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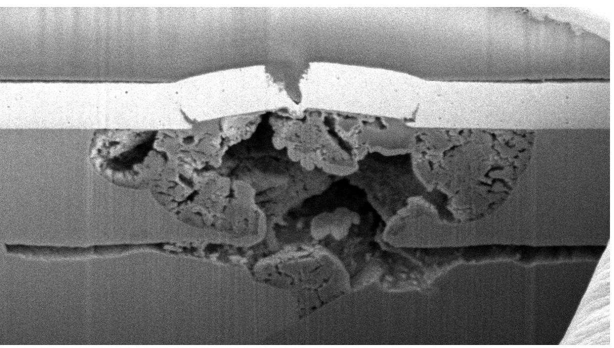
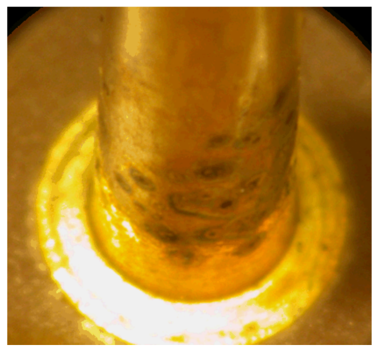
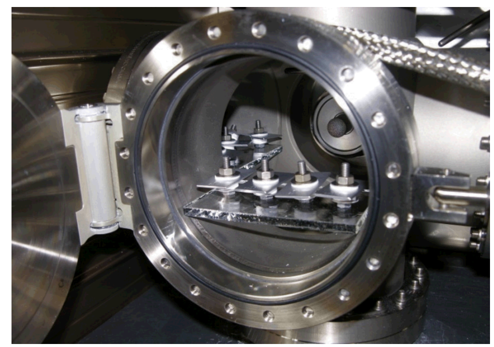
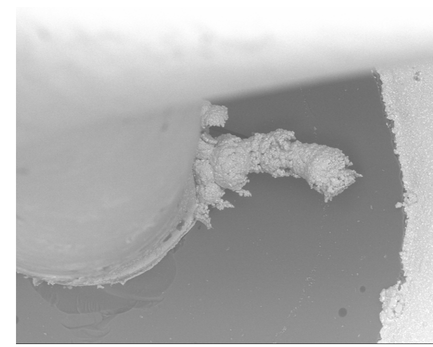

Novel Techniques for the Evaluation of Atmospheric Corrosion

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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What is Corrosion?

- Corrosion is the time-dependent degradation of a materials ability to perform its intended function
  - Generally an electrochemical process for metals
  - Loss of material
  - Reduction of mechanical properties
  - Alteration of surface chemistry/properties
  - Mechanical failure (e.g., cracking)
- The nature of the problem varies depending on the application
- Impact of corrosion can be devastating

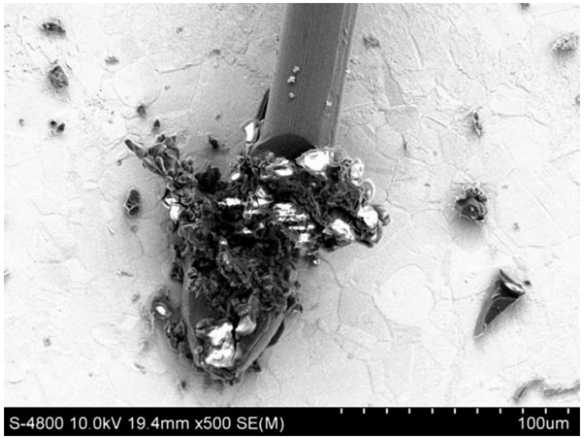
Corrosion Environments

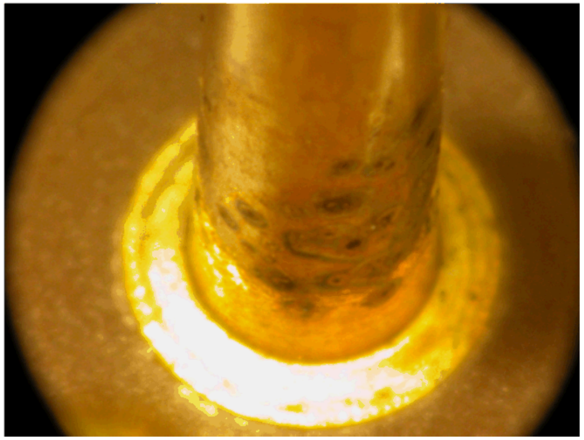
- The corrosion environment determines both the nature of the attack ***and*** the tools that can be used to characterize the relevant processes
- ***Inundated***
  - Bulk liquid phase present and typically controls corrosion reactions
  - Allows use of traditional electrochemical techniques
- ***Atmospheric***
  - No bulk electrolyte
    - Surface environment is defined by the moisture content in the air, as well as contaminants which are delivered either as a gas or as a solid particulate
  - Often the corrosion product causes failure, though for some devices the corrosion can be structural in nature
- ***Primary corrosion mechanism for stockpile applications is atmospheric corrosion***.

Atmospheric Corrosion of Electrical Devices

High Consequence, but Difficult to Interrogate

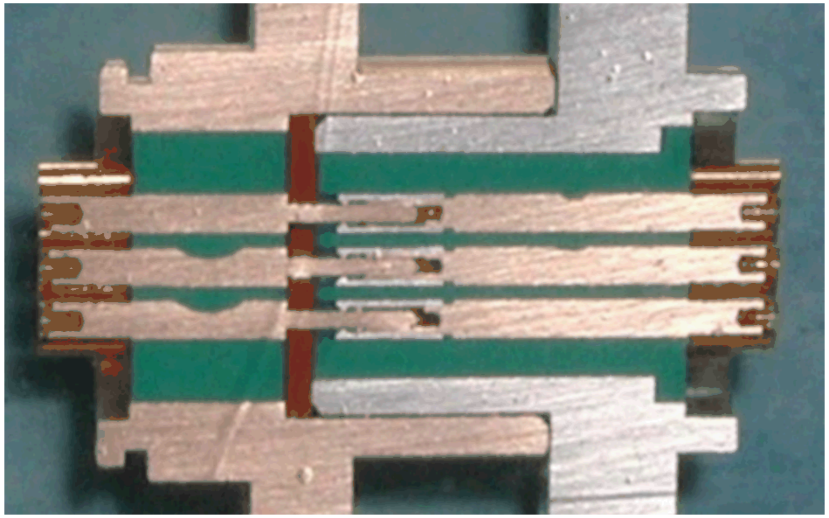
- In microelectronic devices, very small amounts of attack can have a significant impact on performance

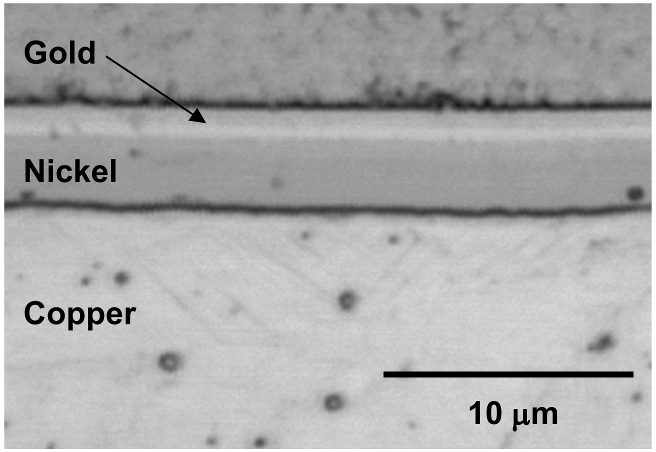




- Conventional approaches to the evaluation of atmospheric corrosion are limited in their ability to quantify the corrosion process in-situ
  - Left with periodically interrupted environmental exposures, or experiments where the corrosion process must be viewed indirectly.

Connector Performance can be Significantly Altered by Corrosion





- Typical connector is noble metal (Au over Ni) plated copper
- Plating is done to provide a high reliability electrical contact
- Unfortunately, plating isn't perfect

Why We Worry About Connectors

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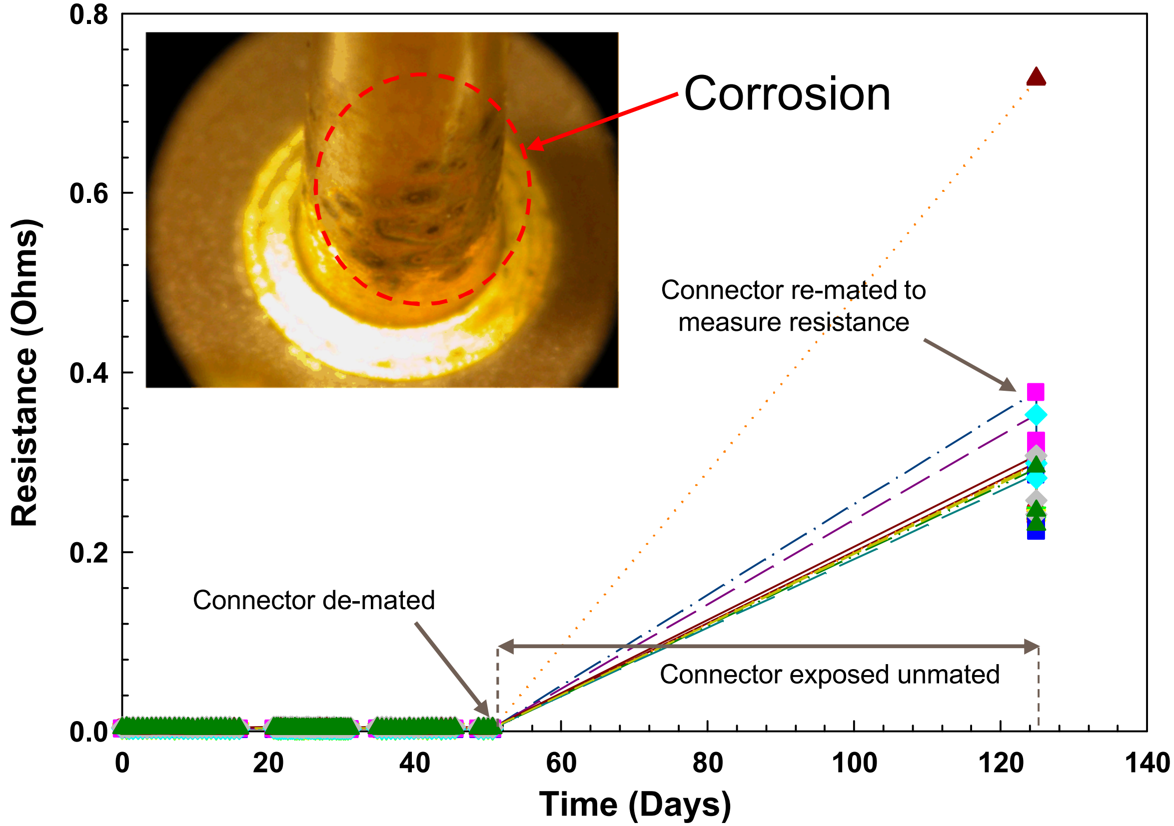
- Gold plated connectors are not unique to the stockpile, NW requirements are differentiating.
  - Very long lifetimes (25+ years) with no diagnostic information
  - Un-energized until they have to work
  - Very high reliability essential
- Industry-driven studies have different priorities
  - Electrical response
  - How thin can we make the gold and still last 5 years…
- A detailed understanding of the degradation process is required for assuring reliability
  - An empirical understanding is not enough!
  - Need an accurate, predictive model to capture long term performance

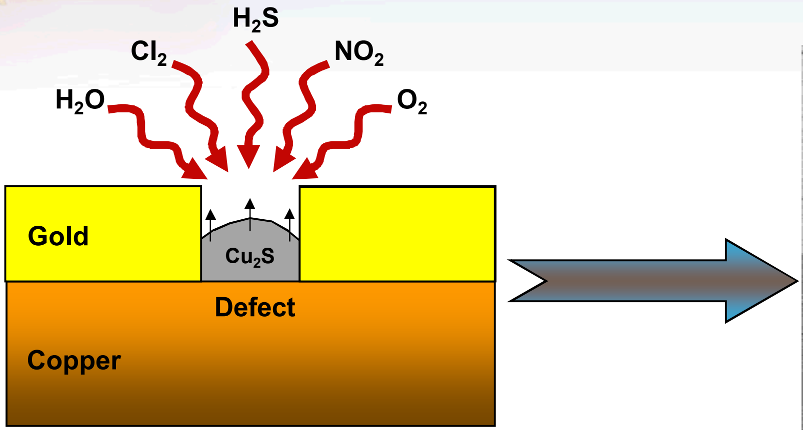
Connector corrosion increases resistance, degrading their signal carrying capability

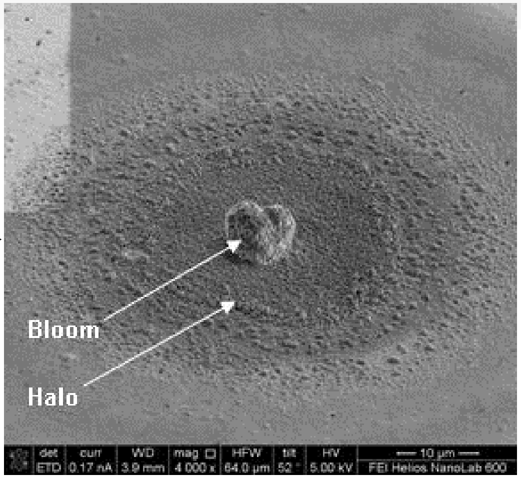


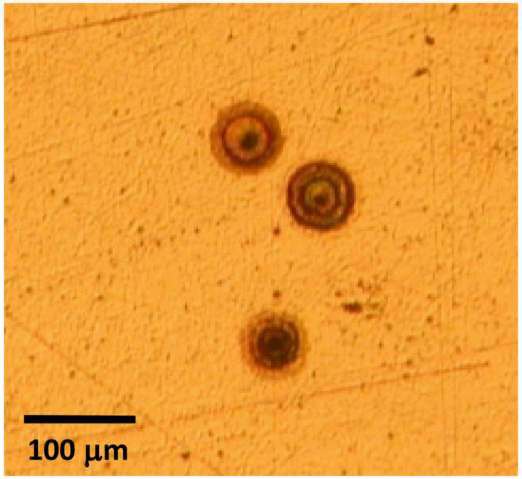
A gold plated connector exposed to a corrosive environment that accelerates corrosion in a relevant way.

- While unmated, significant sulfidation occurred
- Significant increase in resistance upon re-mating the connector.

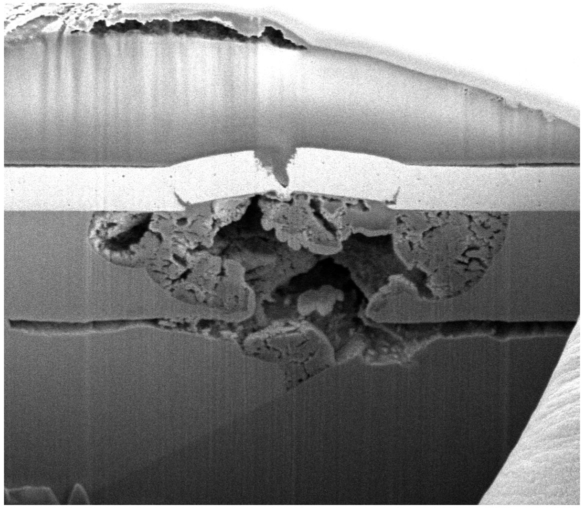
Corrosion Morphology





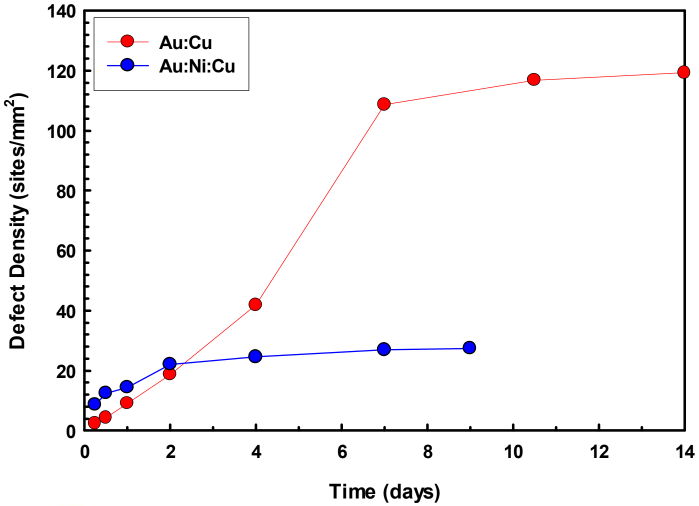


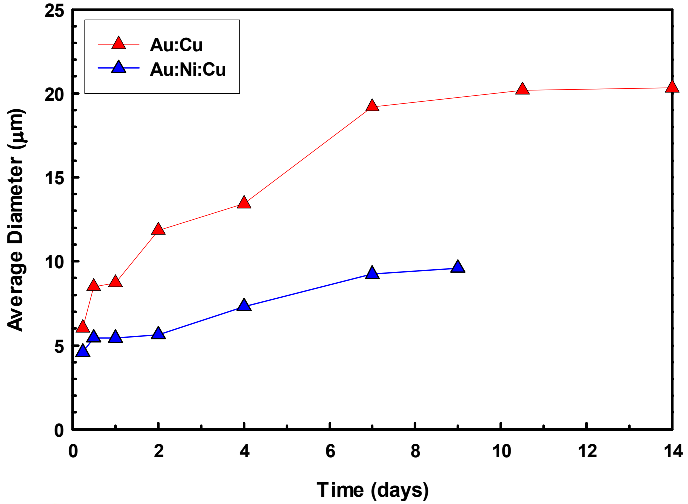
- Contaminants migrate through defects to the underlying copper where they cause corrosion (sulfidation)
- Corrosion product (copper and nickel sulfide) erupts through the defect in the gold
- The sulfide layer is an insulator, so the resistance of a contact made to that surface increases

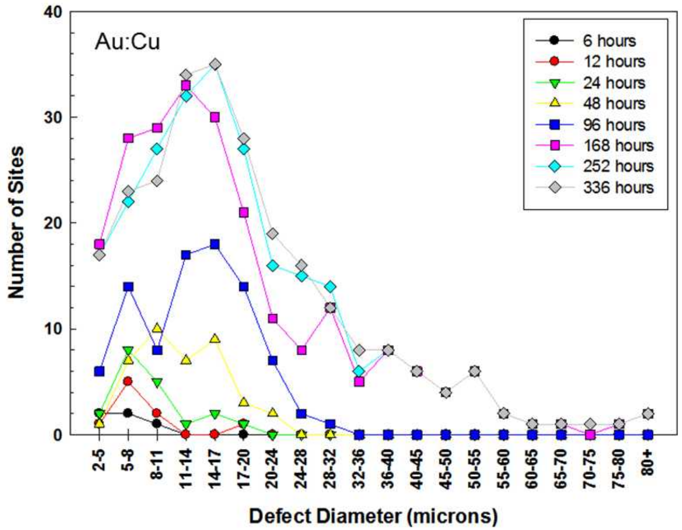


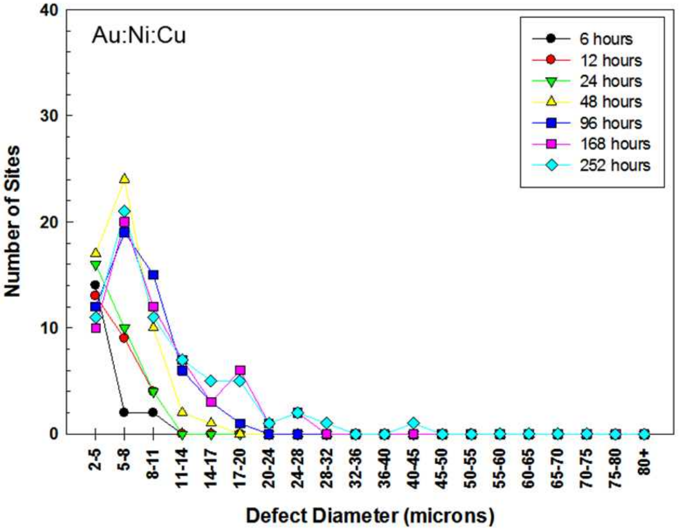
Characterization of the Corrosion Process

- Extensive testing performed to manually characterize the nature of the corrosion process
- Limited ability to assess the behavior of individual sites or to observe corrosion initiation
- Some parameters (e.g., induction time) very difficult to assess









Modeling the Corrosion Process

- Modeling the sulfidation process and it's impact on the overall performance of a gold plated copper connector requires that a number of key phenomena be captured

Bloom Growth Sub-Model
Time dependent probability distribution corrosion sites

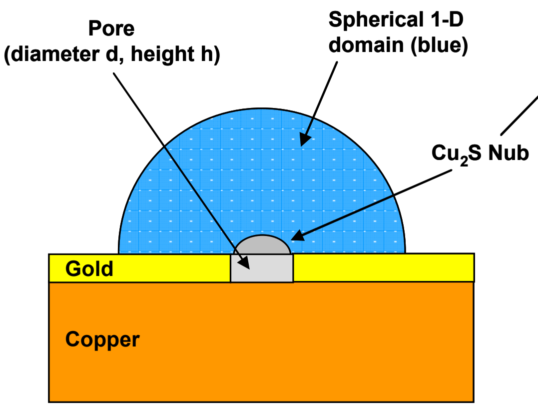
→

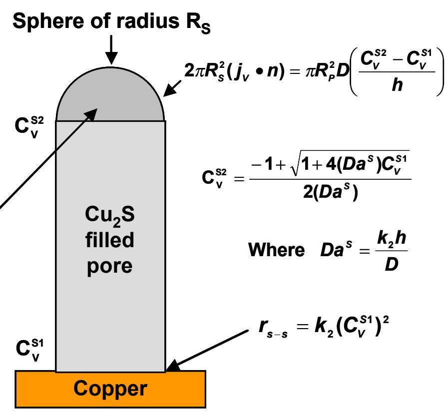
Morphology Sub-Model
Thickness of corrosion product
Distribution of large blooms

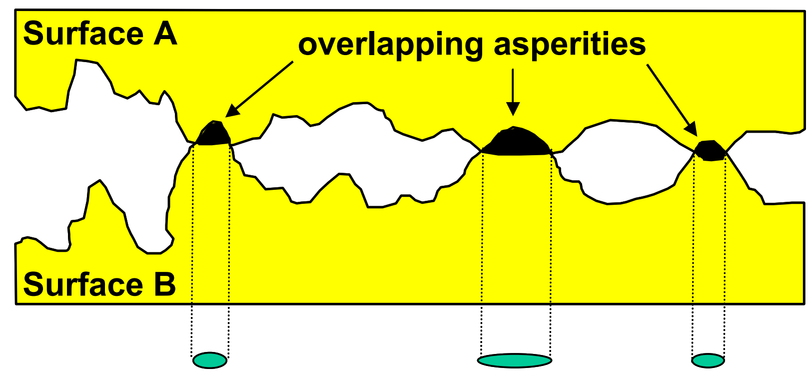
→

Contact Resistance Sub-Model
Cumulative probability distribution of contact resistance as a function of time and environmental conditions

ASC Model (*H. Moffat, A. Sun*)



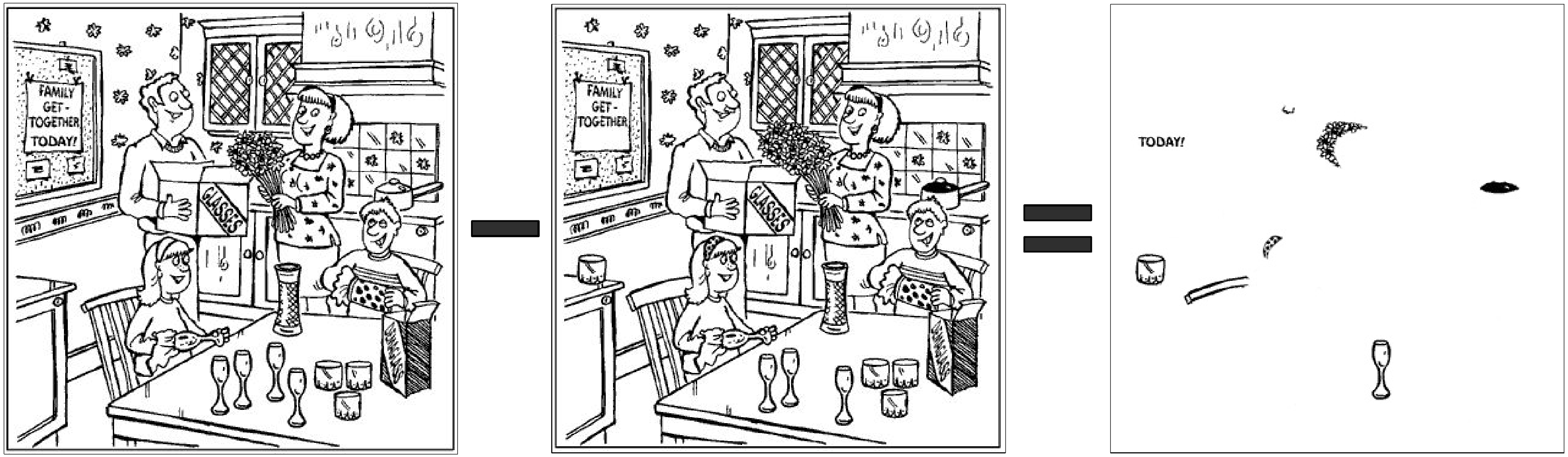




- Many parameters to characterize, but limited data of low fidelity available
- A tool was needed that would enable real time observation of the corrosion process

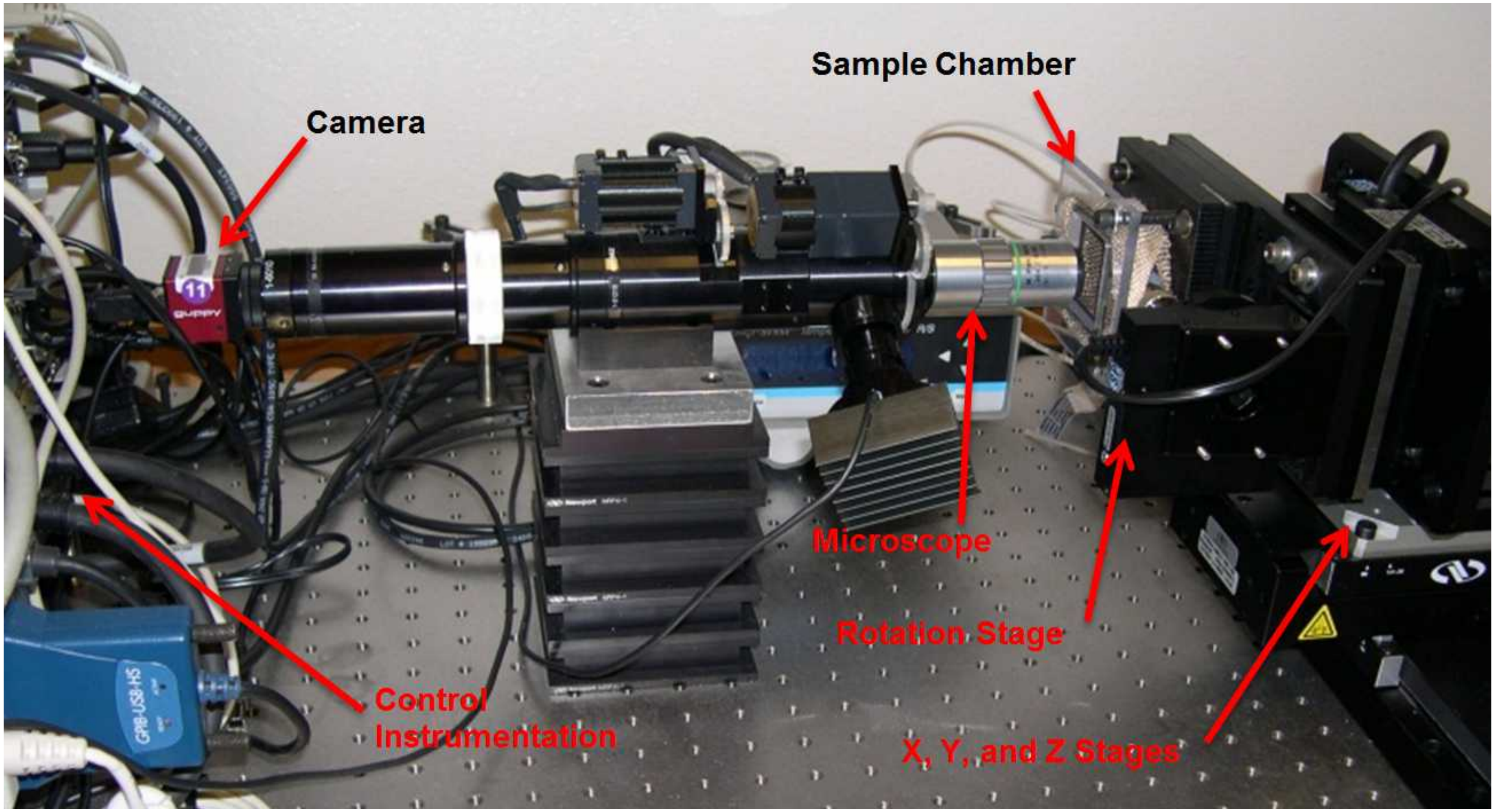
Differential Imaging Technique Developed to Address Data Needs

- Subtraction of an image taken at time *t* from an image taken at time *t+Δt*
  - Eliminate portions of the image which do not change
  - Resultant image nominally contains only those aspects which have changed
  - Can be applied to any imaging technique – not just optical



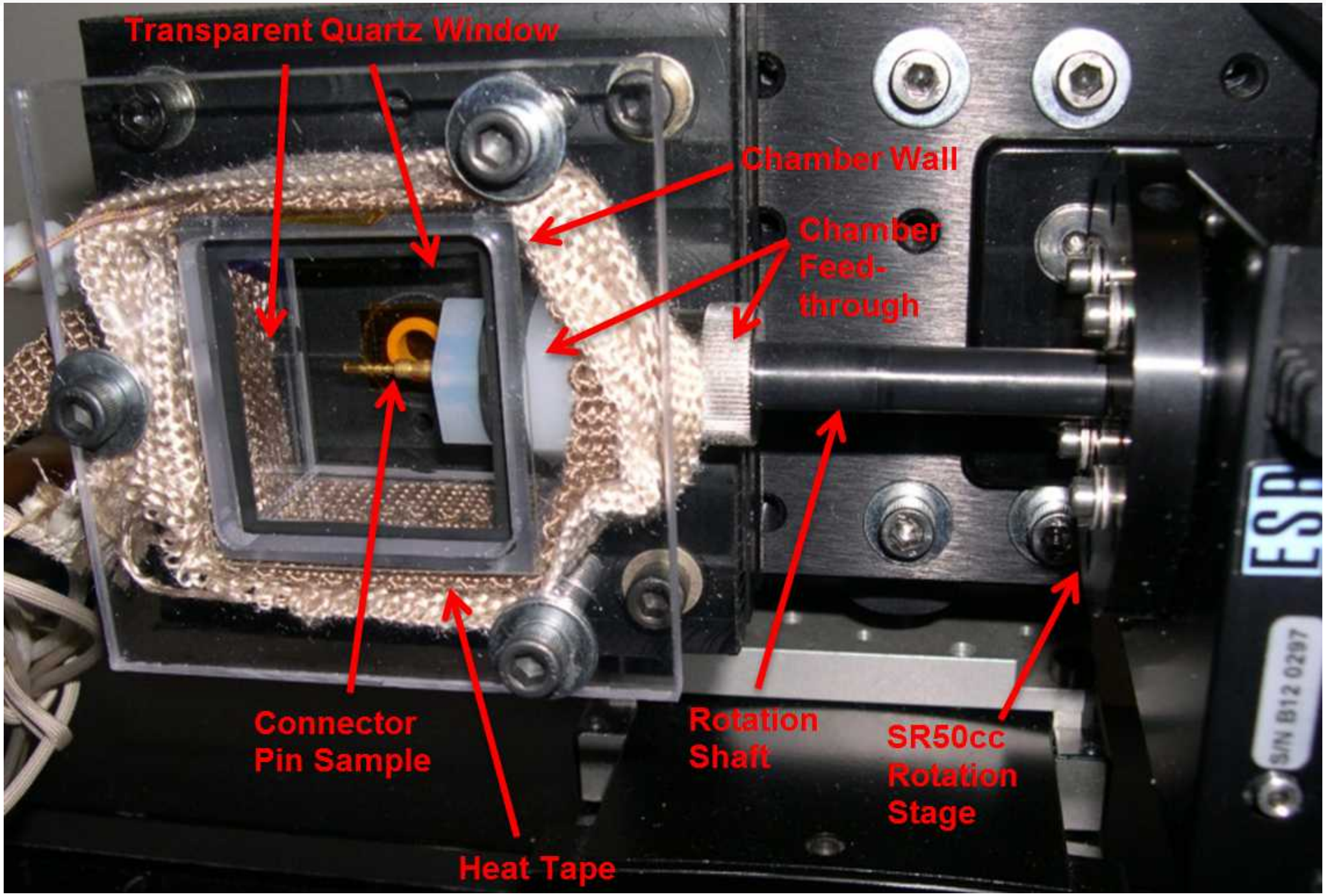
Overall System Configuration

- System is a combination of a precision microscope, an environmental chamber, and a suite of control/analysis software



The Exposure Chamber

(One Example)

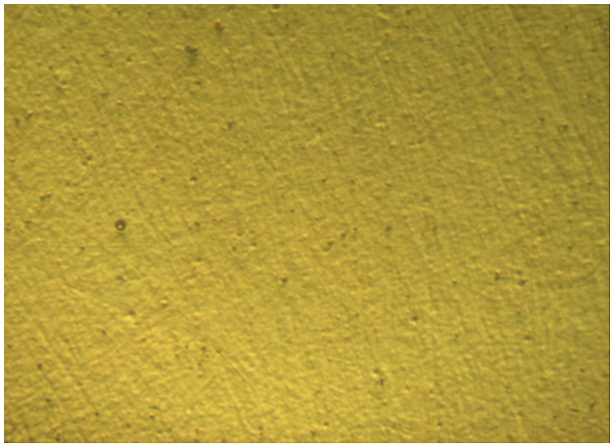


- Chamber design can be tailored to evaluate a wide range of sample geometries

Data Acquisition and Image Analysis Software

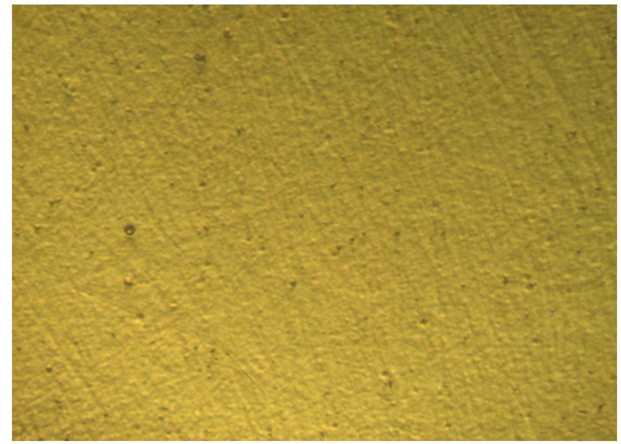
Resolving Individual Defects

Initial Surface (A)



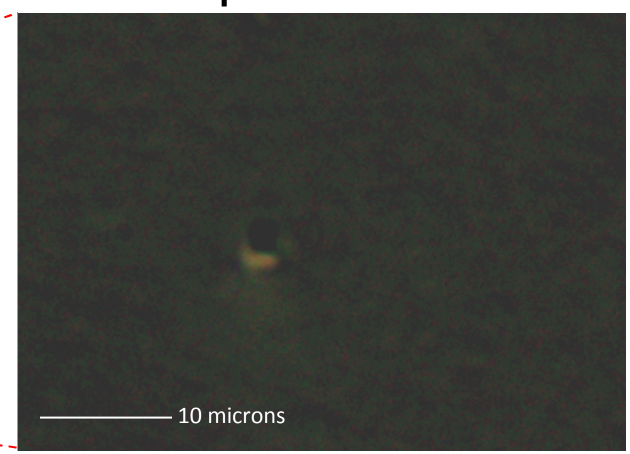
Time

Aged Surface (B)

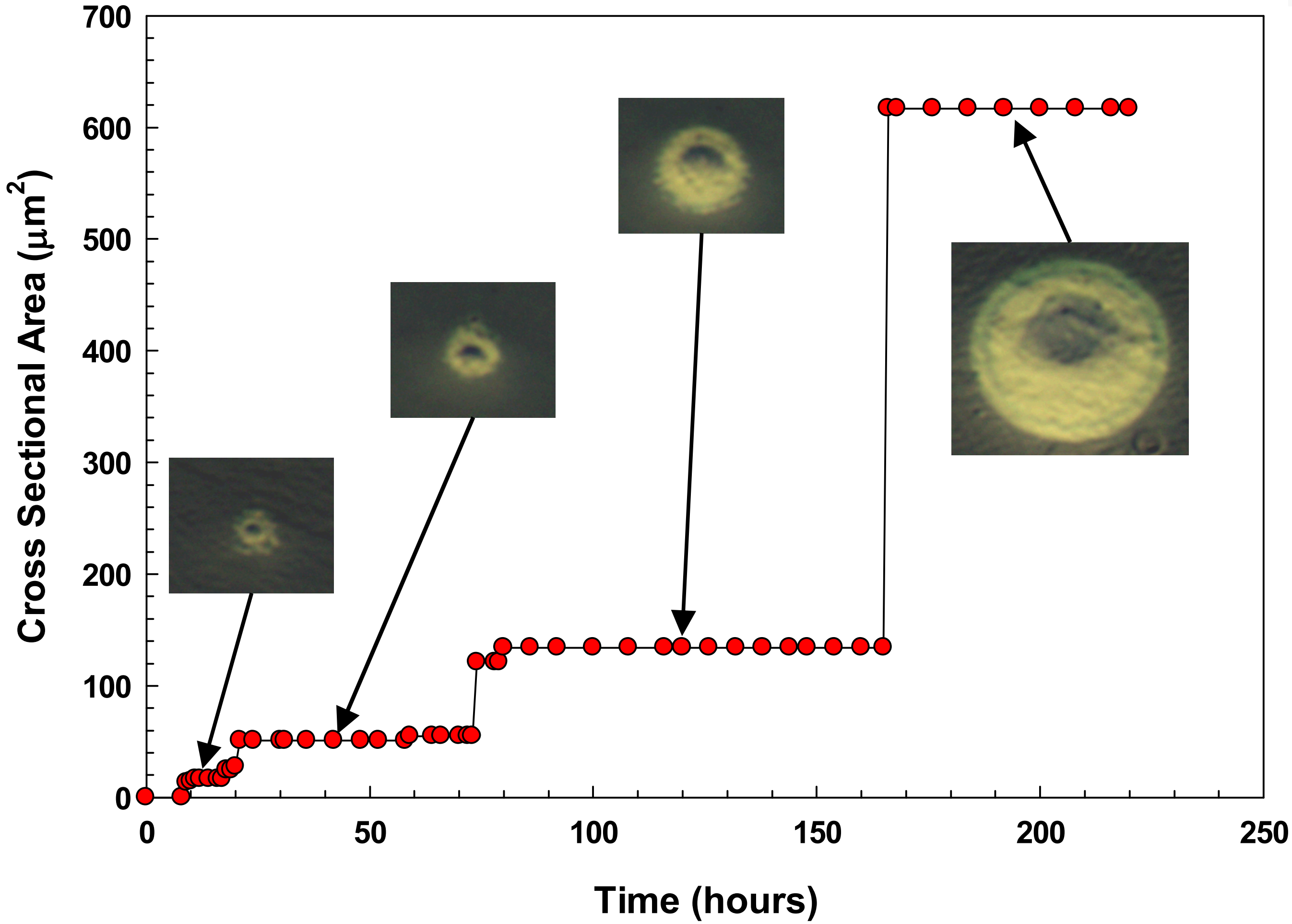


Subtracted Image (B – A)

Close-up of Corrosion Site



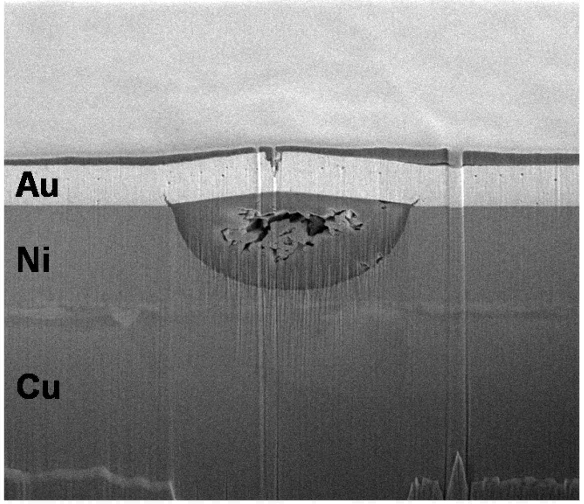
Differential Imagine Enables us to Characterize Individual Corrosion Sites

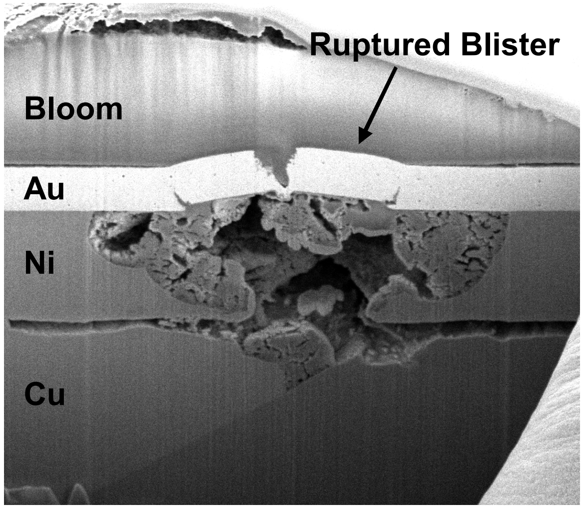


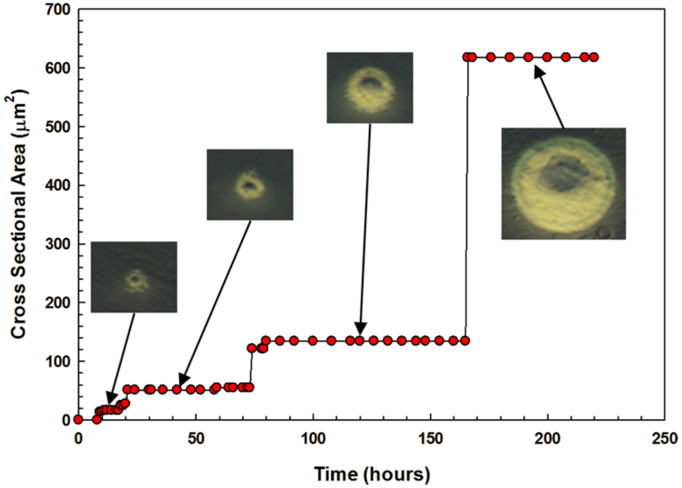
- Growth process is not linear as past studies and prior literature had indicated.

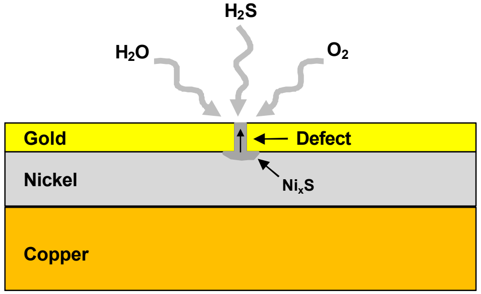
- ***New Discovery***: Non-linear (stepped) growth kinetics
- Now able to quantify key kinetic parameters such as corrosion induction times

Physical Basis for the Multi-Stage Growth Process

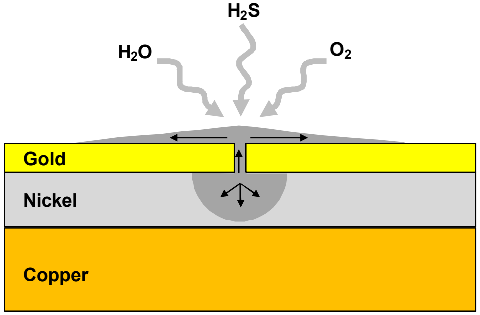




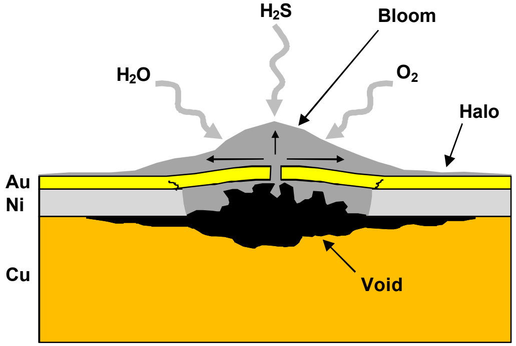




Initiate at defect in Au



Corrosion propagates into Ni



Once Ni is breached, attack of Cu begins – corrosion product erupts onto surface

What Happens When the Cu is Removed:

Early stage growth is similar for Au:Ni plated Alloy 52

3 Weeks, Battelle Class 2 – **Pre-Exposure** = **Corrosion Sites**

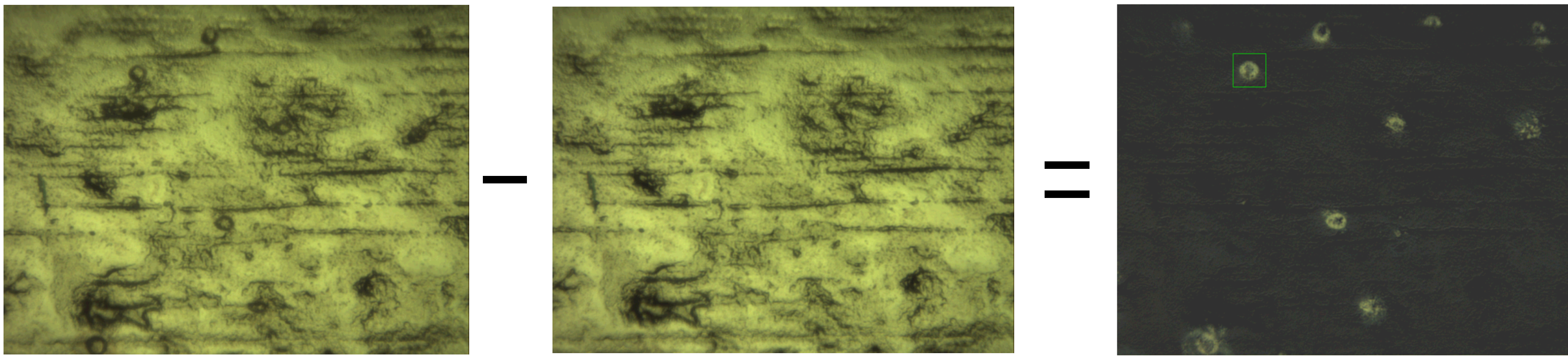


Image width = 250 µm

- Validation of proposed stepped-growth model
  - Take away the copper, and the large increase in the corrosion product layer is not observed
- Images on connector pin shown here demonstrates the ability of the differential imaging system to deconvolute pre-existing surface features from corrosion sites

Improving the Existing Corrosion Model

- What do we do with this new information?
  - Recall – kinetic data available was low fidelity and had an undesirable user bias to it

Bloom Growth Sub-Model
Time dependent probability distribution corrosion sites

Morphology Sub-Model
Thickness of corrosion product
Distribution of large blooms

Contact Resistance Sub-Model
Cumulative probability distribution of contact resistance as a function of time and environmental conditions

Addressing several key areas

- Kinetics of the growth process (stepped vs. linear)
- Induction period of multiple sites
- Number density of pore sites (unbiased assessment)
- Pore size distribution (unbiased assessment)

Summary and Conclusions

- Corrosion of microelectronic connectors has been a significant issue for NW applications
  - Ability to gather reliable kinetic information was limited
  - Existing toolset was insufficient to develop the data needed to create an accurate predictive model.
- Differential imaging system has been developed that enables samples undergoing atmospheric corrosion to be imaged in real time
  - New insights into the corrosion mechanism (e.g., growth process)
  - High fidelity measurements of key parameters (e.g., number density and size distribution of corrosion sites)
- New measurements being integrated into the existing model to improve its ability to be predictive.