SQUID Imaging of Exfoliation and Intergranular Corrosion

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What is the instantaneous rate of corrosion?
How does it depend upon?
• Humidity
• Environment (salt, *etc.*)
• Corrosion abatement technology
• Maintenance
• Metallurgy

SQUIDs can help answer these questions.
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
- **SQUIDs** – detects magnetic field of corrosion currents
  - Can detect *instantaneous* corrosion
  - Difficult to obtain absolute calibration
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 crevice 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.
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 fT/Hz$^{1/2}$)
- Spatial **resolution**: 1 to 3 mm (20 um max)
- **Bandwidth** of DC to 10’s kHz.
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.
The AFCO Corrosion SQUID System
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!
How do the SQUID data correlate with the instantaneous rate of corrosion?

Start with the spatially-integrated magnetic activity (SIMA)

\[
\int_{X}^{Y} \int_{Y}^{X} = \text{SIMA}
\]

\[
\text{SIMA}(t_j) = \sum_{xy} |B(x,y,t_j)| \Delta x \Delta y
\]
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)

$$TSSIMA = \sum_j SIMA(t_j) \Delta t_j$$

TSSIMA correlates well with mass loss, but with a geometry-dependent calibration factor.
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

- Significant increase in magnetic activity when quiescent, existing corrosion is re-initiated.
- No significant difference between distilled water and 0.01-M chloride.
- Significantly more activity generated by distilled water than humid air.

Legend:
- Red triangle: Humid air
- Blue diamond: Distilled water → 0.01-M chloride
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 H₂O 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.
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.
Objective: Exfoliation/IGA

Demonstrate that SQUID magnetometry can provide information regarding the time course of exfoliation/intergranular corrosion attack in aluminum
Preliminary Tests of SQUID Detection of Exfoliation Corrosion

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

Registration coil

Exfoliation Damage Visible on Surface

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Conclusions – Box Stiffener Exfoliation

• SQUIDs can readily detect exfoliation corrosion in 7075 forgings

• Needed
  – Simpler geometry
  – Correlations of SQUID with NDE and metallography
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
Exfoliation Solution

• **ANCIT Solution:**
  – 4 M NaCl
  – 0.6 M KNO3
  – 0.022 M AlCl\(_3\) (as AlCl\(_3\) \cdot 6\text{H}_2\text{O})
  – natural pH ~ 3 to 3.3

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)
SIMA for three holes (VEX001)

- 35 minutes/data point
- Maximum signals after 7-8 hours
- Arrows indicate time of adding solution to the holes
TSMA for three holes (VEX001)

Holes after exposing to solution
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.
- NDE of exfoliation damage does not show intergranular corrosion.
- The evaporation of solution in holes cause crystal accumulate around and inside the holes which may block the reaction.
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

SIMA for Al 7075

- 96 hours elapsed time for the experiment
- ~30 minutes per image and hence SIMA data point
- Maximum signal after 9-10 hours

Downward arrows indicate times of adding solution to the chamber
I. Initiating - eight hours after introducing solution

Upward arrows with (numbers) indicate times of each magnetic image
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
TSMA for Al 7075
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.

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.
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
Future Studies

- Noble metal cathode to drive exfoliation/intergranular corrosion
- Correlate SQUID data with corrosion damage
- Examine factors that affect intergranular corrosion rate
  - Temperature
  - Solution chemistry
  - Corrosion prevention compounds
  - Alloy preparation
  - Sample thickness and rolling direction
- 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
Proposed SQUID Exfoliation Test Geometry

Noble metal Cathode

Electron Flow

B<sub>out</sub> + Ion Current

Intergranular Corrosion

Aluminum

Electrolyte

Noble metal Cathode
We will see the time course of exfoliation/intergranular corrosion
From the Lap-Joint and Box Stiffener studies, we anticipate spatially resolving exfoliation/intergranular corrosion activity!

Riveted Specimen

Spot-welded Specimen
Future Studies

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What Will We Learn?

• Transient driving forces for intergranular/exfoliation corrosion
• External modulation of corrosion rate
• Comparisons to address Critical Unknowns
  – Metallurgy
  – Preexisting damage
  – Onset/offset rates
  – …. 