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Development of Low Stress Binary and Tertiary High-Magnetic Flux Alloy films from Electrolytic Solutions

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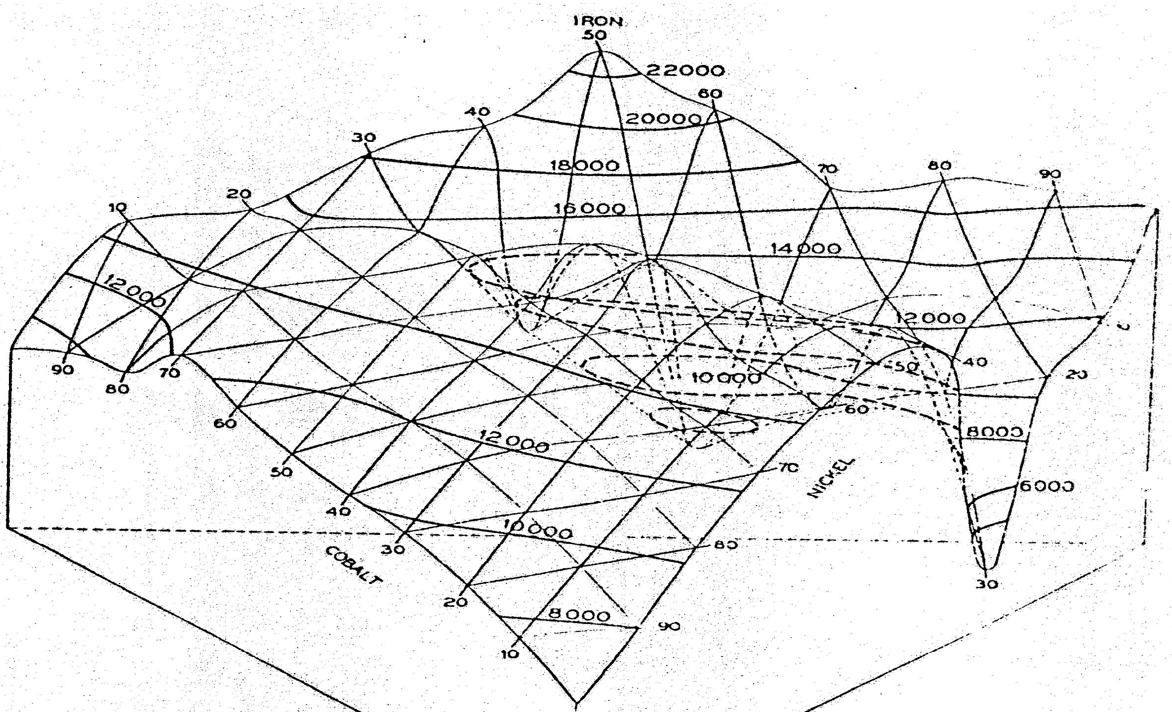
Introduction

Materials are the limitations to technology. The advantages of electrochemical processes for microelectronics have advanced technology in development of materials and alloys with shapes and concentrations deemed impossible by numerous other methods. Areas that have received recent attention are the microfabrication of high-flux magnetic (HFM) alloys and super alloys. Among the greatest challenges that plague researchers today is maintaining the composition of the alloy during electrodeposition.

Overview

- Current limitations as a function of Reaction, Nearstian, and Prandtl boundary layer thickness.
- Anomalous behavior of co-deposited metals.
- Changes in surface concentration as a function of time during fix galvanostatic electrolysis.
- Changes in ionic molar ratios as a function of time.
- Changes in diffusion-layer thickness at limiting current density as a function of time.
- Affluent deposition behaviors of trace ionic species.
- Pulse deposition, “a tool or a hindrance?”

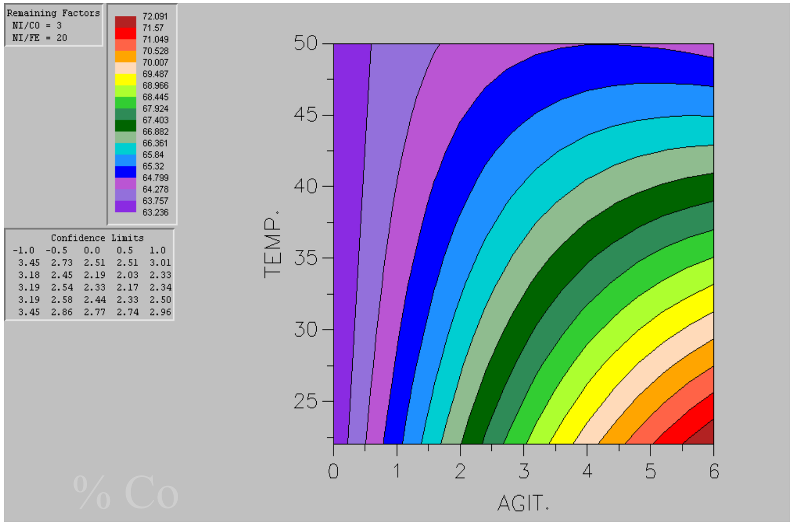
High Magnetic Flux As a Function of Alloy Concentration



H = magnetizing force in gauss

Intrinsic inductions for annealed alloys at $H = 50$.

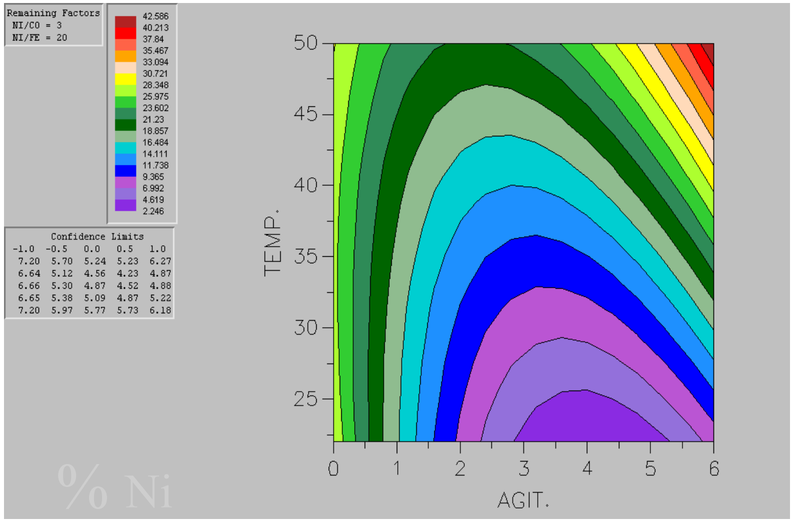
Target: High Magnetic Flux Composition, $(Co_{65}\ Ni_{13}\ Fe_{22})$



Remaining Factors
NI/CO = 3
NI/FE = 20

Confidence Limits

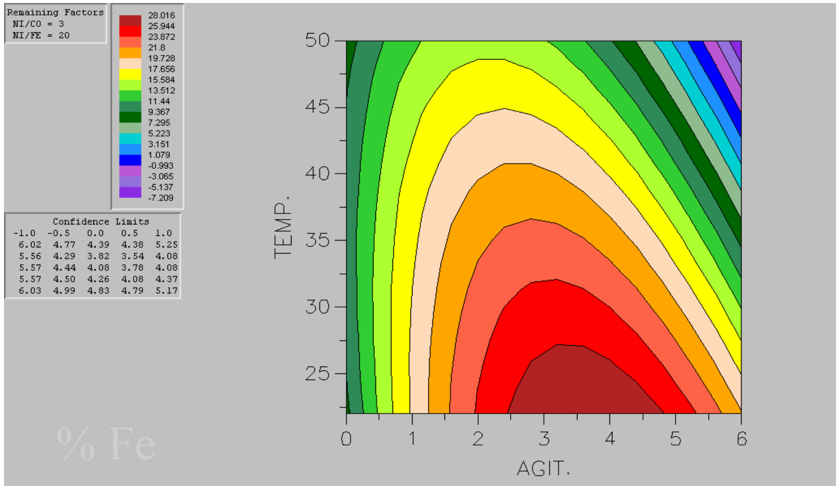
-1.0	-0.5	0.0	0.5	1.0
3.45	2.73	2.51	2.51	3.01
3.18	2.45	2.19	2.03	2.33
3.19	2.54	2.33	2.17	2.34
3.19	2.58	2.44	2.33	2.50
3.45	2.86	2.77	2.74	2.96



Remaining Factors
NI/CO = 3
NI/FE = 20

Confidence Limits

-1.0	-0.5	0.0	0.5	1.0
7.20	5.70	5.24	5.23	6.27
6.64	5.12	4.56	4.23	4.87
6.66	5.30	4.87	4.52	4.88
6.65	5.38	5.09	4.87	5.22
7.20	5.97	5.77	5.73	6.18

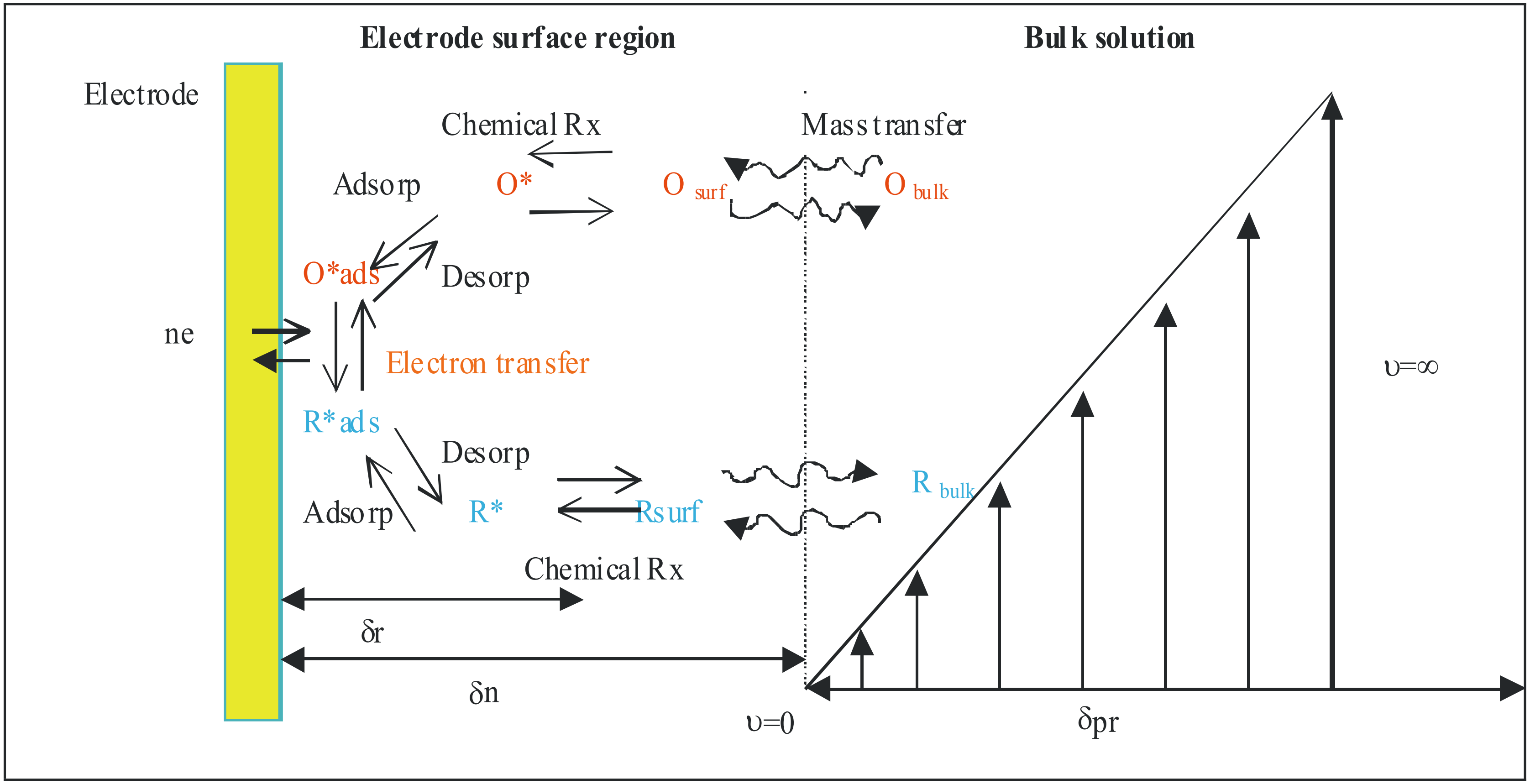


Remaining Factors
NI/CO = 3
NI/FE = 20

Confidence Limits

-1.0	-0.5	0.0	0.5	1.0
6.02	4.77	4.39	4.38	5.25
5.56	4.29	3.82	3.54	4.08
5.57	4.44	4.08	3.78	4.08
5.57	4.50	4.26	4.08	4.37
6.03	4.99	4.83	4.79	5.17

Factors Affecting Electrode Kinetics



Anomalous Behaviors
NiCoFe Ternary Alloy Deposition

- For single ionic specie deposition the more noble species plates out first, Ni>Co>Fe.
- Standard normal potentials.

Ni/Ni^{2+}	-0.257 V.
Co/Co^{2+}	-0.270 V.
Fe/Fe^{2+}	-0.440 V.

- Under iron-group co-deposition, the more noble metal deposition is inhibited while the less noble metal is promoted, Fe>Co>Ni.

Mixed Metal Intermediates According to Zhuang et al.

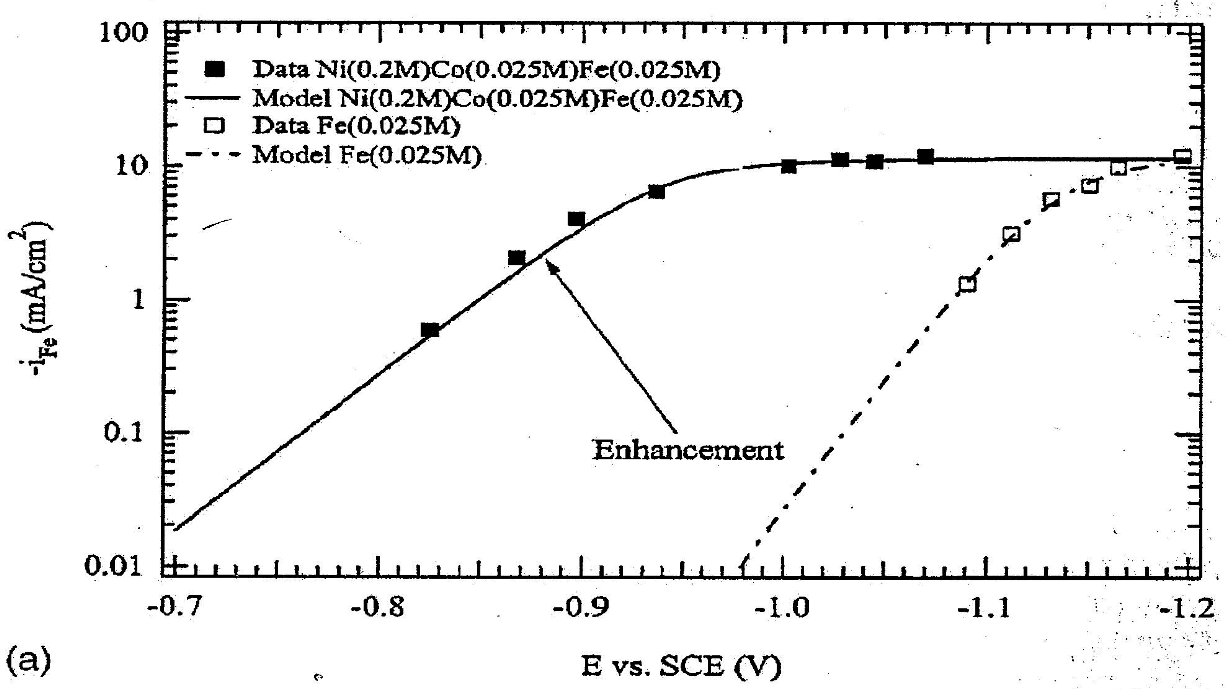
- $\mathrm{Co(ii)} + \mathrm{Ni(ii)} + e \longrightarrow \mathrm{CoNi(iii)}_{ad}$

  $\mathrm{CoNi(iii)}_{ad} + e \longrightarrow \mathrm{Co} + \mathrm{Ni(ii)}$
- $\mathrm{Fe(ii)} + \mathrm{Ni(ii)} + e \longrightarrow \mathrm{FeNi(iii)}_{ad}$

  $\mathrm{FeNi(iii)}_{ad} + e \longrightarrow \mathrm{Fe} + \mathrm{Ni(ii)}$
- $\mathrm{Fe(ii)} + \mathrm{Co(ii)} + e \longrightarrow \mathrm{FeCo(iii)}_{ad}$

  $\mathrm{FeCo(iii)}_{ad} + e \longrightarrow \mathrm{Fe} + \mathrm{Co(ii)}$

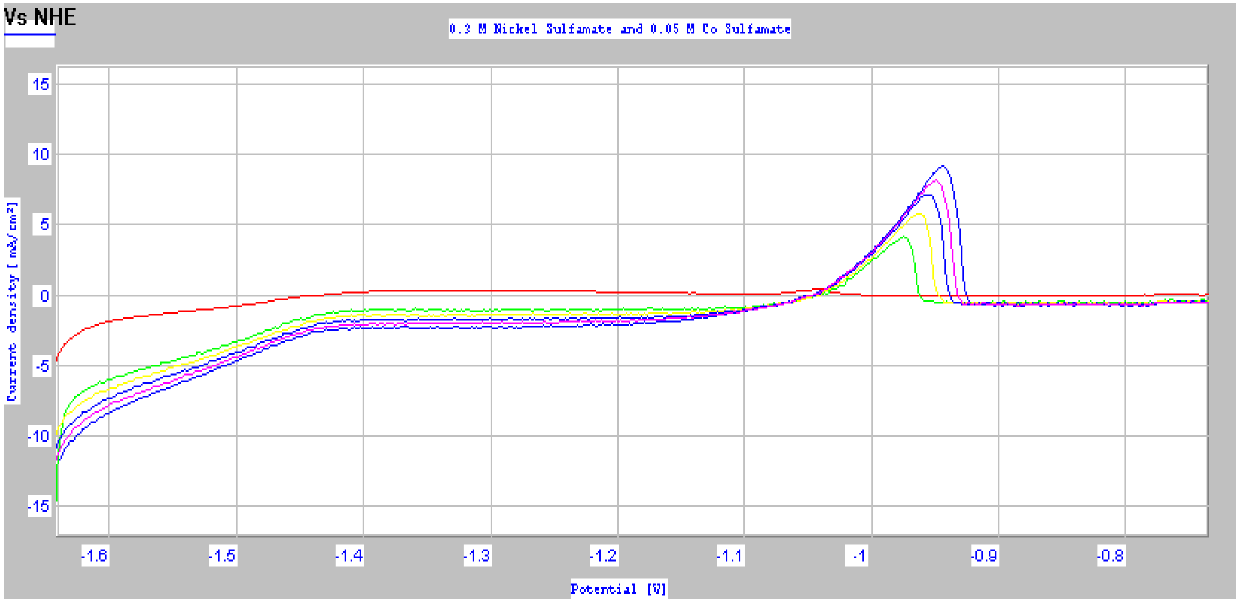
Anomalous Deposition Where Ni and Co Enhance the Partial Current Densities of Fe, Zhuang (2003)



Anomalous Deposition Under Activation Regime

- Potentials more positive than –1.05 V vs. SCE, Ni partial current densities are inhibited.
- Inhibited behavior is a function of Fe^{2+} bulk concentration.
- Depending on bulk concentration, Co^{2+} displays both inhibiting and catalytic region as a function of Fe^{2+} bulk concentration.
- Potentials more negative than –1.05 V vs. SCE, system moves into mass-transport limitations where diffusion controls the partial current densities.

Mass Transport Limited Current Density



Mass transport and charge transfer are two consecutive processes.
The slower of the two processes determines the overall experimentally observed rate.
Distance of charge transfer on the order of 0.5 nm, distances beyond this, species must be transported from the bulk to the surface.

Mass-transport-limited current density $i_L = nFDC/\delta$.
Where nF is charge transferred per mole (C/mol), D is the diffusion coefficient (cm^2/s), C is the bulk concentration ($mole/cm^3$), and δ is the Nernst diffusion layer thickness (cm).
Complexing agent added: sodium citrate 0.5 M.

Ternary Iron Group Deposition Under Diffusion Regime

$\partial C/\partial t = d\partial^2 C/\partial x^2$ under concentration polarization and constant current.

.

BC_1 $t = 0,\ x \geq 0,\ C = C_b$

BC_2 $t > 0,\ x \rightarrow \infty,\ C = C_b$

BC_3 $t > 0,\ (\partial C/\partial x)_{x = 0},\ = j/nFD_i$

.

Sand's (1901) solution, most commonly reported, using Fourier analysis.

.

$$C^s_i = C^b_i - 2j/nF(t/\pi D_i)^{1/2}$$

.

Interestingly, solution using Laplace transform analysis.

$$C^s_i = C^b_i - j/nF(t\pi/D_i)^{1/2}$$

~36% difference

Parameters Used for Concentration Polarization of Ternary Alloy Deposition

Case study.

HMF target: Co 65%, Ni 13%, and Fe 22%, Osaka (2000).

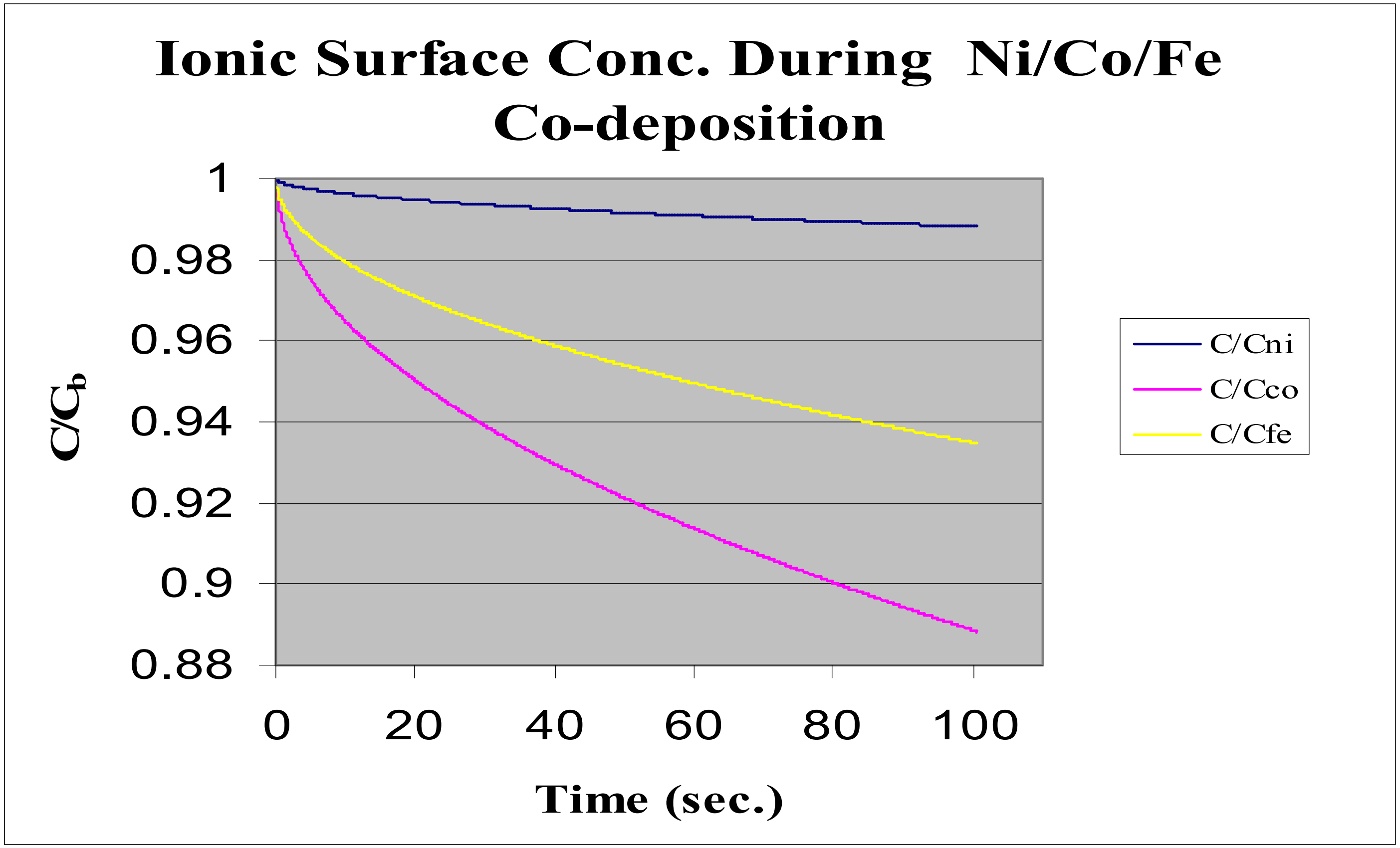
- Nickel Sulfamate $c_{ni}^{2+} = 0.012$ g/cm^3 , Yelton (2003).
- Cobalt Sulfamate $c_{co}^{2+} = 0.061$ g/cm^3.
- Iron Tetrafloroborate $c_{fe}^{2+} = 0.037$ g/cm^3.

Diffusion coefficients @ RT, Zhuang (2003).

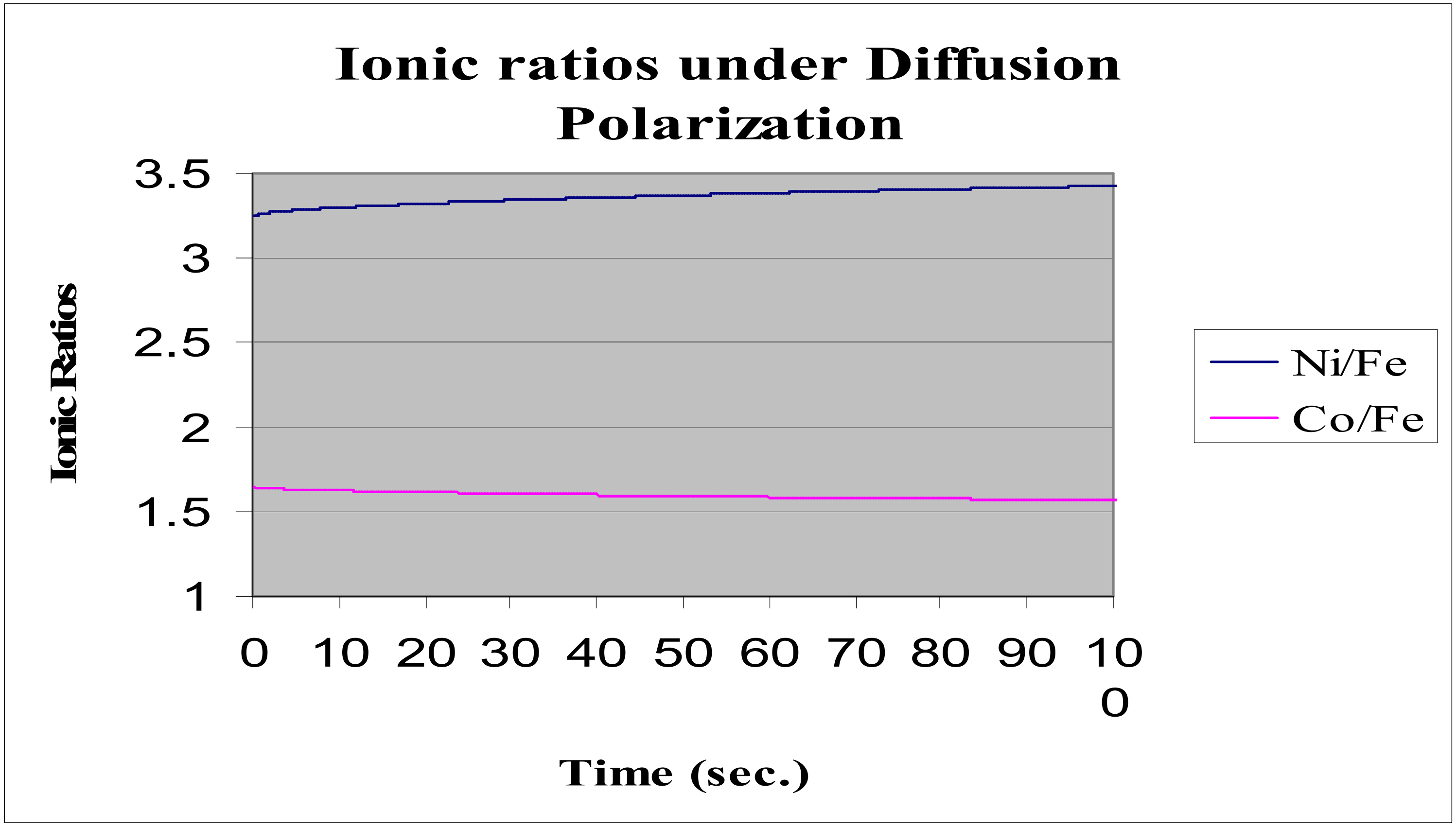
- 2.56 X 10^{-6} cm^2/sec. For Ni, Co, and Fe.

- Partial current density based on 100 ma/cm^2 applied @ 30% effic.
  - Co= 18.6 mA/cm^2, Ni= 3.9 mA/cm^2, and Fe= 6.6 mA/cm^2.

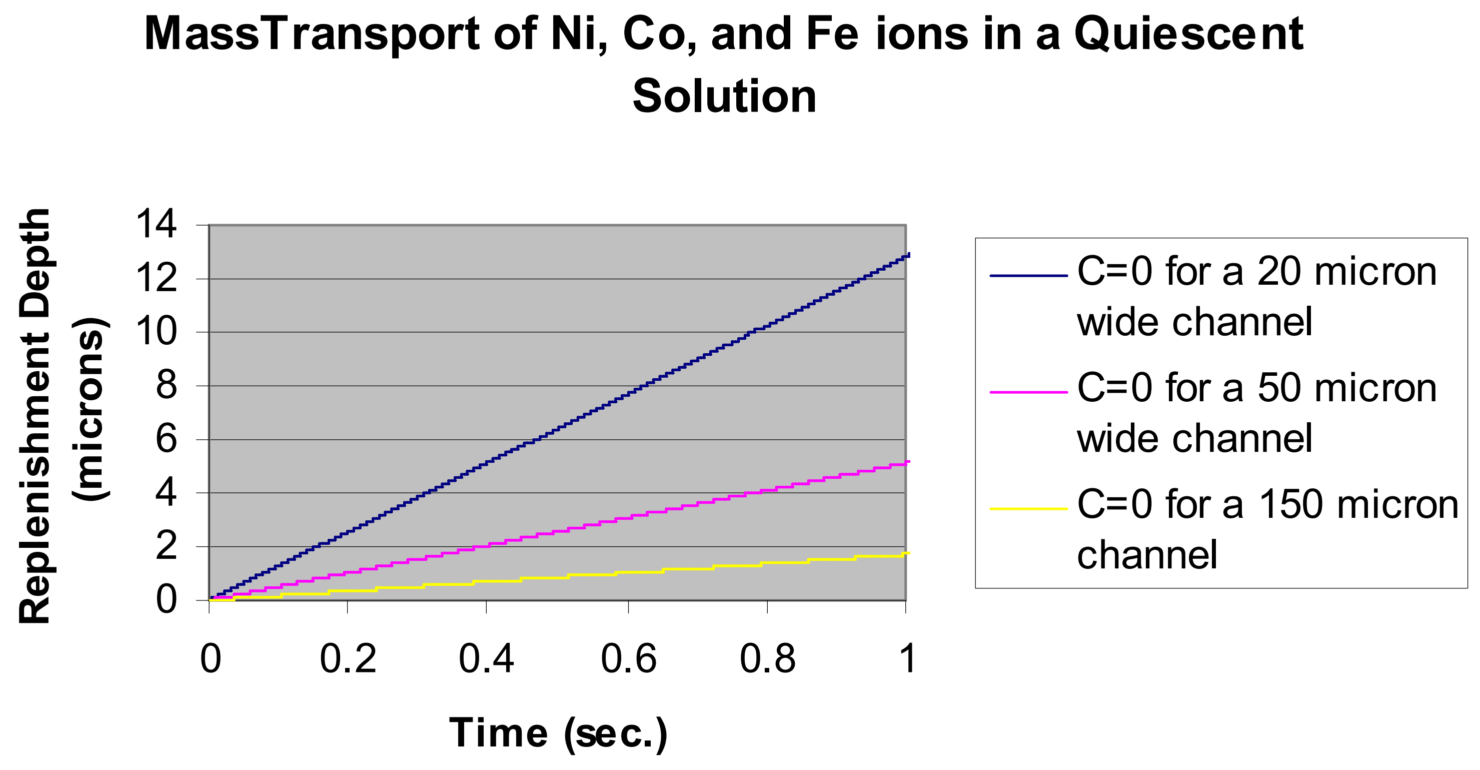
Ionic Surface Concentration Under Fixed Partial Current Density Using Sand's Model



HMF Ternary Alloy Ionic Ratios



Restoration of Depleted Interphase Back to Bulk Ionic Concentrations in Linear Depth As a Function of Time



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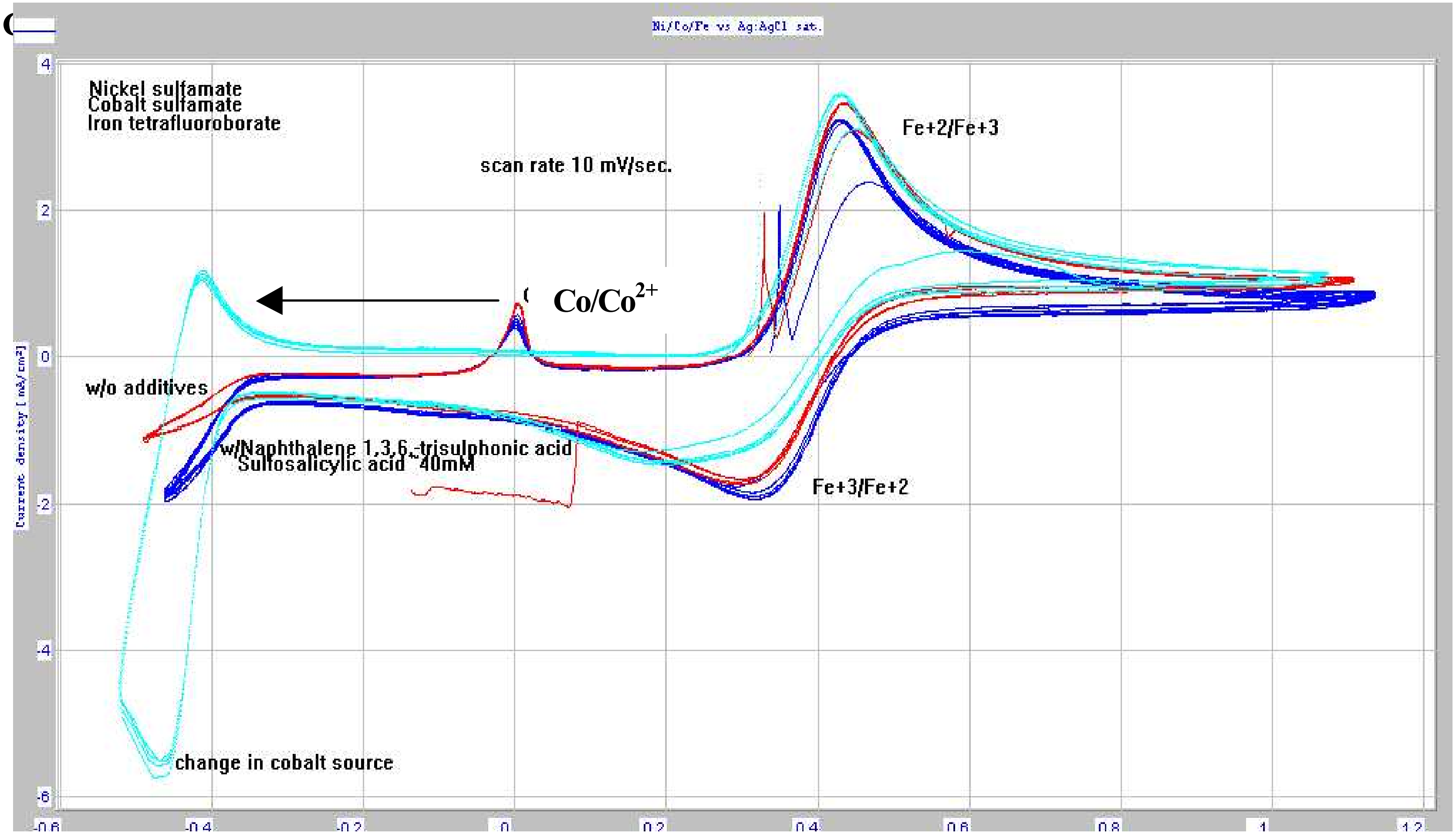
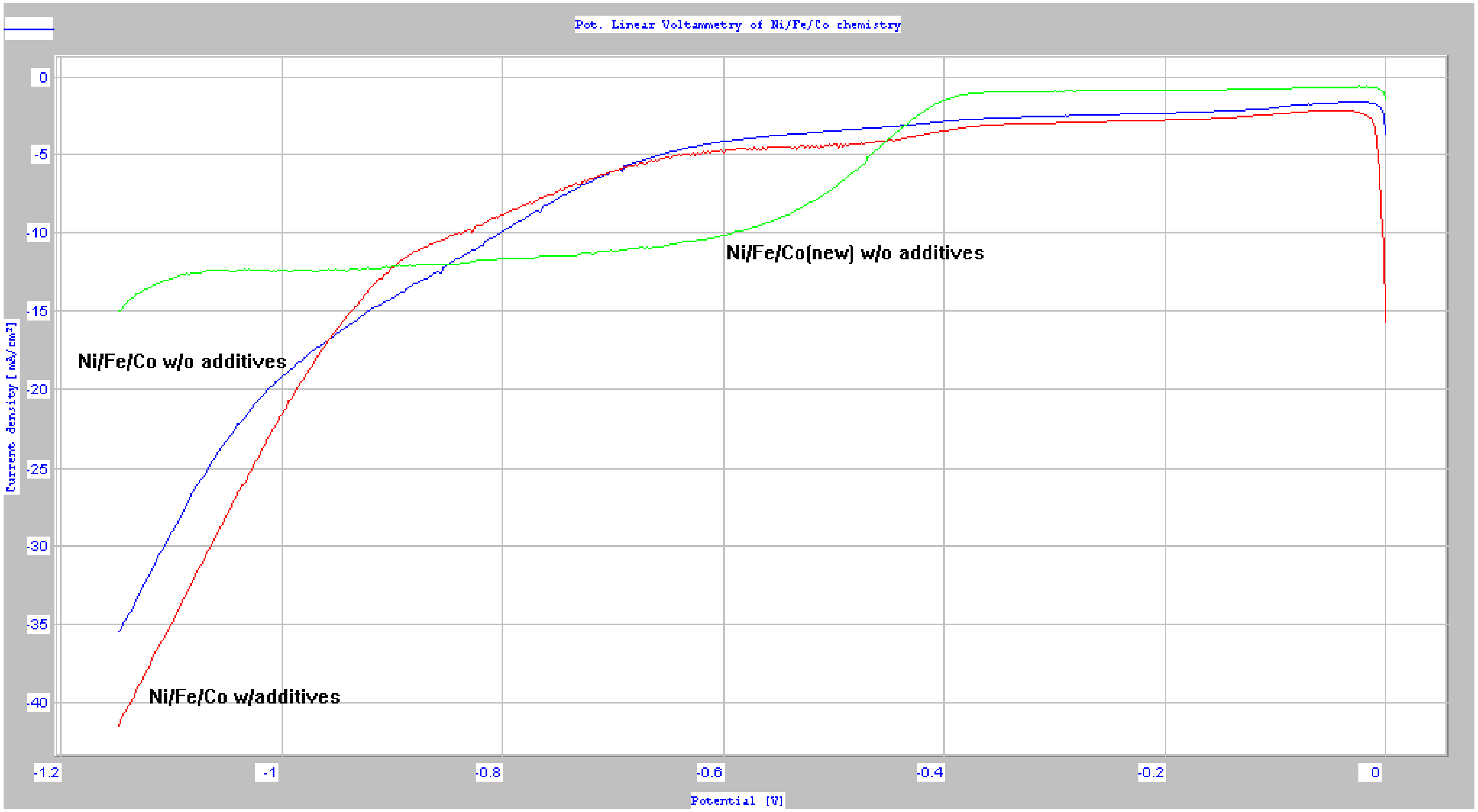
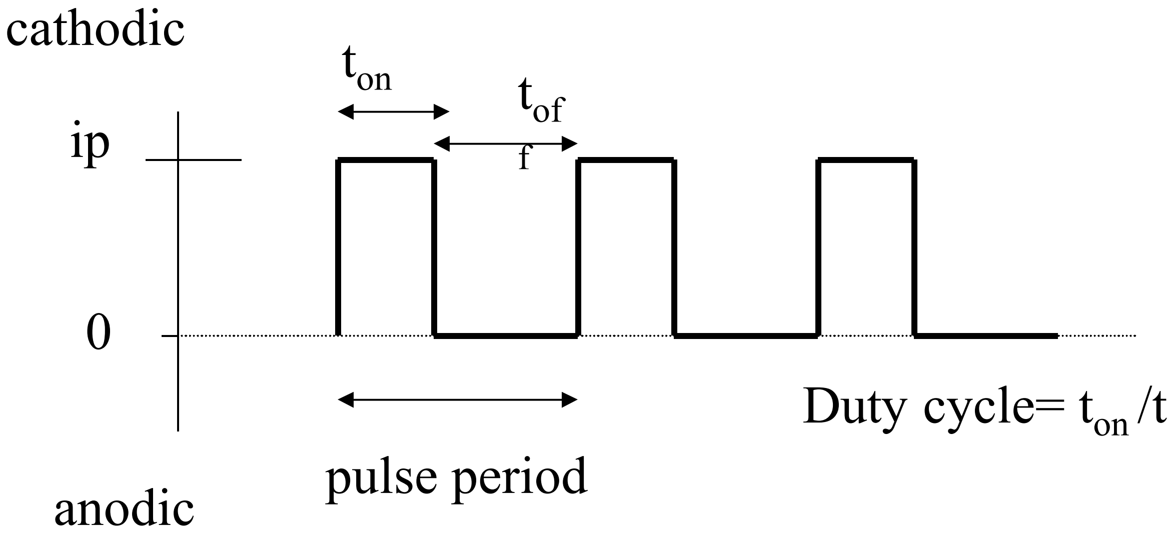
Shifts in Oxidation/Reduction from Trace Ionic Species



Effects of Trace Ionic Species on Rates for Potentials Below H_2 Production Potential



Pulse Deposition, “A tool or a hindrance?”



cathodic

t_{on}

t_{off}

ip

0

pulse period

anodic

Duty cycle= $t_{on} / t_{on} + t_{off}$

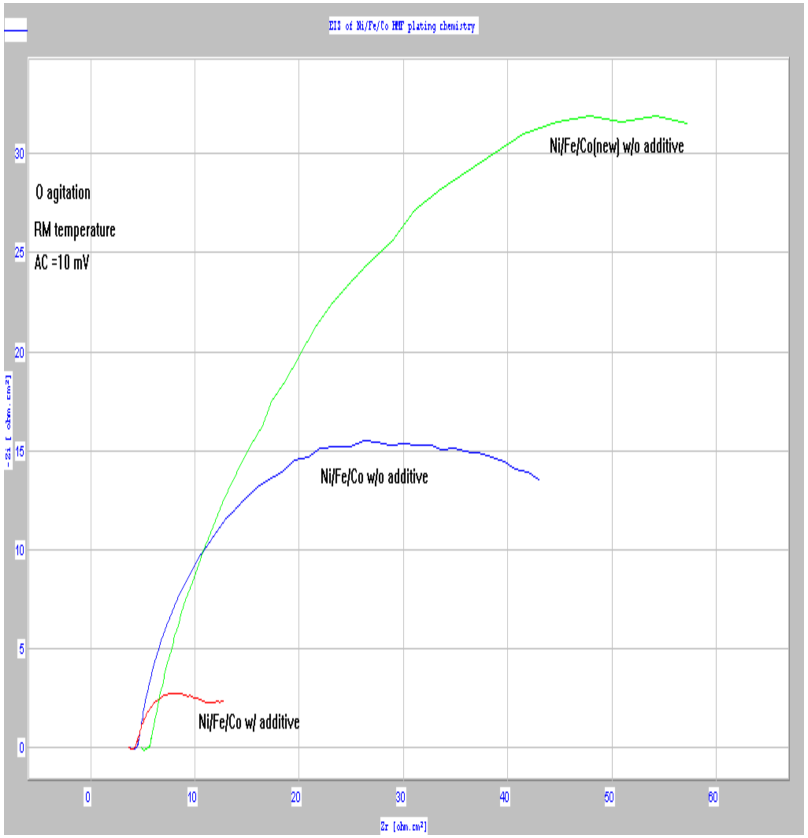
Mass transport and Ionic depletion during on cycle.

Mass transport and Ionic replacement during off cycle.

Crystal phase appears to be a function of duty cycle.

Electrochemical Impedance to identify R_s, R_f, and C_{dl}

- Ni/Fe/Co (blue)
  - R_s (4.5Ω.cm^2),
  - R_f (38.4Ω.cm^2),
  - C_{dl} (46.40 μF/cm^2)
- Ni/Fe/Co w/additives (red)
  - R_s (4.3Ω.cm^2),
  - R_f (7.76Ω.cm^2),
  - C_{dl} (81.98 μF/cm^2)
- Ni/Fe/Co new (green)
  - R_s (5.4Ω.cm^2),
  - R_f (96.42Ω.cm^2),
  - C_{dl} (132.0 μF/cm^2)



Kinetic Parameters from Impedance Measurements

Heterogeneous Reaction occur only at the electrode-electrolyte interface (units of mol.s^{-1} per unit area).

Equilibrium potential is an important reference point in an electrochemical system.

$$O + e^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} R$$

The exchange current density, i_0, is determine using the relationship with the charge-transfer resistance (R_f), $R_{ct} = RT/Fi_0$.

From the exchange current density, i_0, the heterogeneous reaction rate, ν_o, is determine: $\nu_o = i_0/nF$.

Time constant for the electron transfer, $\tau = R_f.C_{dl}$.

Temp.@RT

Ni/Fe/Co w/o additives	**Ni/Fe/Co w/additives**	**Ni/Fe/Co (new)**
i_0=328 μA/cm^2	i_0=1.62 mA/cm^2	i_0=136 μA/cm^2
ν_o = 1.67 nMol. s^{-1}.cm^{-2}	ν_o = 8.23 nMol. s^{-1}.cm^{-2}	ν_o = 0.69 nMol. s^{-1}.cm^{-2}
τ = 1.8 msec.	τ = 640 μsec	τ = 12.7 msec

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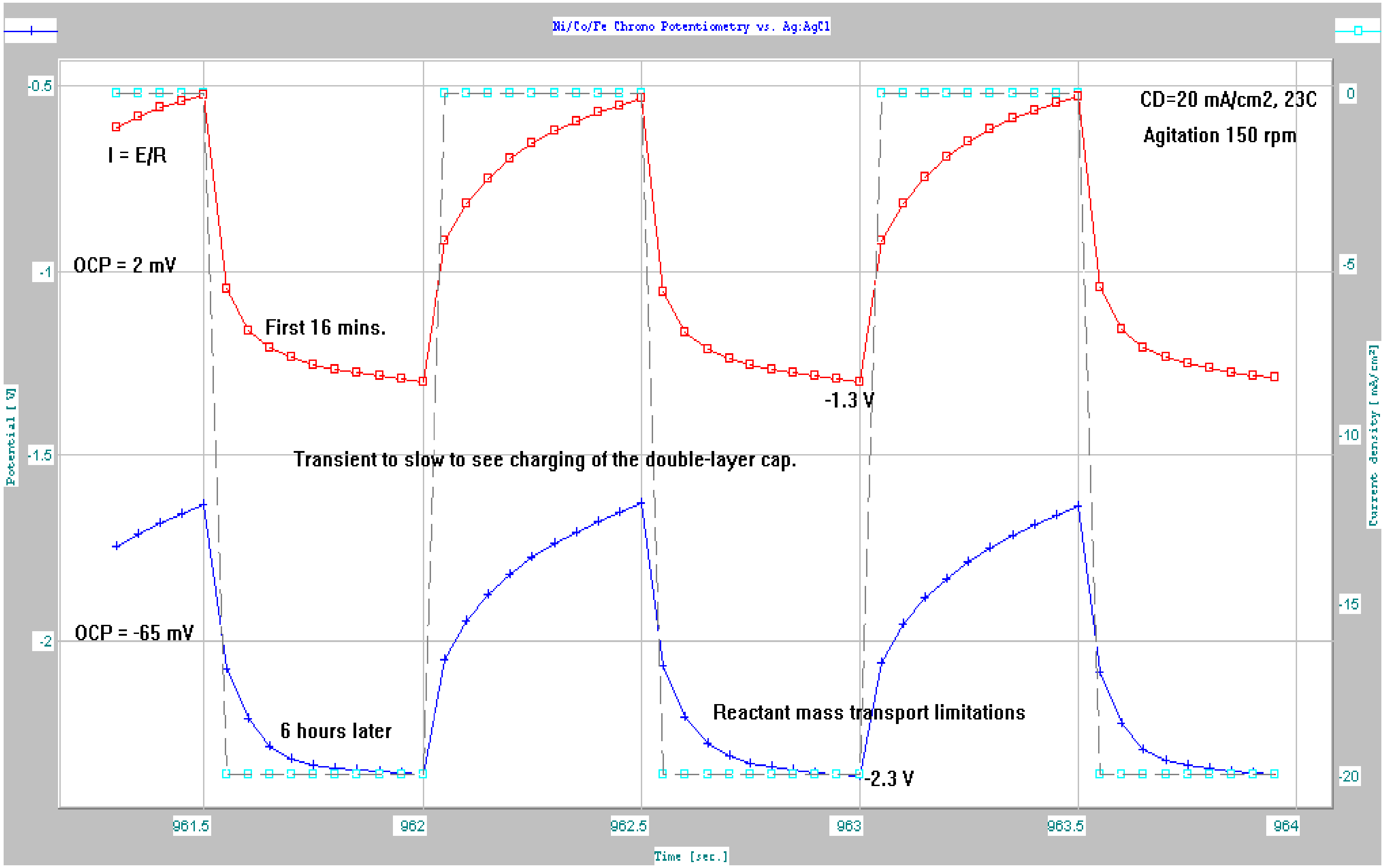
Small Galvanostatic Pulse: Similar Mass Transport Limitations, but Shift in Potentials



CD=20 mA/cm2, 23C

Agitation 150 rpm

I = E/R

OCP = 2 mV

First 16 mins.

-1.3 V

Transient to slow to see charging of the double-layer cap.

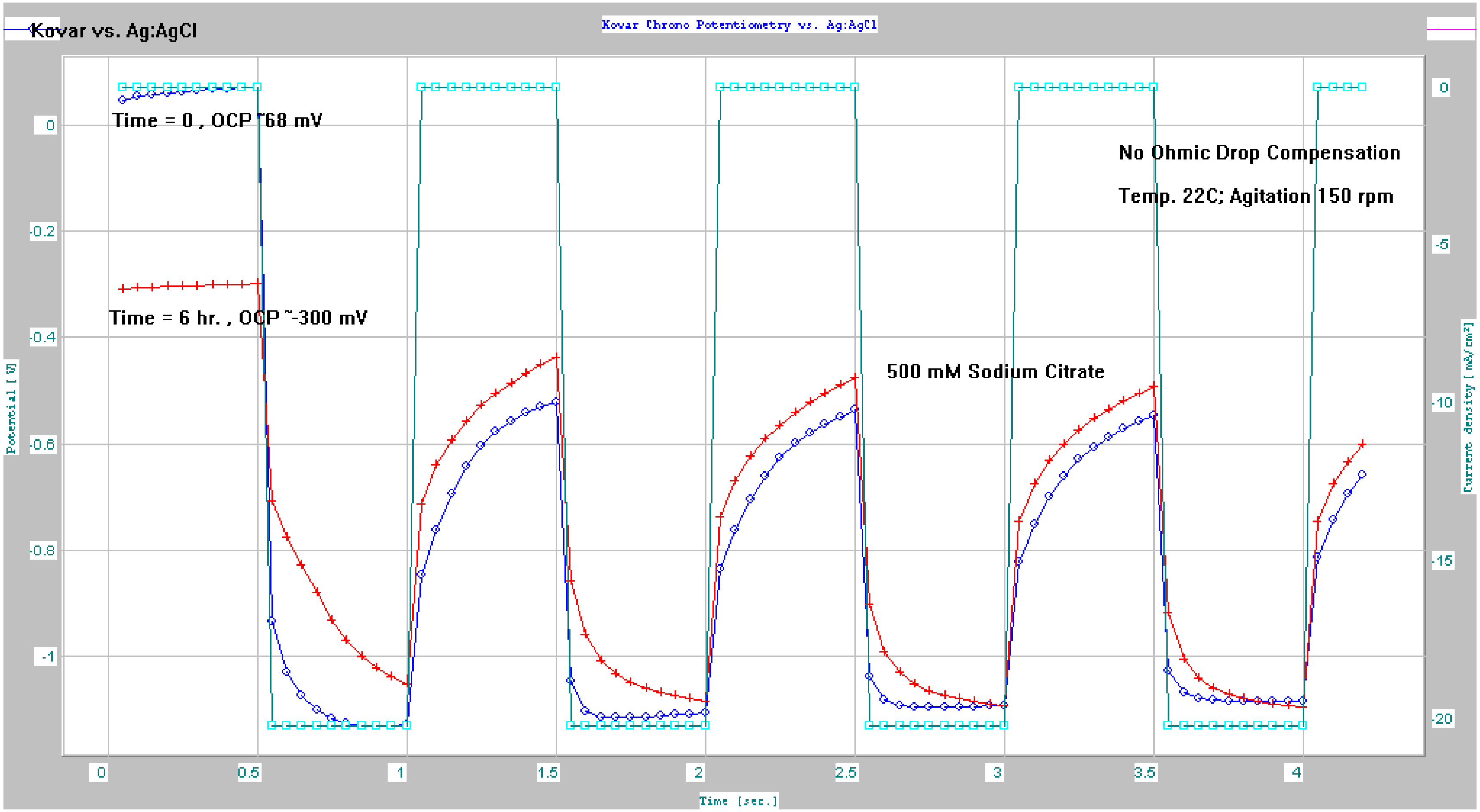
OCP = -65 mV

6 hours later

Reactant mass transport limitations

-2.3 V

Similar Galvanostatic Pulse with Addition of Complexing Agent



Time = 0 , OCP ~68 mV

Time = 6 hr. , OCP ~-300 mV

No Ohmic Drop Compensation

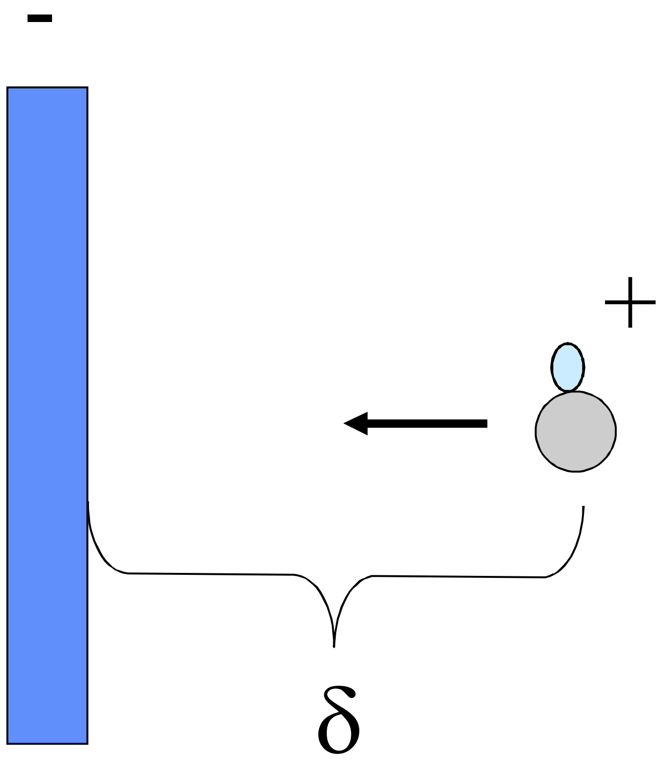
Temp. 22C; Agitation 150 rpm

500 mM Sodium Citrate

Conclusion

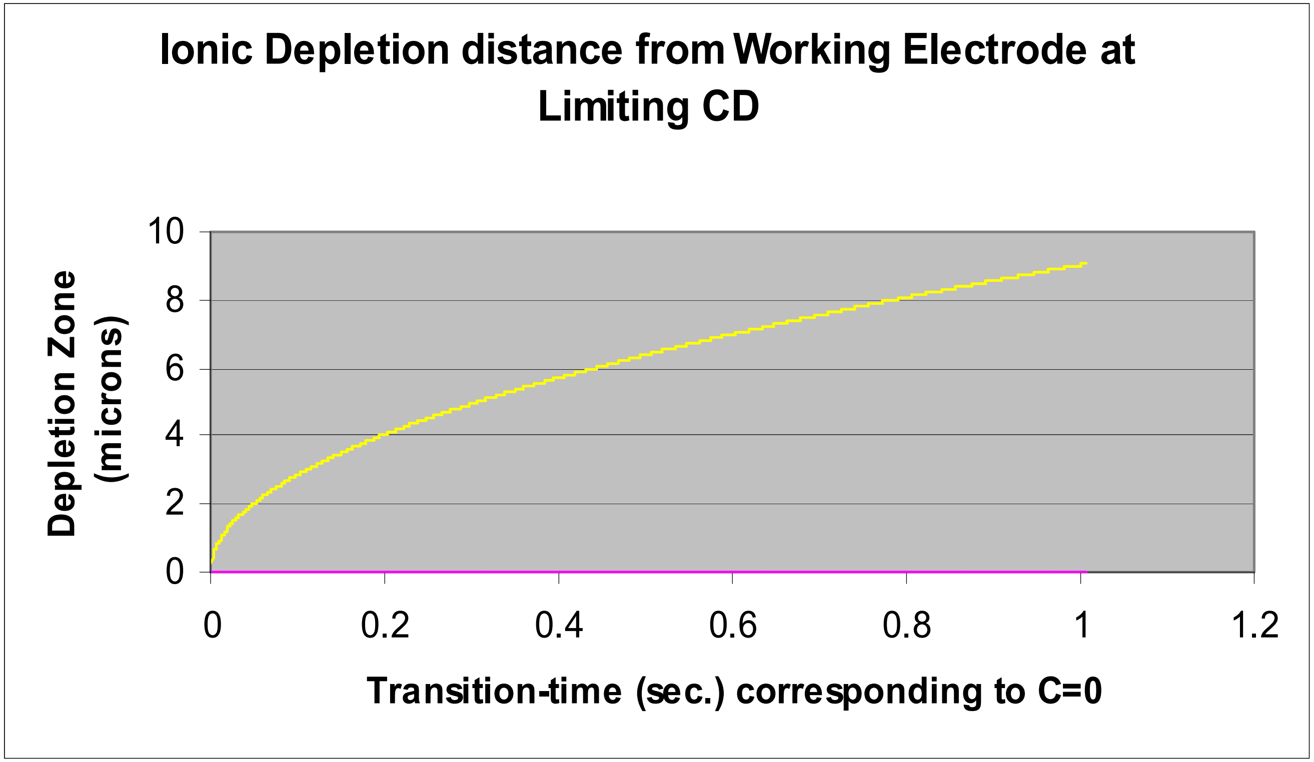
- HMF alloys should not deviate more than 5%.
- Under activation polarization, anomalous behaviors dictate partial current densities.
- Under concentration overpotentials, after 20 sec. the ionic conc. change by ~2% for Ni, ~3% for Fe, and ~5% for Co. Safe for pulses shorter then 20 sec.
- But, ionic species replacement at the cathode is much slower than ionic depletion for channel widths >20 μ; therefore, a pulse “on” cycle should be shorter than “off” cycle.
- Ionic trace species greatly affect quality and kinetics of deposits.
- Literature suggests that HMF properties are a function of crystal phase, which appears to be affected by duty cycle.

Mass-Transport-Limited Current Density
$i_l = nFDC/\delta$

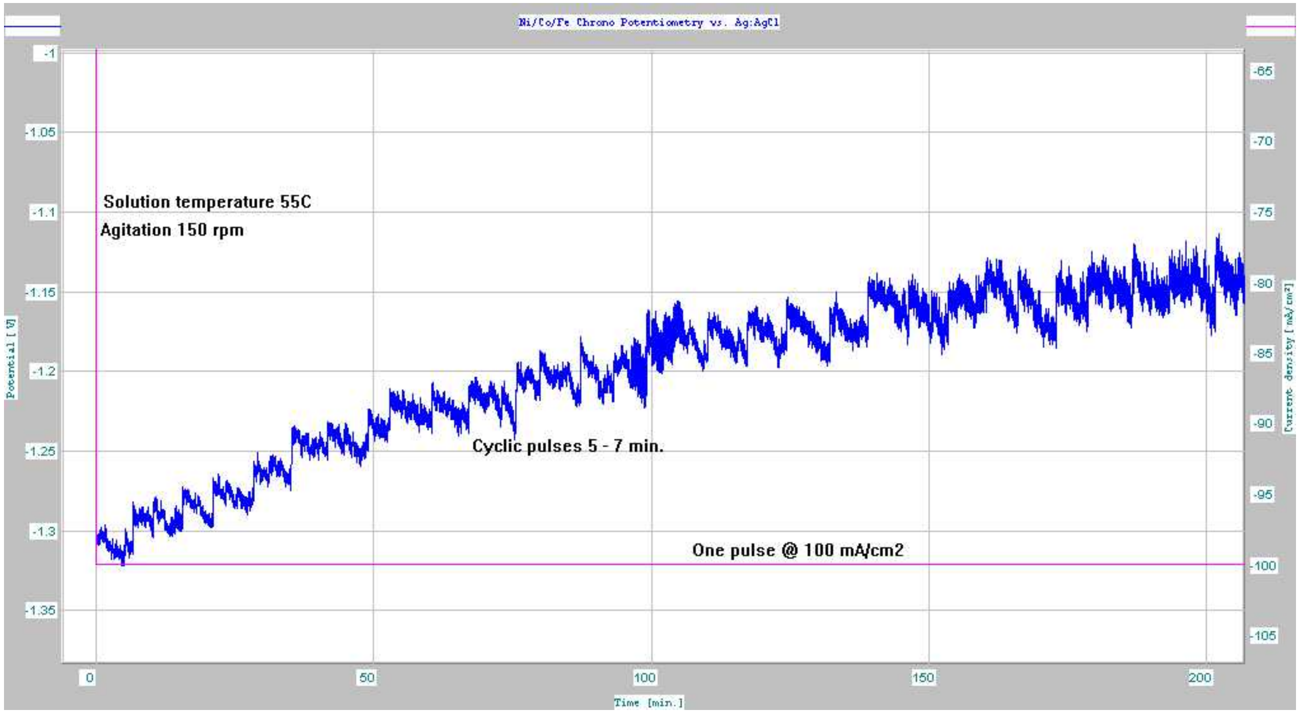


- Stagnate solution 200-300 μ
- RDE 200 rpm ~50μ
- RDE 10^4 rpm ~5–6μ
- Jet flow ~3–5μ
- Typical DXRL channel depth ca. 200 to >500μ
- Channel aspect ratio greatly influences CD
- The need to pulse!

Distance of Ionic Depletion As System Is Driven to Limiting Current Densities



Mass Transport-Limited Potentials and H_2 Surface Coverage Problems



Solution temperature 55C

Agitation 150 rpm

Cyclic pulses 5 - 7 min.

One pulse @ 100 mA/cm2

Uniform Alloy Electroforming of 45/55 Ni/Fe as a Soft Magnetic Material for High-Aspect Ratio MEMS Applications

Figure 1: SEM view of Ni/Fe concentration at .7μ deep

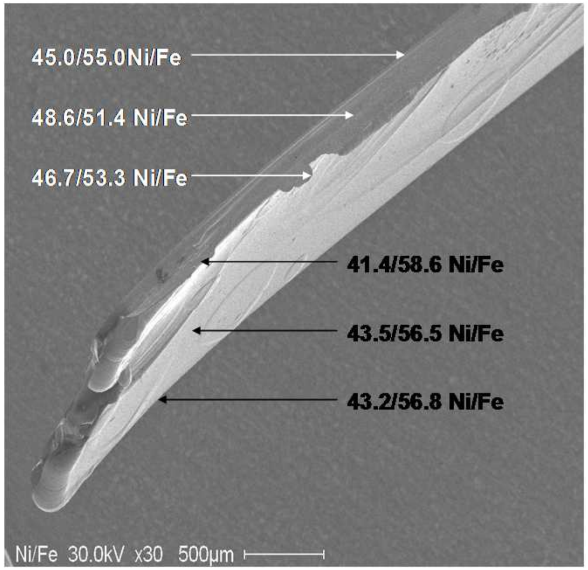


Figure 2: Graph of Magnetization vs. Magnetic Field