CONTRIBUTION OF ELECTROCHEMICAL PROCESSES TO INCREASED HEAD-MEDIA SPACING IN TAPE DRIVES:

Influence of Thin Film Composition on Electrochemical Response
(Supported by NSIC Tape Program)

Fred Spada

CMRR Research Review

May 22, 2002
PROGRAM GOALS

- Evaluate the behavior of head and tape materials to determine if electrochemical processes are responsible for material depletion or deposition at the head-tape interface

- Identify potential incompatibilities among head materials, tape materials, and environmental species that could adversely affect the head-tape separation
WHY FOCUS ON ELECTROCHEMICAL PROCESSES?

• Electrochemically significant potentials at the head-tape interface may arise from:
  
  - charge leakage/stray currents
  - galvanic coupling
  - contact with electrolyte layers produced from environmental species and adsorbed moisture
  - triboelectric charging

• Many chemical processes can be easily initiated when electric potentials are present:

\[ zFE = -\Delta G = RT\ln K \]

\[ \Delta E = 1 \text{ volt implies } 10^{16} \text{ increase in } K \text{ at fixed } T (\Delta T \approx 10^4 K \text{ required to produce the same effect}) \]
SUMMARY OF PREVIOUS RESULTS

• Pole tip corrosion and stain formation appear to be related. Both are observed in NiFe and CoZrTa films exposed to stearic acid at anodic potentials greater than about +400 mV (vs. Ag/AgCl). As previously reported, CoZrTa is more susceptible than NiFe.

• Properties of the stain suggest that it either contains, or is produced by a mechanism that involves metallic soaps, such as

\[ n\text{RCOO}^- + M \rightarrow (\text{RCOO})_nM + ne^- \quad (M= \text{metal, } R= \text{alkyl group}) \]

Waxes and olefins produced via the Kolbe electrolysis

\[ 2\text{RCOO}^- \rightarrow 2\text{CO}_2 + R-R + 2e^- \]

may also be present in thicker films.
1000Å Ni₈₁Fe₁₉
In 0.01M Stearic Acid + Borate Buffer
(Methanol Solvent)

Stain formation and pitting observed after polarization to this potential

No stain formation or pitting up to this potential

E (mV vs. Ag/AgCl wire)
• Some characteristics of electrochemically produced stain on NiFe:

  - light brown in color
  - not soluble in most solvents. Hexane can remove small amount of material in thicker deposits; pyridine can remove almost all of the deposit except a thin molecular layer
  - stain is a poor electrical conductor
  - borate buffer solution without stearic acid does not produce stain (or pitting) on NiFe when polarized up to +1500mV

• These observations suggest that metallic soaps are either intermediates in the mechanism of stain formation or components of the resulting stain

• Electrochemical corrosion of pole tips caused by lubricant hydrolysis products and head staining may be related phenomena
Possible $\text{Co}_{8.8} \text{Zr}_{7} \text{Ta}_{7}$ Electrode Reactions

- Formation of Ta oxide or stearate:
  - $\text{Ta} \rightarrow \text{Ta}^{+5} + 5\text{e}^-$

- Passivation by Co(stearate)$_2$:
  - $\text{Co (stearate)} \rightarrow \text{Co (stearate)}^+ + \text{e}^-$
  - $\text{Co (stearate)}^+ + \text{e}^- \rightarrow \text{Co (stearate)}$

- $E$ (mV vs. Ag/AgCl wire)
• Pourbaix diagrams suggest that electrochemical stability in aqueous solutions at near-neutral pH should decrease in the order Co = Ni > Fe > Ta > Zr.

• How is this trend affected by alloy composition and the presence of stearic acid?
INFLUENCE OF THIN FILM COMPOSITION
ON ELECTROCHEMICAL RESPONSE

• Specimens (compositions determined by EDAX)
  - Sputtered Co_{68}Zr_{5}Ta_{7}
  - Sputtered Co_{90}Fe_{10}
  - Plated Co_{68}Ni_{12}Fe_{23}
  - Sputtered Ni_{81}Fe_{19}

• Ag/AgCl wire “pseudo-reference” electrode

• Pt mesh counter electrode

• Test Solutions (solvent: methanol containing ~0.003M H_{2}O impurity):
  - 0.01M CH_{3}(CH_{2})_{16}COOH (stearic acid)
  - Borate buffer (H_{3}BO_{3} + Na_{2}B_{4}O_{7}) for improved solution conductivity and maintaining neutral pH
  - Air saturated, stagnant
Cathodic → Anodic Portions of Cyclic Polarization Scans
(-1000mV → +1500mV)

\[ \log_{10}(i) \] vs. E (mV vs. Ag/AgCl wire)

- **Co_{68}Zr_{16}Ta_{7}**
- **Co_{80}Fe_{10}**
- **Co_{88}Ni_{12}Fe_{23}**
Cathodic → Anodic Portions of Cyclic Polarization Scans
(-1000mV → +1500mV)

\[ i \text{ (\textmu A/cm}^2) \]

\[ E \text{ (mV vs. Ag/AgCl wire)} \]

- \( \text{Ni}_{91}\text{Fe}_{19} \)
- \( \text{Co}_{65}\text{Ni}_{12}\text{Fe}_{23} \)
Reverse Portions of Cyclic Polarization Scans
(+1500mV → -1000mV)

\[ i \text{ (µA/cm}^2\) vs. Ag/AgCl wire]
• Based on $E_{\text{corr}}$ values and currents in the passive/transpassive regions of the first half of cyclic polarization scans, alloy stability in stearic acid solutions decrease in the order

$$\text{Co}_{65}\text{Ni}_{12}\text{Fe}_{23} > \text{Ni}_{81}\text{Fe}_{19} \approx \text{Co}_{90}\text{Fe}_{10} > \text{Co}_{88}\text{Zr}_{5}\text{Ta}_{7}$$

• Stain formation is most prominent in Fe-containing alloys with both the amount of stain (determined visually) and its passivating characteristics (as measured in the second half of the cyclic polarization scan) decreasing in the order

$$\text{Ni}_{81}\text{Fe}_{19} > \text{Co}_{65}\text{Ni}_{12}\text{Fe}_{23} > \text{Co}_{90}\text{Fe}_{10} > \text{Co}_{88}\text{Zr}_{5}\text{Ta}_{7}$$

• Chemical nature of the stain is still undetermined, but it is presumed to be a metallic soap. X-ray diffraction patterns indicate the stain is either amorphous or poorly crystallized stearate.
X-ray Diffraction Pattern of Ni$_{81}$Fe$_{19}$ in Region Anodically Polarized in 0.01M Stearic Acid Solution ($\lambda = 1.790\text{	extmu}m; \alpha = 3^\circ$ fixed incident angle)

Counts (Arb. Units)

Positions of major reflections in crystalline stearic acid (JCPDS File# 38-1923)

111 (NiFe)

200 (NiFe)
SUMMARY OF Q9 RESULTS

- Thin film magnetic alloys exhibit varying degrees of stability in non-aqueous solutions containing stearic acid. For the alloys studied, those with lower levels of Fe and Ni exhibit the highest corrosion currents at anodic potentials.

- Once anodically formed, stains passivate the alloy surfaces. The passivity of the stain decreases as the Co content of the alloy increases. This may be related to the stability of the metal soap, which is presumed to be a component of the stain.

- Irreversible material losses can occur in a dynamic (i.e., rubbing) environment via reactions such as

\[ n\text{RCOO}^- + M \rightarrow (\text{RCOO})_n M + n\text{e}^- \]

but stains can passivate the alloy surfaces in stagnant environments.

- Future work will include: a) FTIR analysis of electrochemically produced stains and, b) exploring means for eliminating methanol solvent (to eliminate possible interference from side reactions).