Imaging Hidden Corrosion with SQUID Magnetometry

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Aqueous Corrosion Gordon Conference
New London, NH, 17 July 2002
What is a SQUID magnetometer?
Superconducting QUantum Interference Device (SQUID) Magnetometer

- Pickup coil coupled to a SQUID that measures the current induced in the pickup coil.
- A flux-to-voltage converter with unrivaled sensitivity (5-20 f T/Hz\(^{1/2}\))
- Spatial resolution: 1 to 3 mm (20 um max)
- Bandwidth of DC to 10’s kHz.
SQUIDS for Naval NDE and DE

http://unmuseum.mus.pa.us/kraken.htm
SQUIDs for NDE, etc.

- Intrinsic currents
- Remanant fields
- Applied currents
- Thermal currents
- Eddy currents
- Ferromagnetic and stress-related magnetization
- Diamagnetic and paramagnetic susceptibility
This airplane is supposed to fly when it is older than anyone in this room....
Aging Aircraft Corrosion Measurements Using SQUIDs

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How do you quantify hidden corrosion?

- **NDI** – detects corrosion damage and missing metal
  - Measurable material loss may take months
- **Mass Loss** – detects metal loss by weighing
  - Well-suited for determining the average rate over intervals as short as several weeks
  - Cannot be used on old lap joints or exfoliation/IGA
- **Potentiometric measurements**
  - Limited to exposed surfaces
Practical Corrosion Questions

What is the instantaneous rate of hidden corrosion? How does it depend upon?

- Humidity
- Environment (salt, etc.)
- Corrosion abatement technology
- Maintenance
- Metallurgy

SQUIDs can help answer these questions.
1 cm² KC-135
4 mils of metal lost

\[ 10^{-2} \text{cm³} \]

\[
\text{2.7g/m³} \quad \Rightarrow \quad I = \frac{M_o \cdot \tau}{2\pi r} = 100 \text{nA}
\]

\[
B = \frac{M_o \cdot \tau}{\pi r^2} = 20 \text{pT}
\]

200:1 SNR
Why use a SQUID magnetometer?

• There are no established techniques that can measure the rate of hidden corrosion

• There is little knowledge of how corrosion rates are affected by environment, structural condition, flight history, or maintenance procedures.

• Standard electrochemical techniques cannot study the instantaneous rate or distribution of hidden or exfoliation corrosion.

• SQUIDs are ideally suited to map the distribution of hidden corrosion ACTIVITY in an aircraft lap joint or wing plank

• Caution: The mechanisms by which corrosion activity produces the observed magnetic fields are not fully understood
How do you quantify hidden corrosion?
How do you quantify hidden corrosion?

- **NDI** – detects corrosion damage and missing metal
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- **Mass Loss** – detects metal loss by weighing
  - Well-suited for determining the average rate over intervals as short as several weeks
  - Cannot be used on old lap joints or exfoliation/IGA
- **Potentiometric measurements**
  - Limited to exposed surfaces
- **SQUIDs** – detects magnetic field of corrosion currents
  - Can detect *instantaneous* corrosion
  - Difficult to obtain absolute calibration
SQUID Corrosion Measurements: 1990-1995

Active Corrosion

(7075 aluminum alloy in 3.5% NaCl + 50 ppm Cu⁺ solution)

- no solution (before)
- 25 minutes
- 64 minutes
- 105 minutes
- 276 minutes
- 276 minutes
- 1403 minutes
- 2786 minutes

- no solution (after)
SQUID Sensitivity for Weak or Deep Corrosion

SQUIDs can detect corrosion of aluminum in 1 ppm NaCl

SQUIDs can detect corrosion of aluminum through 1 cm of metal or air

Conclusions from AFOSR-URI studies

• SQUIDs are suited for the periodic, non-destructive analysis of corrosion test specimens where the corrosion activity is not directly accessible to a potentiostat, *e.g.*, corrosion that is hidden under a thick coating or one or more layers of metal.

• SQUIDs may be the only technique to detect these hidden *currents* non-destructively and instantaneously.

• The external magnetic field does not reflect all of the internal corrosion activity, *i.e.*, there are field cancellation effects.
SQUID Corrosion Measurements in the Laboratory

- This is a laboratory technique for determining the rates of hidden corrosion under different conditions.
- This is NOT an NDI tool!
- It is highly unlikely that this technique can be applied to intact aircraft on the flight line!

http://seawifs.gsfc.nasa.gov/OCEAN_PLANET/SQUID/clyde_hosing_mantle.jpg
The AFCO Corrosion SQUID System
SQUID-Specific Questions

How do the SQUID data correlate with the instantaneous rate of corrosion?

How do the SQUID data correlate with total mass loss?

How do the SQUID images correlate with corrosion damage images?
How do the SQUID data correlate with the instantaneous rate of corrosion?

Start with the spatially-integrated magnetic activity (SIMA)

\[
\text{SIMA}(t_j) = \sum_{xy} |B(x,y,t_j)| \Delta x \Delta y
\]
Ideally, SIMA is proportional to the instantaneous corrosion activity, i.e. corrosion rate.
How do the SQUID data correlate with mass loss?

Use the temporally-summed spatially-integrated magnetic activity (TSSIMA)

\[ TSSIMA = \sum_j \text{SIMA}(t_j) \Delta t_j \]

TSSIMA correlates well with mass loss, but with a geometry-dependent calibration factor.
SIMA and TSMA with the UVa LJSS cocktail . . . .
Old Lap Joints

http://www.tenhand.com/squid/cuttlefish-squid.jpg
Corrosion Rates in Old Lap Joints
Protocol 3 exposure sequence

Step 1: Humid Air (98% RH)
Step 2: Distilled Water
Step 3: 0.01 M Chloride
Step 4: 0.1 M Chloride

- Bake-out before each step
- Degauss after each bake-out
- Each step is repeated three times for all specimens
SQUID Images

Step 1: Humid Air (98% RH)

Step 2: Distilled Water

Step 3: 0.01 M Chloride

Step 4: 0.1 M Chloride
Summed Magnetic Activity Versus Time for Old Aircraft Lap Joints

- Reproducible dry background
- Varied activity depending upon lap joint, corrosive solution, and time
- Reproducible dry background
Lap Joint SIMA vs Environment

![Graph showing magnetic activity over time for humid air and distilled water with 0.01-M chloride.]

- **Humid air** vs **Distilled water with 0.01-M chloride**

  - **No significant difference between distilled water and 0.01-M chloride**

  - **Significant increase in magnetic activity when quiescent, existing corrosion is re-initiated**

  - **Significantly more activity generated by distilled water than humid air**
Spot-Welded Compared with Riveted: Cumulative activity map

Riveted Specimen

Spot-welded Specimen

Can identify internal structure apparently associated with spot welds compared with that of rivets
Summed Magnetic Activity Versus Time for Old *Riveted* Lap Joints

- 0.01 M chloride shows higher activity
- Distilled H$_2$O activates the chemistry within the lap joint
- Low activity in 98% relative humidity air
Summed Magnetic Activity Versus Time for Old Spot-Welded Lap Joints

- Distilled H$_2$O activates the chemistry within the lap joint
- 0.01 M chloride shows lower activity than distilled water
- Low activity in 98% relative humidity air
Spot-Welded Compared With Riveted: Ratio of TSSIMA

- If an old lap joint is hydrated with distilled water, the chemicals already in the lap joints may be more important in the short term than what is added externally.
- There may not be a strong dependence upon the concentration of externally-applied chloride.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Spot-Welded Average</th>
<th>Riveted Average</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humid air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distilled water</td>
<td>1594% increase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01 M Cl⁻</td>
<td>50% increase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M Cl⁻</td>
<td>10% increase (not significant)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diagram:
- Spot-welded average
- Riveted average
- 11% decrease (not significant)
- 27% decrease (not significant)
- n = 4
Old Lap Joint Conclusions

• SQUIDs can make useful measurements of instantaneous electrochemical activity in lap joints that are not possible with any other technique.

• These data are reproducible phenomenological representations of corrosion activity.

• We can assess the effects of moisture and NaCl on old riveted and spot-welded lap joints.

• There may not be a strong dependence upon the concentration of externally-applied chloride.

• Kelly 1, SQUID 1
Is the magnetic signal proportional to corrosion?

http://www.tenhand.com/squid/squid1.jpg
Characterization Studies
Afshin Abedi and John Wikswo

Examine the relationship between magnetic fields and the underlying corrosion activity

• Controlled **uniform corrosion**
  – 7075-T6 aluminum disks with mylar and epoxy masks
  – NaOH for uniform corrosion
  – Control corrosion area and pH
Galvanic cell with current loop
A SQUID as a Scanning, Zero-Resistance Ammeter
Afshin Abedi and John Wikswo
Plan View and TSMA Image

- Cu
- Al
- 3.5% NaCl

mm

nT/hr

14

0
Galvanic Corrosion and a SQUID as a Scanning, Zero-Resistance Ammeter

- Spatially-integrated magnetic activity (SIMA) correlates well with the current that is required to produce the observed magnetic field in the small coil.
And how do the magnetic signals scale with corroding area and pH?
Uniform Corrosion Setup

Afshin Abedi and John Wikswo
Uniform Corrosion Setup

- 7075-T6 aluminum disks
- NaOH for uniform corrosion
- Control of corrosion area and pH
Corrosion versus Corroding Area

- Mass Loss correlates with Exposed area ($R^2=0.97$)
- TSSIMA correlates with exposed area ($R^2=0.76$)
- TSSIMA correlates with mass loss ($R^2=71$)
Corrosion versus pH (19 mm spot)

- Mass Loss correlates with NsOH ($R^2=0.89$)
- TSSIMA correlates with NaOH ($R^2=0.56$)
- TSSIMA correlates with mass loss ($R^2=55$)
- TSSIMA greater for non-uniform corrosion (red) than for uniform corrosion (blue)
Uniform vs Heterogeneous Corrosion

http://www.tenhand.com/squid/squid5.gif
Hidden, Inhomogeneous Corrosion

0.01M NaOH

Corrosive Solution

Cryogenic Dewar & SQUID

Sample

Sample Chamber

Polyurethane Wick
TSIMMA vs Mass Loss

- CMF in regular time intervals above a 70-mm diameter, 0.8-mm thick, 7075-T6 aluminum disk submerged in a 0.5-M NaOH solution.

\[ \text{TSSIMA} = 0.29 \Delta m \]

\[ R^2 = 0.90 \]
Exposed, Homogeneous Corrosion
0.1M NaOH
TSIMA vs Mass Loss

TSSIMA = 0.29 $\Delta m$
$R^2 = 0.90$

TSSIMA = 0.10 $\Delta m$
$R^2 = 0.78$
Just how sensitive are SQUIDS?

http://www.tenhand.com/squid/squid-okeanos1.jpg
The Sensitivity of SQUID Magnetometers for Determining the Instantaneous Penetration Rate of Hidden Corrosion

Robert G. Kelly, Grant Skennerton, Afshin Abedi, John P. Wikswo
Simulated Lap Joints

- 76 mm x 76 mm 2024-T3 lap joint, N=6
- Weigh
- Hi-lock fasteners
- 0.1 M NaOH
- Disassemble
- Clean
- Reweight

![Graph showing Mass Loss vs. TSSIMA (μT-mm²-hr)]

\[ y = 0.8445x - 0.9564 \]

\[ R^2 = 0.7506 \]
SQUID magnetometers can detect ..

- mass loss rates as low as 0.8 mg/cm²-y
- uniform penetration rate of 0.12 mils per year
- $3.5 \times 10^{-4}$ mils per day (3 µm/yr or 9 nm/day).
- **Kelly 2, SQUID 2**
Preliminary Tests of SQUID Detection of Exfoliation Corrosion

http://www.tenhand.com/squid/spacesquid.jpg
Preliminary Tests of SQUID Detection of Exfoliation Corrosion

Yu Pei Ma, John Wikswo

• Sample
  – Horizontal stabilizer carry through box stiffener
  – Aircraft MDS - KC-135
  – Material: 7075-T6 Forging

• Protocol
  – SQUID above flat side (side not shown)
  – Scan in air for baseline recording
  – Submerge distilled water and scan for one week
Horizontal Stabilizer Carry Through Box Stiffener with Square Registration Coil

Registration coil

Exfoliation Damage Visible on Surface
Close-Ups of Exfoliation Damage
Exfoliation Damage Visible on Surface

Ultrasound and Temporally Summed Magnetic Activity (TSMA) After One Week of Exposure

Registration coil
Conclusions – Box Stiffener Exfoliation

• SQUIDs can readily detect exfoliation corrosion in 7075 forgings
• Deb Peeler chopped up our sample… ; ( 
• Needed
  – Simpler geometry
  – Correlations of SQUID with NDE and metallography
SQUID Imaging of Exfoliation and Intergranular Corrosion

John P. Wikswo and Yu Pei Ma
Vanderbilt University

Kevin Cooper, Luna Innovations, Inc.,
James Suzel, S&K Technologies
Robert Kelly, University of Virginia
Luna/S&K/VU Protocol E1

- Samples: Kaiser 0.350 7075-T6 (lot 274371) 4” wide by 10” long, grain lengthwise.
- Holes: three 3/8” holes approximately 1/8” deep and 2” apart.
- Coated twice everywhere except sides of holes with XP-2000 sealant; 0.040-0.050 bare aluminum on hole sides
- Holes filled with ANCIT solution
- Anticipate 1-3 mm of penetration in 48-96 hours.
Sample VEX001
SQUID Images During Exfoliation Corrosion Development

- Corrosion activity visible within 5 hours of exposure and reach maximum about 7.5 hours
- Time-dependence of corrosion differs from hole to hole over short time intervals (Frame #12 vs #15, and #66 vs #69)
Exfoliation Solution

• ANCIT Solution:
  – 4 M NaCl
  – 0.6 M KNO3
  – 0.022 M AlCl3 (as AlCl3 \cdot 6H2O)
  – natural pH \sim 3 \text{ to } 3.3

TSMA for three holes (VEX001)

Holes after exposing to solution
TSMA for three holes (VEX001)

Holes after exposing to solution
SIMA for three holes (VEX001)

- 35 minutes/data point
- Maximum signals after 7-8 hours
- Arrows indicate time of adding solution to the holes
Protocol E1 Conclusions

• SQUID can see corrosion in well sample, with clear time-dependence over 96 hours
• TSMA images of individual hole is consistent with the corrosion activity
• The evaporation of solution in holes cause crystal accumulate around and inside the holes which may block the reaction.
• NDE of damage does not show intergranular corrosion.
• Kelly 2, SQUID 3
VU Protocol E2 - Edge Test

Sample: 4.8 mm thick Al 7075-T6 aluminum, 69.5 x 69.5 mm
Coated everywhere with epoxy and plastic film except 1/3 of one edge
Uncoated edge is exposed to ANCIT solution for 96 hours
Exfoliation Solution

• ANCIT Solution:
  – 4 M NaCl
  – 0.6 M KNO3
  – 0.022 M AlCl3 (as AlCl3 · 6H2O)
  – natural pH ~ 3 to 3.3

I. Initiating - eight hours after introducing solution

Upward arrows with (numbers) indicate times of each magnetic image

(1) 3.28 hour (#7)  (2) 4.55 hour (#10)  (3) 6.23 hour (#14)  (4) 7.93 hour (#18)
II. Developing --- changing polarity

Upward arrows with (numbers) indicate times of each magnetic image
III & IV. Adding new solution accelerates corrosion

Upward arrows with (numbers) indicate times of each magnetic image
Microscopic Photo

(a) Surface of the edge  
(b) Possible exfoliation  
(c) Pitting corrosion
Metallographic Examination

The exposed edge (non-masked) was the S-T plane. Arrow indicates direction of observation for metallography samples.

There is not a significant amount of attack of either of the two specimens. Low magnification visual observations are suggestive of only slight surface attack of the exposed region (i.e., non-epoxyed area). Cross-sectional metallographic examination also did not reveal visible attack, despite successive grinding, polishing and examination. Neither exfoliation nor intergranular corrosion was observed. Samples were wet polished to 1200 grit.
TSMA for Al 7075
Current Flow in
Exfoliation Test E2??

Electron Flow

+ Ion Current

Intergrannular Corrosion

Aluminum

Electrolyte
Magnetic Activities After Draining

1. Before draining the corrosion at the side surface produce a dipolar magnetic signal.

2. 24 hours after draining the corrosion continues and the signal becomes a monopole.

3. The corrosion develops into the metal, even the cross-sectional metallographic examination did not reveal visible attack.
Possible Intergranular Corrosion Activity After Draining

(28) 25.91 hrs after draining

Macroscopic electron flow

Microscopic electron flow

Aluminum
Protocol E2 Conclusions

• Edge-exposed square sample with square fluid reservoir
  – Simple geometry will allow quantitative analysis
  – Readily accessible corrosion face for damage characterization
  – Epoxy-Mylar coating more effective than red paint
    • Mechanically robust
    • Blocks corrosion
    • Can be removed chemically

• Distinct magnetic signature from corrosion
  – Field distribution correlates with exposed corrosion edge
  – Temporal fluctuations in activity correlate with addition of solution
  – Corrosion activity reaches steady state in approximately 24 hours
  – Ideal for tracking response to environmental change

• Neither exfoliation nor intergranular corrosion was observed

• Kelly 2, SQUID 4
Proposed SQUID Exfoliation E3 Geometry

Noble metal Cathode

Electron Flow

B_{out}

+ Ion Current

Intergranular Corrosion

B_{in}

Aluminum

Electrolyte

Noble metal Cathode
There are, however, some loose ends..

http://courses.washington.edu/mb351/squid02/dsc02865.jpg
The measured magnetic fields are one to two orders of magnitude smaller due to cancellation of fields from small-scale corrosion circuits.
Problem

- A zeroth-order model of corrosion has a thin electrochemical layer between two metallic sheets, with the electrochemical current perpendicular to the layer.
Simple vector calculus shows...
Three models for corrosion currents that produce magnetic fields
A very small demonstration...

http://www.tenhand.com/squid/carribean-reef-squid.jpg
Uniform Corrosion Test, Insulated, Off-Center Hole, E26-S39
SQUIDs see current flowing though out the metal, and are sensitive to when the current is deflected by internal conducting boundaries.
Effects of Geometry on Magnetic Signals Due to Corrosion

http://www.ucpress.edu/books/pages/8342/squid.html  Loligo Opalescens.jpg
Effects of Geometry on Magnetic Signals Due to Corrosion

Eimutis Juzeliunas,
John P. Wikswo, and Yu Pei Ma
Institute of Chemistry, Lithuania
Vanderbilt University
The experimental setup of the magnetic imaging system for static electrolyte flow conditions in 2024 Al
Experimental Set Up
Measurement Cell

AA 2024 sample under G-10 cover

corrosion cell (plexiglass)
solution outlet

rubber seal

solution inlet

sample A

sample B

sample C
Sample

AA2024 sample in naturally aerated 3.5% NaCl solution
Four Measurements

Asymmetric sample A (SIMA = 147 nTmm²)

Symmetric sample B (SIMA = 34 nTmm²)

Sectioned asymmetric sample C (SIMA = 28 nTmm²)

0.1 mA current through sample A
Geometry Conclusions

- Asymmetric sample A produces a larger magnetic signal than does symmetric sample B. The ratio is 147/34 (4/1).
- Due to the dish geometry, the magnetic signal is mainly due to the electron flow inside the AA 2024 sample.
- The corrosion reaction causes a potential difference inside the Al sample associated with the electron flow inside the sample.
- The sectioned sample shows localized current flow which produces much less magnetic signal.
- ?? Does the corrosion rate depend upon geometry? Mass loss measurements are required!
Summing it up…

http://www.tenhand.com/squid/illex.jpg
What have we learned?

• We can image the magnetic fields from hidden corrosion
• Since we are measuring current, we have an instantaneous indication of corrosion activity
• Magnetic fields can detect corrosion currents associated with nA/cm voltage gradients in metals
• We are very sensitive to metal/insulator edges
• For a given geometry, the summed magnetic activity is proportional to mass loss
• There are cancellation and symmetry effects that deserve careful attention in experimental design and data analysis/interpretation
Future Studies

- Noble metal cathode to drive exfoliation/intergranular corrosion
- Correlate SQUID data with corrosion damage
- Examine factors that affect intergranular corrosion rate
  - Solution chemistry
  - Corrosion prevention compounds
  - Alloy preparation
  - Sample thickness and rolling direction
  - Temperature
- Examine samples with long-term corrosion
  - Signals from deep penetration
  - Dependence on deep corrosion rate on external environment and baking
  - Spatial correlation between TSMA and extended corrosion damage
- Current imaging instead of TSMA
- Higher spatial resolution SQUID images with SQUID microscope
Future Studies, Con’t

- Magnetic fields from streaming currents/potentials
- Dependence of corrosion on oxygen and flow
- Biofilms
- Corrosion inside copper pipes
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– S&KT (John Wensits)

Collaborators
– Yu Pei Ma, Afshin Abedi, Grant Skennerton, Delin Li (Vanderbilt)
The Mathematics of Magnetic Imaging

The Law of Biot and Savart

\[ \mathbf{B}(\mathbf{r}) = \frac{\mu_0 I}{4\pi} \oint \mathbf{d}l' \times \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \]
SPATIAL FILTERING AND CURRENT IMAGING
THEORETICAL APPROACH

\[ J_s(x, y) \quad (a) \]

\[ \text{FFT} \]

\[ j_s(k_x, k_y) \quad (b) \]

\[ \text{filter} \]

\[ \mu_d \frac{k - k_z}{2k_y} \]

\[ v_z(k_x, k_y) \quad (c) \]

\[ \text{FFT}^{-1} \]

\[ B_z(x, y) \quad (d) \]

\[ \text{Add Noise} \]

\[ J_s(x, y) + \text{Noise} \quad (h) \]

\[ \text{FFT}^{-1} \]

\[ j_s(k_x, k_y) + \text{noise} \quad (g) \]

\[ \text{window} \]

\[ \frac{1 + \cos \frac{k - k_z}{k_{max}}}{2} \quad k < k_{max} \]

\[ 0 \quad k > k_{max} \]

\[ \text{filter}^{-1} \]

\[ \mu_d \frac{2k_y k_z}{k_{max}} \]

\[ v_z(k_x, k_y) + \text{noise} \quad (f) \]

\[ \text{FFT}^{-1} \]

\[ B_z(x, y) + \text{Noise} \quad (e) \]