Film Stress and Magnetic Properties of Nickel, Cobalt, Iron and Iron-Cobalt Alloy Electrodeposits

*by S. Kelcher, D-Y. Park, B-Y. Yoo and N.V. Myung**

Nano- / Micro-ElectroMechanical Systems (NEMS/MEMS), including microactuators, sensors, micromotors and frictionless microgears use magnetic materials, because electromagnetically-actuated NEMS/MEMS are more stable for high force and large actuation gap applications. In addition to NEMS/MEMS, there is also great interest in fabrication of nanostructured magnetic materials (e.g., multilayers, nanowires, nanotubes, nanorods and nanoparticles) to apply in nanodevices, including nanoelectronics, spintronics, drug delivery and bio-separation. In order to integrate magnetic materials to devices, properties (e.g., magnetic, mechanical and electric properties, film stress and corrosion resistance) and deposition processes (e.g., operating temperature, pH) must be "tailored". In particular, good magnetic properties with minimum film stress are essential for magnetic materials for successful integration to magnetic-NEMS/MEMS. In the present studies, various low-stress iron group metals and iron-cobalt alloy thin films were developed. The effect of deposition parameters on film compositions, surface morphology, magnetic properties and film stress of electrodeposits were investigated using scanning electron microscopy (SEM), the flexible strip method and vibrating sample magnetometry (VSM). In general, low stress iron group metals and iron-cobalt alloys were electrodeposited by applying low current density and high operating temperature in an additive-free acidic chloride bath. Magnetic properties including coercivity and squareness were strongly influenced by film stress.

Nuts & Bolts: What This Paper Means to You

This work is a part of AESF Research Project #114, which deals with one of AESF's emerging technology areas, MEMS, or micro-electromechanical systems technology. Here we're making microsensors, micromotors and frictionless microgears, and the focus is on plated magnetic deposits, including iron, nickel, cobalt and iron-cobalt alloys. The work explores the conditions necessary to make low-stress films with the best magnetic properties from an additive-free chloride bath.

The ever-increasing demand for faster, smaller and less expensive electronic systems, such as integrated circuits (ICs), microelectromechanical systems (MEMS) and computer hard disk drives (HDDs), have resulted in the development of cost-effective processes. The incredible rate of increasing aerial density of HDDs (100% per year) is a good example of current trends in this technology. In order to meet this strong demand for HDDs, soft magnetic materials with high magnetic saturation (M_S) are under active investigation by several research groups.[1]

In the case of NEMS/MEMS, hard and soft magnetic materials are used in microactuators, sensors, micromotors and frictionless microgears because electromagnetically-actuated NEMS/MEMS are more stable for high force and large gap applications. These are more robust in harsh environments (*e.g.*, dust, humidity) and can be actuated with low cost voltage controllers.[2-7] The shapes, structures and functionality can be very different depending on the application.

Recently, there has been great interest in fabrication of nanostructured magnetic materials (*e.g.*, multilayers, nanowires, nanotubes, nanorods and nanoparticles) to apply in nanodevices including nanoelectronics, spintronics, drug delivery and bio-separation.

Figure 1 shows a few examples of the authors' previous NEMS/MEMS devices with integrated electrodeposited materials. Figures 1(a) and (b) show the microforce-detected nuclear magnetic resonance (μFD-NMR) images to identify chemical compounds for *in-situ* planetary exploration and nickel nanowires for magnetic and biomedical applications (*e.g.*, protein separation), respectively. The nickel nanowires were fabricated by combining a nanotemplate and electrodeposition. Figures 1(c) and (d) show the LIGA** fabricated scroll pump for vacuum

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** *LIGA is an acronym from German words for lithography, electroplating and molding.*

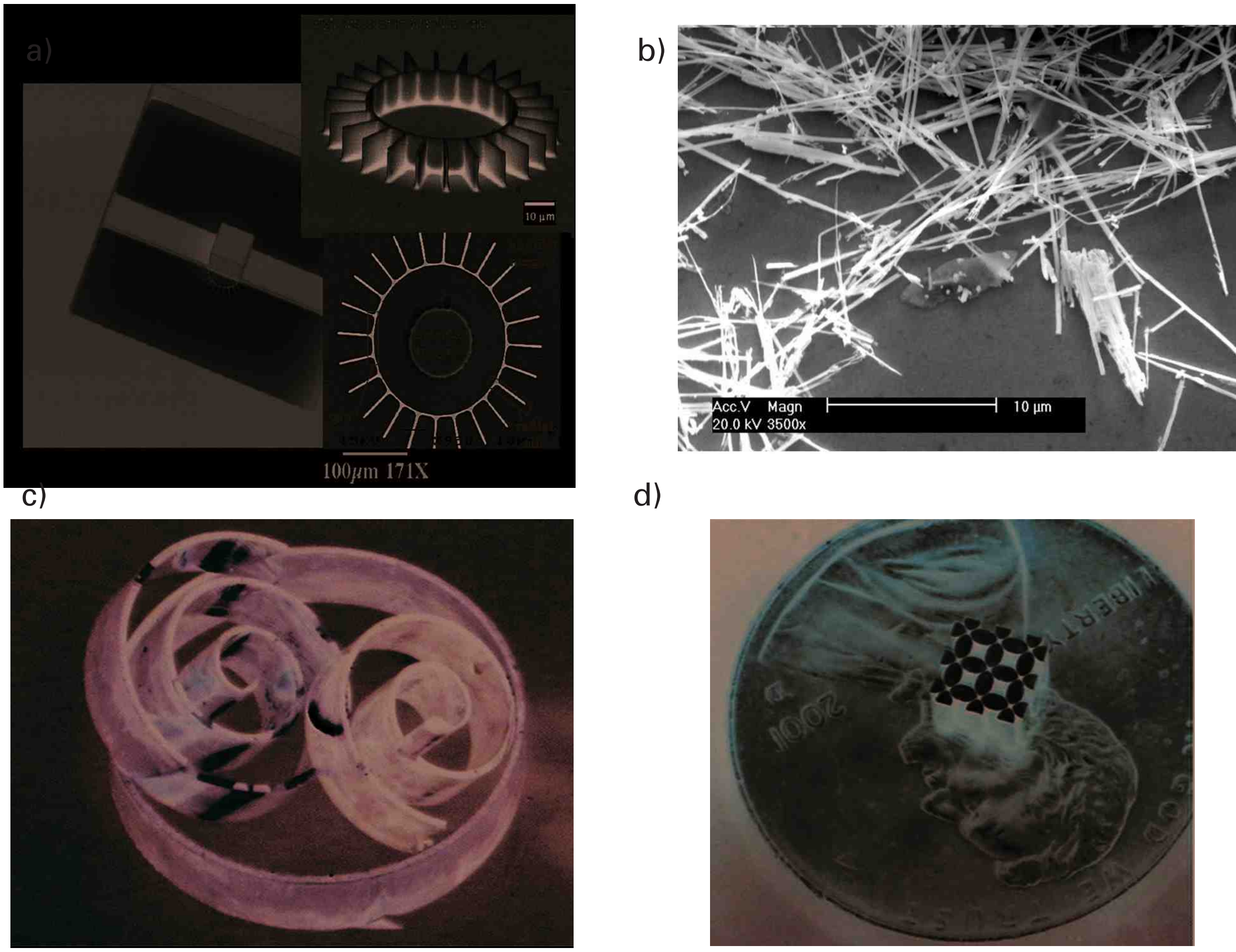

Figure 1—A few examples of electrodeposited MEMS devices and nano-engineered materials: (a) Micro-force detector nuclear magnetic resonance (µFD-NMR); (b) electrodeposited nickel nanowires using template synthesis methods. The diameter and length of the nanowires are approximately 200 nm and 30 µm long; (c) miniature scroll vacuum roughing pump using electroformed nickel from sulfamate baths. The height of the scroll is 3 mm; (d) miniaturized two-dimensional quadrupole mass filter for a micro-GC/MS instrument using electroformed copper from sulfate acid baths. The height of the quadrupole mass filter is 3 mm.

roughing pump and the two-dimensional 3 × 3 quadrupole mass filter, respectively, for a miniaturized gas chromatograph/mass spectrometer (GC/MS). The height of these devices is 3 mm. As shown in the figures, the layer thickness can vary from a few nanometers to a few millimeters depending on the application. In addition, the magnetic materials and deposition processes must be "tailored" to be compatible with other MEMS processing including photo-resistive patterning, vacuum deposition and chemical and physical etching.

There are many different ways to deposit and integrate magnetic materials into devices, including vacuum deposition (*i.e.*, sputtering, e-beam evaporation, chemical vapor deposition, molecular beam epitaxy) and electrochemical deposition (*i.e.*, electro- and electroless deposition). Compared to vacuum processes, electrochemical processing is well-suited to fulfill the requirements of high yield, cost-effective processes.

Electrochemical processes have many advantages, including precisely controlled room temperature operation, low energy requirements, rapid deposition rates, the capability of handling complex geometries, low cost and simple scale-up with easily maintained equipment. In addition, the properties of materials can be "tailored" by controlling solution compositions and deposition parameters. Because of these advantages, electroplated soft magnetic materials such as NiFe and CoNiFe have been widely used as recording head materials by the computer hard drive industry.[8] In the case of magnetic-MEMS/NEMS, the magnetic layers must also have good adhesion, low-stress and corrosion resistance, and be thermally stable with excellent magnetic properties.

Even though there are many studies on electrodeposited iron group metals and alloys, there has been a lack of systematic studies to develop low stress films and to relate magnetic properties with film stress and deposit compositions. In this paper, we investigated and compared the effect of solution compositions and electrodeposition parameters on the nature of the films in terms of their compositions and stress, structure and magnetic properties.

Experimental

Nickel, iron, cobalt and iron-cobalt alloys were electrodeposited from the various plating solutions listed in Table 1. Calcium chloride was used as the supporting electrolyte in order to enhance the current efficiency. Solution pH was maintained between 0.3 and 0.4 with HCl or NaOH. The low pH was essential in order to prevent the oxidation of ferrous ions (Fe^{+2}) to ferric ions (Fe^{+3}). Even at the low solution pH, the current efficiency was in the range of 90 to 100%, and was independent of current density. Dense deposits resulted under these conditions.

Experiments were conducted at different operating temperatures, from 23°C to 70°C (73°F to 158°F) with no stirring. The effect of the Fe^{+2}/Co^{+2} ratio in solution on the deposit composition of iron-cobalt alloy films was investigated by varying the Fe^{+2} and

Table 1
Solution Compositions of Nickel, Cobalt, Iron and Iron-Cobalt Alloys

Solution	Molar Composition
Ni	1.5M $NiCl_2$ + 1.0M $CaCl_2$
Co	1.5M $CoCl_2$ + 1.0M $CaCl_2$
Fe	1.5M $FeCl_2$ + xM $CaCl_2$ (x = 0.0, 0.25, 1.0)
Fe-Co	yM $FeCl_2$ + (1.5-y)M $CoCl_2$ + 1.0M $CaCl_2$ (y = 0.0 to 1.5M)

Co^{+2} concentration while holding the total iron group metal ion content at 1.5M. Copper-beryllium substrates with surface areas of 7.74 cm^2 (1.2 $in.^2$) were used. Iron, cobalt or nickel were used as soluble anodes for the alloy baths. The current density was varied from 2.5 to 60 mA/cm^2 (2.3 to 55.7 A/ft^2) with a fixed total charge of 60 Coulombs. Surface morphology and film compositions were examined using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. Magnetic properties of electrodeposited films were measured with a vibrating sample magnetometer with an applied magnetic field from -1.5 to 1.5 Telsa*** at room temperature. Film stress was measured by a flexible strip method.[9]

Results & discussion

Electrodeposited nickel, cobalt and iron films

Figures 2 and 3 show the dependence of film stress, magnetic properties (*i.e.*, coercivity and squareness) of electrodeposited nickel and cobalt films as a function of current density at a fixed temperature of 70°C (158°F). Film stress in the electrodeposited films is an important factor for MEMS using LIGA processes. In many cases, this film stress could exceed the strength of the film, resulting in cracking, deformation of devices and interfacial failure. As shown in Figs. 2(a) and 3(a), the film stress of electrodeposited nickel and cobalt films increased monotonically as current density increased. For example, electrodeposited nickel and cobalt film stress increased from 70 to 202 MPa (10.2 to 29.3 kpsi) and from 105 to 202 MPa (15.2 to 29.3 kpsi) with an increase in deposition current density from 2.5 to 60 mA/cm^2 (2.3 to 55.7 A/ft^2), respectively.

*** *A Telsa (T) is a unit of magnetic induction. One Telsa equals one Newton-Meter/Ampere (0.74 lbf-ft/A).*

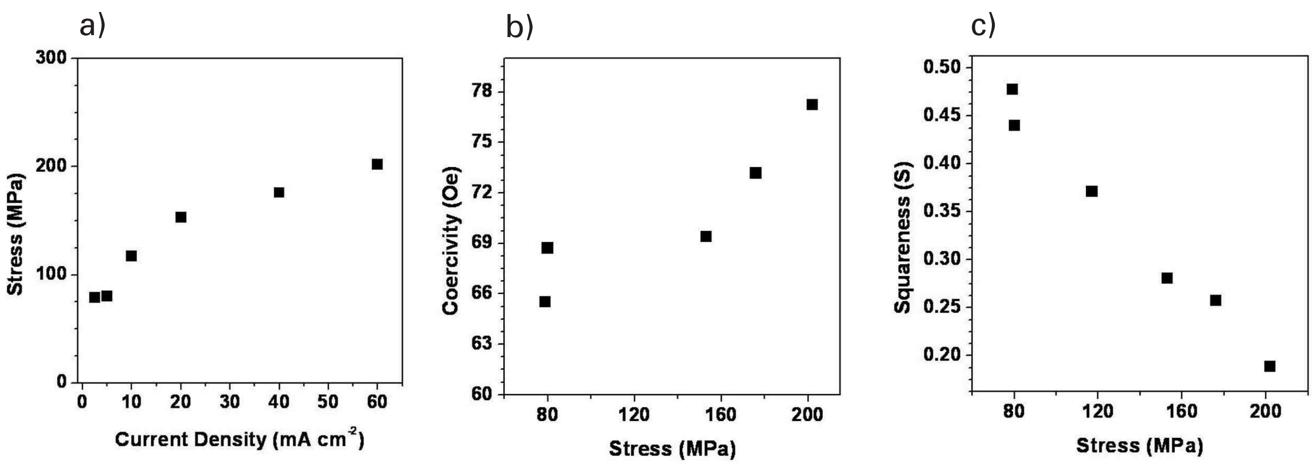

Figure 2—(a) Residual stress, (b) coercivity and (c) squareness [remanence (M_R)/magnetic saturation (M_S)] of electrodeposited nickel films as a function of current density. Solution pH and operating temperature were 0.3 and 70°C (158°F), respectively.

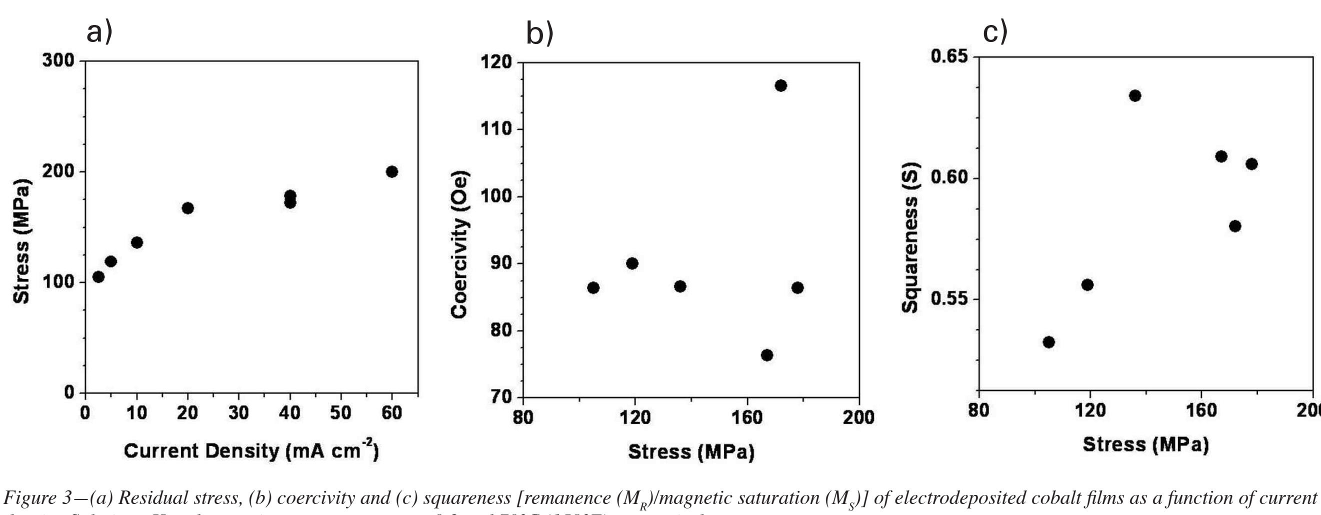

Figure 3—(a) Residual stress, (b) coercivity and (c) squareness [remanence (M_R)/magnetic saturation (M_S)] of electrodeposited cobalt films as a function of current density. Solution pH and operating temperature were 0.3 and 70°C (158°F), respectively.

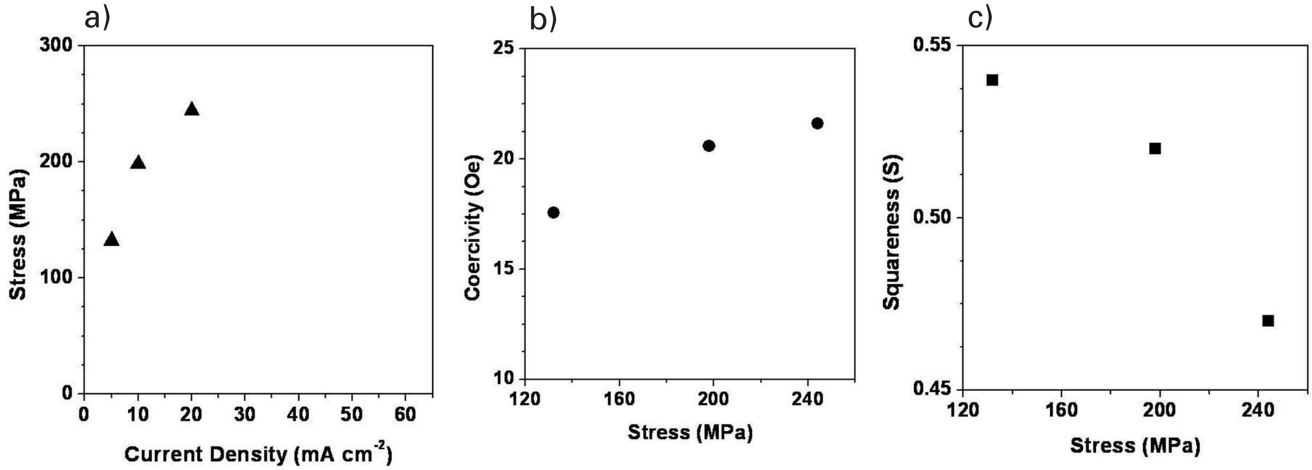

Figure 4—(a) Residual stress, (b) coercivity and (c) squareness [remanence (M_R)/magnetic saturation (M_S)] of electrodeposited iron films as a function of current density. Solution pH and operating temperature were 0.3 and 70°C (158°F), respectively.

Magnetic saturation values (M_S) of electrodeposited nickel and cobalt films were 0.6 and 1.8 T, respectively. These results were independent of electrodeposition conditions and in agreement with bulk data, as expected. Coercivity (H_C)† and squareness ($S = M_R/M_S$)†† were dependent on the deposition conditions, since they are extrinsic magnetic properties dependent on the film microstructure, including grain size, preferred orientation and stress. As shown in Figure 2(b), the coercivity of electrodeposited Ni films increased with increasing film stress, which indicates that magnetoelastic energy was the dominant anisotropy energy in the electrodeposited Ni films. Squareness decreased, as expected from the literature, since tensile stress causes a magnetic curve to be less square when magnetoelastic energy is the dominant anisotropy energy [Fig. 2(c)]. Unlike electrodeposited nickel films, there were no clear relationships between coercivity and film stress in electrodeposited cobalt films, which indicated that magnetoelastic energy was not the dominant anisotropy energy [Fig. 3(b)]. In contrast to electrodeposited nickel films, squareness increased with increasing film stress in such cobalt films [Fig. 3(c)].

Figure 4 shows the dependence of film stress, magnetic properties (*i.e.*, coercivity and squareness) of electrodeposited iron films as a function of current density at a fixed temperature of 70°C (158°F). Film stress in the iron electrodeposits increased monotonically as current density was increased. For example, electrodeposited iron film stress increased from 120 to 240 MPa (17.4 to 34.8 kpsi) with an increase in deposition current density from 5 to 20 mA/cm^2 (4.6 to 18.6 A/ft^2), respectively. Magnetic saturation values (M_S) of electrodeposited iron films were 2.1 T, independent of electrodeposition conditions. As shown in Fig. 4(b), the coercivity of electrodeposited iron films increased with increasing film stress, which indicates that magnetoelastic energy was the dominant anisotropy energy. Squareness was decreased in electrodeposited iron films, since tensile stress causes a magnetic curve to be less square when magnetoelastic energy is the dominant anisotropy energy [Fig. 4(c)].

Figure 5 shows the SEM micrographs of electrodeposited iron films at different current densities [5, 10 and 20 mA/cm^2 (4.6, 9.3 and 18.6 A/ft^2)] at 50°C (122°F). As shown in these figures, surface morphologies for the iron films were influenced by deposition temperature. Low current density promoted grain growth, while high current densities promoted nucleation and produced smaller grains. Higher deposition temperatures [*i.e.*, 70°C (158°F), not shown in the figure] promoted larger grain growth than lower deposition temperatures did.

Electrodeposited iron-cobalt films

Iron-cobalt alloy thin films of varying composition were electrodeposited by varying the Fe^{+2}/Co^{+2} ratio in solution, while maintaining the total iron group metal ions constant at 1.5M. Figure 6

† *The intensity of the magnetic field needed to reduce the magnetization of a ferromagnetic material to zero after it has reached saturation.*

†† *The remnant magnetization force after the magnetic field was reduced to zero divided by magnetic saturation.*

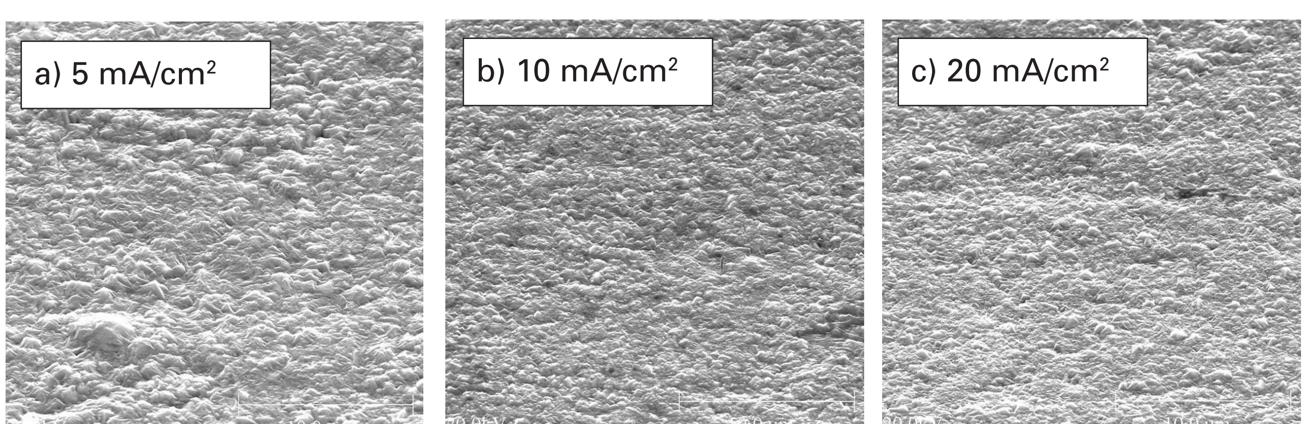

Figure 5—SEM micrographs of electrodeposited iron films at different current densities: (a) 5 mA/cm^2 (4.6 A/ft^2), (b) 10 mA/cm^2 (9.2 A/ft^2) and (c) 20 mA/cm^2 (13.8 A/ft^2); Temp. = 50°C (122°F).

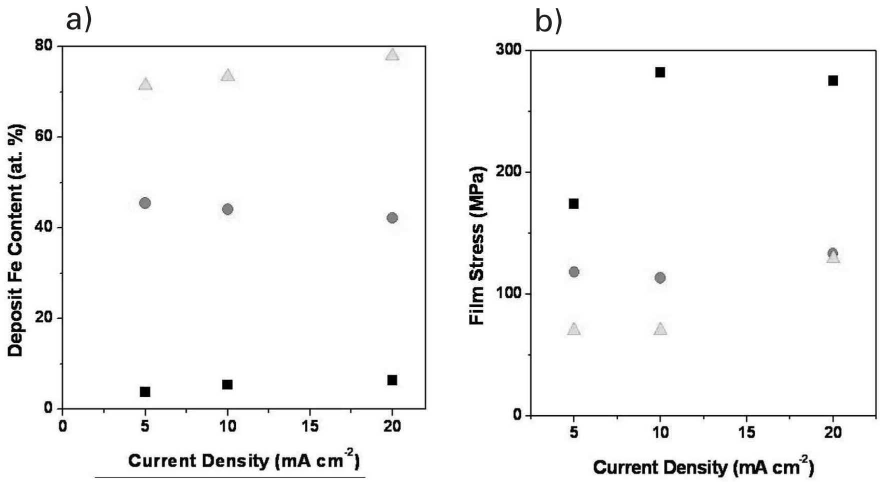

Figure 6—Deposit iron content and film stress as a function of solution composition at different current densities [5 to 20 mA/cm² (4.6 to 18.4 A/ft²)]; Temp. = 70°C (158°F): ■ *0.15M Fe^{+2} + 0.135M Co^{+2};* ● *1.05M Fe^{+2} + 0.45M Co^{+2};* ▲ *1.275M Fe^{+2} + 0.125M Co^{+2}.*

shows (a) the deposit Fe content and (b) film stress as a function of solution composition at various current densities. As shown in Fig. 6(a), the deposit iron content increased with increasing Fe^{+2}/Co^{+2} ratio, as expected. The maximum film stress in the iron-cobalt thin films was observed at a deposit iron content of 5 to 10 atomic %.

Figure 7 shows SEM micrographs of electrodeposited iron-cobalt films with different film compositions at a current density of 5 mA/cm² (4.6 A/ft²). As shown in the images, the surface morphology of the iron-cobalt films dramatically changed with the iron-cobalt film composition. The grain size increased with an increase in iron content. Small grains were observed in 3.8 Fe / 96.2 Co films [Fig. 7(a)]. The film film stress in the iron-cobalt films decreased with increasing grain size. An earlier report[10] had also demonstrated that electrodeposited mixed phase iron-cobalt alloys produced films with smaller grain size. Magnetic saturation of iron-cobalt alloys increased with increasing in deposit iron content. For example, magnetic saturation values of 1.6 T, 1.9 T and 2.0 T were measured for iron-cobalt electrodeposits with deposit iron contents of 3.8%, 35.1% and 45.4%, respectively.

Figure 8 shows the film stress of iron-cobalt films as a function of film thickness. As expected, the film stress decreased with increasing film thickness. High initial stress is attributed to lattice and grain size mismatch between the deposits and the underlying substrate.[9] Film stress decreased to a steady state value as the deposit increased in thickness.

Conclusion

The electrodeposition of nickel, cobalt, iron and iron-cobalt alloys thin films from additive-free acidic chloride baths with calcium chloride as a supporting electrolyte was investigated. In general, low film stress was achieved by operating at a low current density and higher temperature. SEM micrographs indicated that these conditions promoted grain growth over nucleation. Magnetic properties, including coercivity and squareness, were strongly influenced by film stress. Coercivity in electrodeposited nickel and iron films increased with increasing film stress while squareness decreased, indicating that magnetoelastic energy was the dominant anisotropy in electrodeposited nickel and iron films. No such trends were observed in electrodeposited cobalt films, which indicated that other anisotropy energies (*e.g.*, crystal anisotropy) were dominant. In the case of iron-cobalt thin films, film composition played an important role in determining film stress.

Acknowledgements

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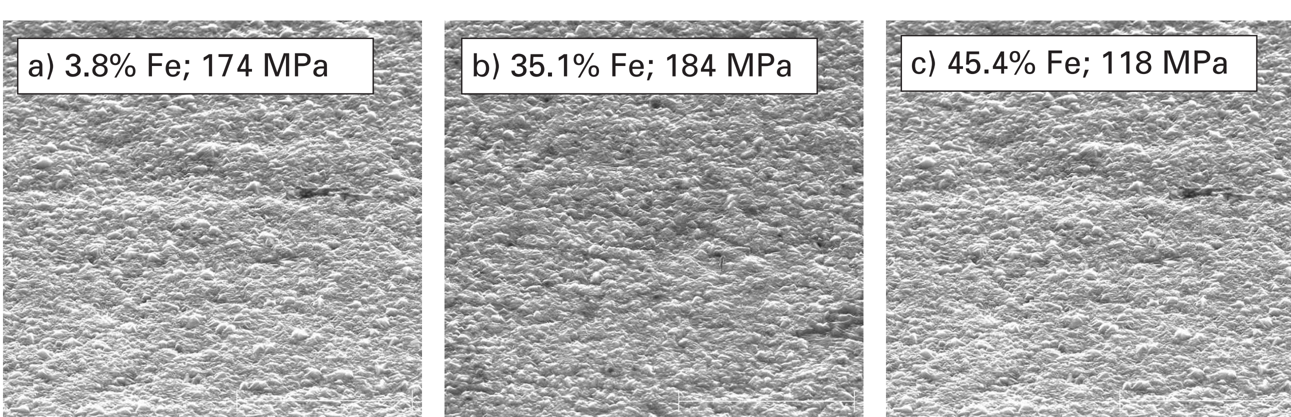

Figure 7—SEM micrographs of electroformed iron-cobalt films: (a) 3.8% Fe, (b) 35.1% Fe, (c) 45.4% Fe; CD = 5 mA/cm² (4.6 A/ft²) and Temp. = 66 to 68°C (151 to 154°F).

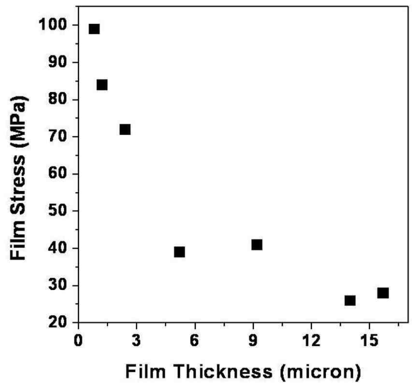

Figure 8—Residual stress of iron-cobalt electrodeposits as a function of film thickness: iron-cobalt films were electrodeposited from 1.275M $FeCl_2$ + 0.225M $CoCl_2$ + 1.0M $CaCl_2$; pH = 0.3; Temp. = 70°C (158°F).

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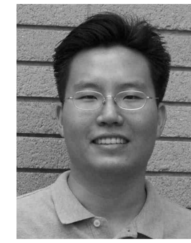
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