Rust with 21st Century Tools

L. D. Marks
Northwestern University
Astor Lecture
Acknowledgements I

Ahmet Gulec  Xiao-xiang Yu  Yifeng Liao  James Rondinelli
Acknowledgements II

Pooja Panjiri

Alex Lin

Yifeng Liao

Emily Hoffman
Suppose every human vanished

Wait 10,000 years, what would be left?

Plastics -- some
Buildings – crumbled
Metals – almost all gone

Except 4th Century Iron Pillar in Delhi protected by a thin iron hydrogen phosphate hydrate¹ due to a high level of phosphorus in the cast iron.

Estimated corrosion of the pillar is 50-500 μm over 1600 years

Understanding Atomic Scale Structure in Four Dimensions to Design & Control Corrosion Resistant Alloys

Corrosion

~ $1 Trillion/year

Nanoparticles

$20-70 Billion/year

Corrosion versus Nanoparticles Publications
Corrosion effects many materials
Arthritis and Hip Replacement

Cause of Disability (U.S. 2005)

8.5 M (19%)

- Arthritis or rheumatism
- Heart trouble
- Mental or emotional problem
- Deafness or hearing problem
- Blindness or vision problem
- Cancer
- Back or spine problems
- Lung or respiratory
- Diabetes
- Stiffness
- Stroke
- Others
Intergranular Corrosion of CoCrMo implants

Images courtesy of J. Jacobs, Rush
Understanding Atomic Scale Structure in Four Dimensions to Design & Control Corrosion Resistant Alloys

Multiple processes occurring over wide spatial and temporal scales control the nucleation, stability, and utility of oxide scales. An integrated multiscale modeling combined with real and reciprocal space experimental characterization tools is required to fully understand and predict corrosion processes.
Some of the gaps

Many surface science studies

Atoms  Atom Clusters  Nanometer scale defects  Micrometer scale defects  Mesoscale defects

0.1 nm  1 nm  10 nm  100 nm  1 µm  10 µm  100 µm

Exp

Model

Understanding Atomic Scale Structure in Four Dimensions to Design & Control Corrosion Resistant Alloys
The Opportunity

There has been an explosion of tools to image materials at the atomic scale and accurately calculate their behavior.

Combine advanced characterization and theory to solve complex problems.
Overview: Three Topics

- What is Corrosion?
- Theoretical Results for a New Early Stage Mechanism
- Corrosion at the Multiscale: Grain Boundary Sensitization of CoCrMo Hip Implants
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What is Corrosion?

A process in which a solid, especially a metal, is eaten away and changed by a chemical action, as in the oxidation of iron in the presence of water by an electrolytic process.

Collins English Dictionary

Example:

Iron going to Iron Oxide (Rust)

Rusted Deck and Ventilation
Equipment
Source: www.corrdefense.org
Basic Chemical Components

- Oxidation of a metal by the environment – typically O₂ either at high temperatures or in aqueous environment

\[ M + \frac{1}{2}O_2 \rightarrow M^{2+} + O^{2-} \rightarrow MO \text{ thin film} \]

- Growth of the metal oxide thin film limits the use of the metal in service

Typical protective Cr₂O₃ layer on NiCrAl superalloys
Oxide growth

Nucleation (~1nm)
Surface Chemistry and Structure matter

Thin scales (~10nm)
Strong electric field drives the oxide growth.

Intermediate
Complex region, not as yet well understood in detail

Thick scales (>1μm)
When the scale thickness greatly exceeds the Debye length, growth is well described by the Wagner theory.¹

¹Wagner. Phys. Chem. B 1933, 21, 25
³Xu., Rosso, & Bruemmer. PCCP. 2012, 14(42), 14534–9.
⁴Cabrera and Mott, Rep. Prog. Phys. 12, 163
Typical Failure Mechanisms

Occur via a runaway of corrosion locally

Pitting corrosion
Often around defects, precipitates

Crevice Corrosion
Trapped solution, pH can go small (very acid)

\[ M^+(aq) + H_2O \rightarrow MOH + H^+ \]
Typical Failure Mechanisms

Intergranular Corrosion
Often called “sensitization”
Literature says it is due to reduction of protective elements (e.g. Cr) in ~100 nm around grain boundaries

Stress Corrosion Cracking
Combination of normal corrosion + stress, sometimes due to hydrogen incorporation but can be more complex
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The Cabrera-Mott Model

- Electrons pass freely from the metal to the oxide surface to ionize oxygen
  - Creates a **uniform** field within the oxide, which leads to a shift in the Fermi level of the oxide

\[
D = (\text{coverage})(\text{charge})_{\text{surface}}
\]

![Diagram of ideal surface, oxide film, and grounded electrode with O2 pressure. A layer of adsorbed ions provides the surface charge and the voltage across the oxide.](image)
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Band structure evolution

**BEFORE Absorption**

- $E_{v_{ac}}$
- $E_{CB}$
- $E_{F}$
- $E_{G}$
- $E_{VB}$

**O$_2$ 2p level**

**TM 3d – O 2p**

**surface**

**metal**

**oxide**

**AFTER electron transfer + absorption**

- $1/2O_2(Gas) + 2e(Metal) \rightarrow O_2^-$
- $\Delta V=1-3V$
- Mott Potential

- O$_2$ 2p level

- Electric field = $V/x$ (MV/cm or $>$)

Microscopic mechanisms

- Energy gain due to work function difference between metal and oxygen, plus attractive Coulomb potential of negative $O^{n-}$ and metal
- Energy gain drops as oxide thickness increases
- Potential difference drives ionic transport across the oxide film

### Oxygen interstitials
- Into oxide

### Oxygen vacancies
- Out

### Metal interstitials
- Into oxide

### Metal vacancies
- Out

### Electron (hole) transport
- Across the film
Cabrera-Mott model

Issues

- Is this general?
  - Other oxides?
  - Other structures, surfaces?
- Does is matter which oxide is used?
  - Al₂O₃ has Al³⁺ -- which has no available electrons
  - Most relevant oxides involve transition metals, with partially filled d-bands
Consider a more complex model

- KISS (Keep it Simple Stupid) model
- Base metal, Al, fcc

- NiO – simple cubic, albeit slightly complex electronic structure

- Assume simple cube-cube epitaxy, bulk Al lattice parameter (strain the NiO)
- GGA+U (standard)
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Models

Slab models (150+ atoms) with varying interfacial O compositions

NiO
12 layers, 48 atoms

Al
10 layers, 20 atoms

Layer z=10
O : Al = 0 (pristine)

Layer z=10
O : Al = 1 : 2 (1/2)

Layer z=10
O : Al = 2 : 2 (1)
Monomolecular $O_2$ adsorption on the surface

Initial Model

NiO 1~12 layers

Al 10 layers, 40 atoms

AFM (11-1) The spin-parallel Ni atoms underneath

Spin-down Ni

Spin-up Ni

Al

O

Ni hollow

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Monomolecular O$_2$ absorption energies

The absorption energy increases (becomes unfavorable) as the thickness of NiO increases.

The charge density differential after O$_2$ molecule adsorption.

\[ E_{O_2\text{~absorption}} = E_{\text{surface with O}_2} - E_{\text{clean surface}} - E_{O_2} \]
The O-O distance of adsorbed $O_2$ molecule decreases as the thickness of NiO increases.

- Large charge transfer, $O_2^{2-}$
- Limited charge transfer, $O_2$
But....

Absorption energy (eV)

Number of layers

-3.5
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0

Four interfical O
Two interfical O
Without interfical O

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Transfer of charge from Al to surface Ni

Understanding Atomic Scale Structure in Four Dimensions to Design & Control Corrosion Resistant Alloys
Interfacial dipole at buried interface is positive towards external NiO surface, hence a larger bonding of $O_2^{n-}$ – reduces the Mott Potential.
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Interfacial Dipole and Surface Charge

- **Interfacial dipole (eV/A)**
  - with four interfical O
  - with two interfical O
  - without interfical O

- **Charge/atom (e)**
  - Four interfical O
  - Two interfical O
  - No interfical O

Graphs showing the relationship between the number of layers and the interfacial dipole and charge/atom for different conditions.
Take Home message

Passive metal is very different from an active metal with d-electrons, where behavior can be tuned by changing buried interface.
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CoCrMo Alloys

- THR: wrought alloy (C<0.1%)
- HSR: cast alloy (C: 0.15% -0.4%)

### Chemical Composition

<table>
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<tr>
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<th>ASTM F1547/HC</th>
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<tr>
<td>Co</td>
<td>Balance</td>
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<tr>
<td>Cr</td>
<td>26-30 %</td>
<td>26-30 %</td>
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<tr>
<td>Mo</td>
<td>5-7 %</td>
<td>5-7 %</td>
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<tr>
<td>Mn</td>
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<td>0-1 %</td>
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<td>Si</td>
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<tr>
<td>N</td>
<td>0-0.25 %</td>
<td>0-0.25 %</td>
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</table>

Clayton JBJS 2008;90:1988
Corrosion of Implants

- CoCrMo implants corrode approximately 0.01 mm per year
- >350K/year total hip replacements performed in the US
Multiscale Analysis in Practice
Methods

As-received, wrought
3-5 um FCC matrix grains
High number density of second phases
Heavily twinned

Solution annealed, same crystal structure
FCC matrix grains up to 100-300 um
Fewer second phase regions / unit area
(some carbide/intermetallic dissolution)
Heavily twinned

Accelerated electrochemical corrosion tests (in vitro)
Low Carbon CoCrMo

Very few localized pits

Faster overall rate of corrosion

Low-carbon alloy subject to general corrosion which attacks the entire surface
Wrought Alloy (not annealed)

Pitting corrosion everywhere

Before

After
Annealed 1150 C/2hr

Pits have corroded *around* second phases (phase boundaries) but not the second phases themselves.
Longer Anneal (1150 C/24 hr)

Pits localized at phase boundaries and at some grain boundaries
EBSD to determine orientation

uncorroded  corroded  uncorroded  corroded
Corrosion is at high-energy boundaries

(Twins)

Increasing GB Energy
Add 3D profilometry
Depth Information

Depth vs. Grain Boundary Interfacial Energy

Depth vs. Width
Conventional view of intergranular corrosion.
What controls corrosion at a grain boundary?

Hypotheses

- Grain boundary energy
  - Coincidence site lattice
- Grain boundary composition
  - Sensitization

Sensitization is when the chromium of the matrix gets tied up in a carbide so the Cr$_2$O$_3$ protective layer can no longer form.
FIB TEM sample

Grain 1
Grain 2

Grain boundary

Pt FIB coating sensitized region

carbide

50 μm

1 μm
Large Precipitates: 0.68 of Cr

<table>
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<tr>
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<th>Co (at%)</th>
<th>Cr (at%)</th>
<th>Mo (at%)</th>
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<tr>
<td>Matrix</td>
<td>64.48</td>
<td>30.62</td>
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<td>Carbide</td>
<td>19.28</td>
<td>67.16</td>
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<tr>
<td>Sensitization</td>
<td>70.44</td>
<td>20.99</td>
<td>8.57</td>
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Medium Precipitates: 0.96 Cr

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<tr>
<td>Matrix</td>
<td>64.52</td>
<td>28.31</td>
<td>7.17</td>
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<tr>
<td>Carbide</td>
<td>38.74</td>
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<tr>
<td>Sensitization</td>
<td>66.33</td>
<td>26.48</td>
<td>7.19</td>
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Small Precipitates: 1.0 Cr

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<th>Cr (at%)</th>
<th>Mo (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>63.56</td>
<td>30.89</td>
<td>3.80</td>
</tr>
<tr>
<td>Carbide</td>
<td>59.95</td>
<td>33.00</td>
<td>4.88</td>
</tr>
<tr>
<td>Sensitized</td>
<td>63.56</td>
<td>30.89</td>
<td>3.80</td>
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</table>
Sensitization in Implants

\[
\Delta E_{GB} = -1.5 \text{ to } -5.4 \times 10^{-19} \text{ Jnm}^{-1}
\]
\[
\Delta E_{Seg} = -1.8 \text{ to } -8.4 \times 10^{-19} \text{ Jnm}^{-1}
\]

Both grain boundaries and segregation matter
Simple Qualitative Model

- Maps to a kinetic-Wulff shape

\[
sin(\theta) = \frac{v_{side}}{v_{GB}} \sim \frac{\Delta\mu_{side}}{\Delta\mu_{GB}}
\]

\[
\tan(\theta) = 0.5 \times \frac{\text{Width}}{\text{Depth}}
\]
What does this mean?

- Depletion of Cr is small – not conventional sensitization
- Grain boundary energy and chemical terms from segregation are comparable
- Cannot explain via conventional models
- Grain boundaries are only *initiators* of corrosion, then crevice corrosion
Summary

There is plenty of room at the bottom of Rust

- Atomic scale processes are not fully understood
- Many details are different from simpler models
- Electronic mechanisms go beyond the simple approaches such as Cabrera-Mott
- Even phenomena as “well understood” as grain boundary sensitization are not...
Questions?