Sac/CoFe}}^S\), as the linear combination between the surface energy of CoFe grains without adsorbed saccharin phase \(\gamma_{\text{CoFe}}^S\) and surface energy of CoFe grains with the maximum saccharin coverage, \(\gamma_{\text{Sac/CoFe}}^S(1)\), viz.

\[
\gamma_{\text{Sac/CoFe}}^S = \theta \cdot \gamma_{\text{Sac/CoFe}}^S + (1 - \theta) \cdot \gamma_{\text{CoFe}}^S
\]  

(7)

Using the same analogy, the grain boundary energy of grain boundaries formed after zipping process of the grains with an arbitrary saccharin coverage \(\gamma_{\text{Sac/CoFe}}^{\text{GB}}\) can be expressed as

\[
\gamma_{\text{Sac/CoFe}}^{\text{GB}} = \theta \cdot \gamma_{\text{Sac/CoFe}}^{\text{GB}} + (1 - \theta) \cdot \gamma_{\text{CoFe}}^{\text{GB}}
\]  

(8)

Here, the term \(\gamma_{\text{Sac/CoFe}}^S\) represents the energy of the grain boundary formed by zipping of the two CoFe grain surfaces with the maximum saccharin coverage \((\theta = 1)\). Now, we can define the driving force for the zipping process of the CoFe grains (Fig. 4B) with adsorbed saccharin phase having an arbitrary coverage \(\theta\) as

\[
\Delta \gamma(\theta) = \gamma(\theta)^S_{\text{Sac/CoFe}} - \gamma(\theta)^S_{\text{CoFe}} - \frac{1}{2} \gamma(\theta)^{\text{GB}}_{\text{Sac/CoFe}}
\]  

(9)

Substituting Eqs. (7) and (8) into Eq. (9) yields a more transparent expression for \(\Delta \gamma(\theta)\):

\[
\Delta \gamma(\theta) = \Delta \gamma_{\text{CoFe}} - \theta \cdot (\Delta \gamma_{\text{CoFe}} - \Delta \gamma_{\text{Sac/CoFe}})
\]  

(10)

Here, the term \(\Delta \gamma_{\text{Sac/CoFe}}\) represents the driving force for grain zipping process where the saccharine coverage of the grain surface is maximum \((\theta = 1)\). The driving force for the grain zipping process with adsorbed saccharin phase is thus a strong function of saccharin coverage. Using the form of Eq. (6) we can now define the maximum tensile stress developed in electrodeposited CoFe films with an arbitrary coverage of adsorbed saccharin phase as

\[
\sigma_{\text{avr, CoFe}}^{\text{max}}(\theta) = 8 \frac{\Delta \gamma(\theta)}{d_c}
\]  

(11)

Combining Eqs. (6)–(10) and (11) and defining the new term \(\Delta \gamma = \Delta \gamma_{\text{CoFe}} - \Delta \gamma_{\text{Sac/CoFe}}\), the final form of the analytical model for...
maximum tensile stress in electrodeposited CoFe films is presented as
\[
\sigma_{\text{AVRG}}(\theta) = \sigma_{\text{AVRG,CoFe}} - 8 \frac{\Delta \gamma^*}{d} \cdot \theta
\]  
(12)

The physical meaning of the \( \Delta \gamma^* \) term is the difference in driving force for grain zipping between the grains with clean “saccharin-free” surface and grains with maximum coverage of adsorbed saccharin phase, \( \theta = 1 \). The \( \sigma_{\text{AVRG,CoFe}} \) is the maximum tensile stress in CoFe films electrodeposited from the saccharin-free solution. It is defined by Eq. (6) and it can be measured experimentally, Fig. 3. It is evident that the second term on the right side of Eq. (12) represents the reduction of the stress level due to the saccharin adsorbed phase on the CoFe surface. It is the direct function of saccharin coverage.

For practical purpose, it is convenient to express the saccharin coverage on the CoFe surface in terms of its concentration in the solution. Earlier work [16,17] has shown that saccharin adsorption on CoFe surface can be represented well by the Langmuir adsorption formalism:
\[
\theta = \frac{B \cdot c_{\text{Sac}}}{1 + B \cdot c_{\text{Sac}}}
\]  
(13)

In the above expression \( B \) is the equilibrium adsorption constant while \( c_{\text{Sac}} \) is the concentration of saccharin. Substituting Eq. (13) into Eq. (12) yields
\[
\sigma_{\text{AVRG}}(c_{\text{Sac}}) = \sigma_{\text{AVRG,CoFe}} - 8 \frac{\Delta \gamma^*}{d} \cdot \frac{B \cdot c_{\text{Sac}}}{1 + B \cdot c_{\text{Sac}}}
\]  
(14)

The values of \( d \) and \( \sigma_{\text{AVRG}} \) are known (Figs. 2 and 3) while the parameters \( B \) and \( \Delta \gamma^* \) are determined from the model fit to the \( \sigma_{\text{AVRG}} \) vs. \( c_{\text{Sac}} \) data, Fig. 3B. From the fit we determined the values of \( B = 20.5 \pm 0.5 \text{L}^{-1} \) and \( \Delta \gamma^* = 1.0 \pm 0.1 \text{m}^{-2} \). The analytical model formulated by Eq. (14) represents the \( \sigma_{\text{AVRG}} \) vs. \( c_{\text{Sac}} \) experimental trend well. The extracted value of the term \( B \) could be used to verify validity of the Langmuir adsorption formalism (Eq. (13)) for our modeling consideration. For \( c_{\text{Sac}} = 1 \text{g L}^{-1} \) and \( B = 20.5 \pm 0.5 \text{L}^{-1} \) we calculate that the expected saccharin coverage during CoFe film growth is \( \theta = 0.95 \pm 0.01 \). Previously, discussing our EIS measurements of \( c_{\text{Dk}} \) in Fig. 1B, we have determined that saccharin coverage on the CoFe surface during electrodeposition of CoFe films is \( \theta = 0.96 \) (at \( \varepsilon = -1.1 \text{V} \)). The concurrence between EIS data and estimate of Eq. (13) for \( B = 20.5 \pm 0.5 \text{L}^{-1} \) is obtained for 0.12 g L\(^{-1}\) saccharin concentration as well. The remarkably good agreement between EIS measurements of \( \theta \) and calculations using Eq. (13) supports use of the Langmuir adsorption formalism for interpretation of the saccharin adsorption process during electrodeposition of CoFe films.

The obtained value of \( \Delta \gamma^* (1.0 \pm 0.1 \text{m}^{-2}) \) from the model fit to the experimental data is positive and smaller than the value of \( \Delta \gamma^* \text{CoFe} (1.125 \pm 0.1 \text{m}^{-2}) \). This implies that \( \Delta \gamma^* \text{Sac/CoFe} < \Delta \gamma^* \text{CoFe} \) and \( \Delta \gamma^* \text{Sac/CoFe} = 0.125 \pm 0.1 \text{m}^{-2} \). The obtained \( \Delta \gamma^* \text{Sac/CoFe} < \Delta \gamma^* \text{CoFe} \) inequality supports our initial assumptions and physical picture on which we based our modeling approach. The adsorbed saccharin additive significantly lowers the driving force for grain zipping process. In fact, it is clear that stress reduction in electrodeposited CoFe films is due to saccharin adsorption on CoFe surface. The physical origin of this effect can be explained as follows. The CoFe surface with adsorbed saccharin molecules is likely to have surface bonds saturated by adsorption process effectively reducing the CoFe surface energy. In contrast, the grain boundaries that are formed by zipping of the CoFe grains/surfaces covered with adsorbed saccharin phase are likely to have more defects; less atom-atom coordination and lower atom packing density. These grain boundaries have higher grain boundary energy as compared to the grain boundaries formed during zipping process of “clean” CoFe surfaces. Therefore, saccharin’s impact on stress reduction in electrodeposited CoFe films is, indeed, thermodynamic in nature.

![Fig. 5. Coercivity dependence on growth stress of \( 0.3 \times 10^6 \text{m}^{-1} \) thick CoFe films. The solid line is to guide an eye. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)](image)

3.4. Stress vs. coercivity of CoFe films

The CoFe films have a relatively large value of magnetostriction [35]. Because of that, the high levels of intrinsic stress developed during the growth of CoFe films can substantially alter their magnetic anisotropy. The CoFe films with high stress levels very often do not exhibit low coercivity which limits their application for magnetic device fabrication [1]. In order to assess the effect of growth stress in CoFe films on their coercivity, the coercivity measurements were performed on 9 CoFe films electrodeposited from solution containing different saccharin concentrations. All CoFe films had the same thickness (\( d_\text{film} = 0.3 \times 10^{-6} \text{m} \) and their in-plane \( M-H \) loops were obtained by VSM to determine their coercivity. These results are correlated with measured stress levels in CoFe films obtained from cantilever bending measurements. The results are presented in Fig. 5. As expected, the largest coercivity value was measured for the sample with correspondingly the highest level of stress. This sample was electrodeposited with saccharin-free solution, and serves as reference against which the other samples were compared (\( \sigma_{\text{AVRG}} = 420 \times 10^6 \text{Pa} \), \( H_\text{c} = 110 \text{Oe} \)). As the saccharin concentration is increased, the \( \sigma_{\text{AVRG}} \) of CoFe films have gradually decreased to 130 \( \times 10^6 \text{Pa} \) having reduced value of \( H_\text{c} \). The \( H_\text{c} \) vs. \( \sigma_{\text{AVRG}} \) relation in this range of the data represents a linear trend (red line, Fig. 5). The observed trend is expected. The reducing stress levels in the CoFe films result in reduced contribution of magnetoelastic anisotropy energy to the overall anisotropy energy of the CoFe films and the decrease in coercivity. However, for CoFe films with stress level \( \sigma_{\text{AVRG}} \leq 130 \times 10^6 \text{Pa} \) an increase in \( H_\text{c} \) values is observed. Previous work of Riemer et al. and George et al. have reported results where the increasing concentration of saccharine leads to increase of the CoFe films coercivity after certain threshold value of saccharine concentration is exceeded [5,17]. Considering that the growth stress in CoFe films is a decreasing function of saccharine concentration (Fig. 3) the \( H_\text{c} \) vs. \( \sigma_{\text{AVRG}} \) trend in Fig. 5 is not surprising.

The increase in \( H_\text{c} \) with further decrease of \( \sigma_{\text{AVRG}} \) below 130 \( \times 10^6 \text{Pa} \) cannot be explained using stress induced anisotropy change arguments. Perhaps, the increasing \( H_\text{c} \) with decreasing \( \sigma_{\text{AVRG}} \) can be explained by more detailed consideration of the saccharin incorporation phenomenon [4,5,16,17]. The magnetic decoupling of the CoFe grains due to saccharin related inclusion precipitation at the grain boundaries has an antagonistic effect on
the coercivity of CoFe films. The two seemingly opposite effects of saccharin on coercivity of CoFe films could result in the observed minimum in $H_c$ vs. $\sigma_{AVRG}$ dependence, i.e. an optimum saccharin concentration producing the CoFe films with the lowest coercivity values, [5,7]. At this point, more work is necessary to understand the entire $H_c$ vs. $\sigma_{AVRG}$ relation and to develop its accurate phenomenological description.

4. Conclusions

The effect of saccharin as a stress reducing additive in electrodeposition process of CoFe films was found to be thermodynamic in nature. The saccharin adsorption on the growing CoFe surface during electrodeposition effectively changes the driving force for the CoFe grain zipping process and consequently it changes the maximum level of stress in CoFe films. The control of the CoFe stress levels is achieved by effective control of saccharin coverage of the CoFe surface. This can be realized either by control of the deposition potential, i.e. potential for saccharin adsorption, or through the control of the saccharin concentration in solution. The latter approach is explored in detail. The analytical model describing the maximum stress level in CoFe films as a function of saccharin concentration is developed (Eqs. (12) and (14)) and used to analyze our experimental data. The model is mathematically applicable to other magnetic films–saccharin systems where the growth stress vs. saccharin concentration dependence exhibits a decreasing trend, [9,12]. The Langmuir adsorption model is confirmed to be a very good representation of the saccharin adsorption on CoFe surface during electrodeposition process. This finding should be of general importance for modeling of saccharin adsorption during electrodeposition of other magnetic films [3,7,15–17].

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References