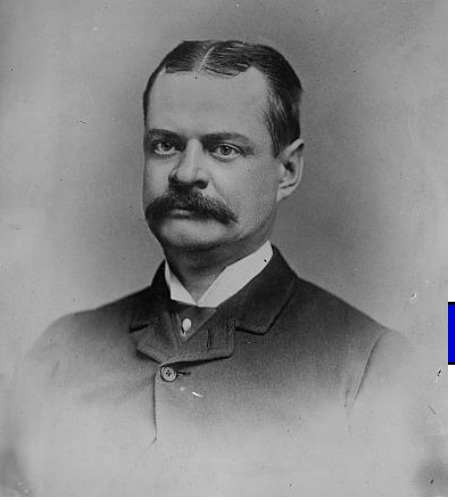


William Waldorf Astor,
1st Viscount Astor

Rust with 21st Century Tools

L. D. Marks

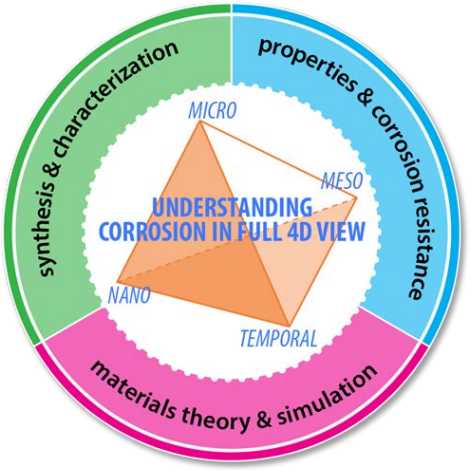
Northwestern University

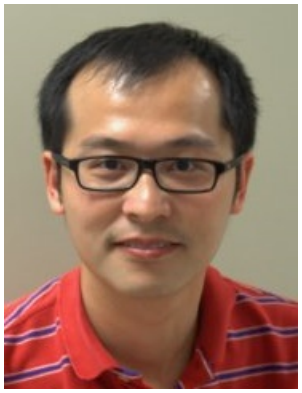
Astor Lecture

Acknowledgements I

Ahmet Gulec

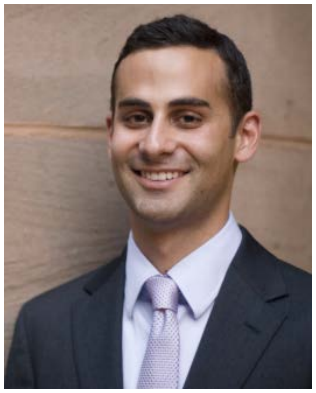
Xiao-xiang Yu





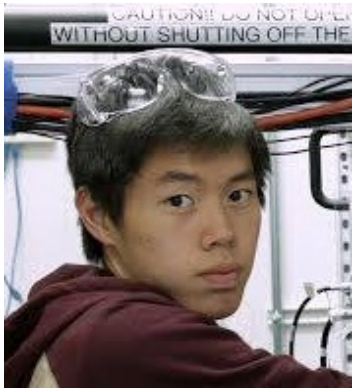
Yifeng Liao

James Rondinelli



Acknowledgements II

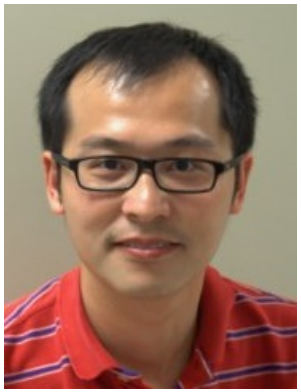
Pooja Panjiri



Alex Lin

Emily Hoffman

Yifeng Liao



Suppose every human vanished

Wait 10,000 years, what would be left?

Plastics -- some

Buildings – crumbled

Metals – almost all gone

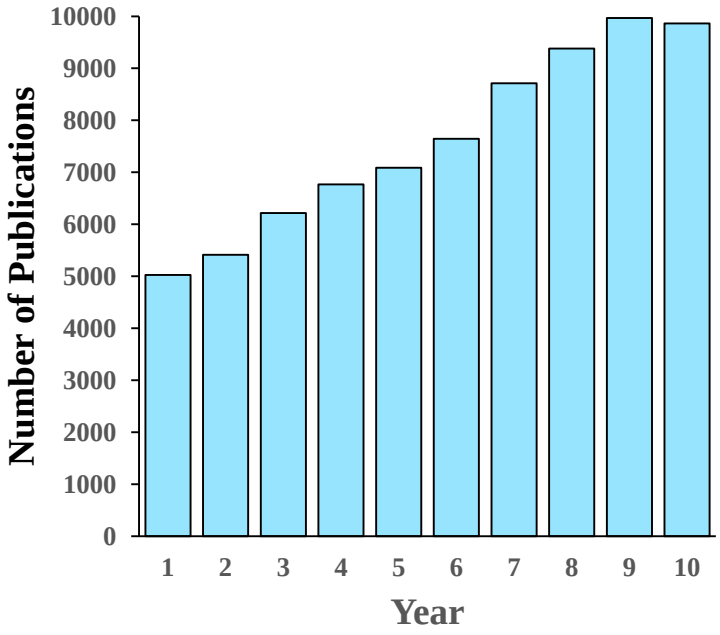
Except 4th Century Iron Pillar in Delhi protected by a thin iron hydrogen phosphate hydrate[1] due to a high level of phosphorus in the cast iron.

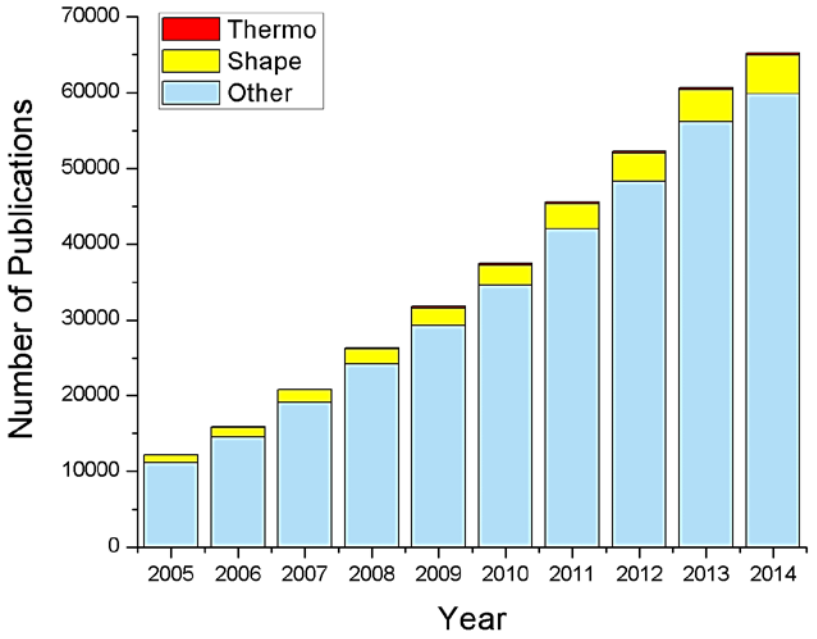
Estimated corrosion of the pillar is 50-500 µm over 1600 years

The 4th Century Iron Pillar in Delhi
Source: bertatih.wordpress.com

[1]Balasubramaniam R. On the corrosion resistance of the Delhi iron pillar. Corrosion Science. 2000;42(12):2103-29

Corrosion versus Nanoparticles Publications





Corrosion

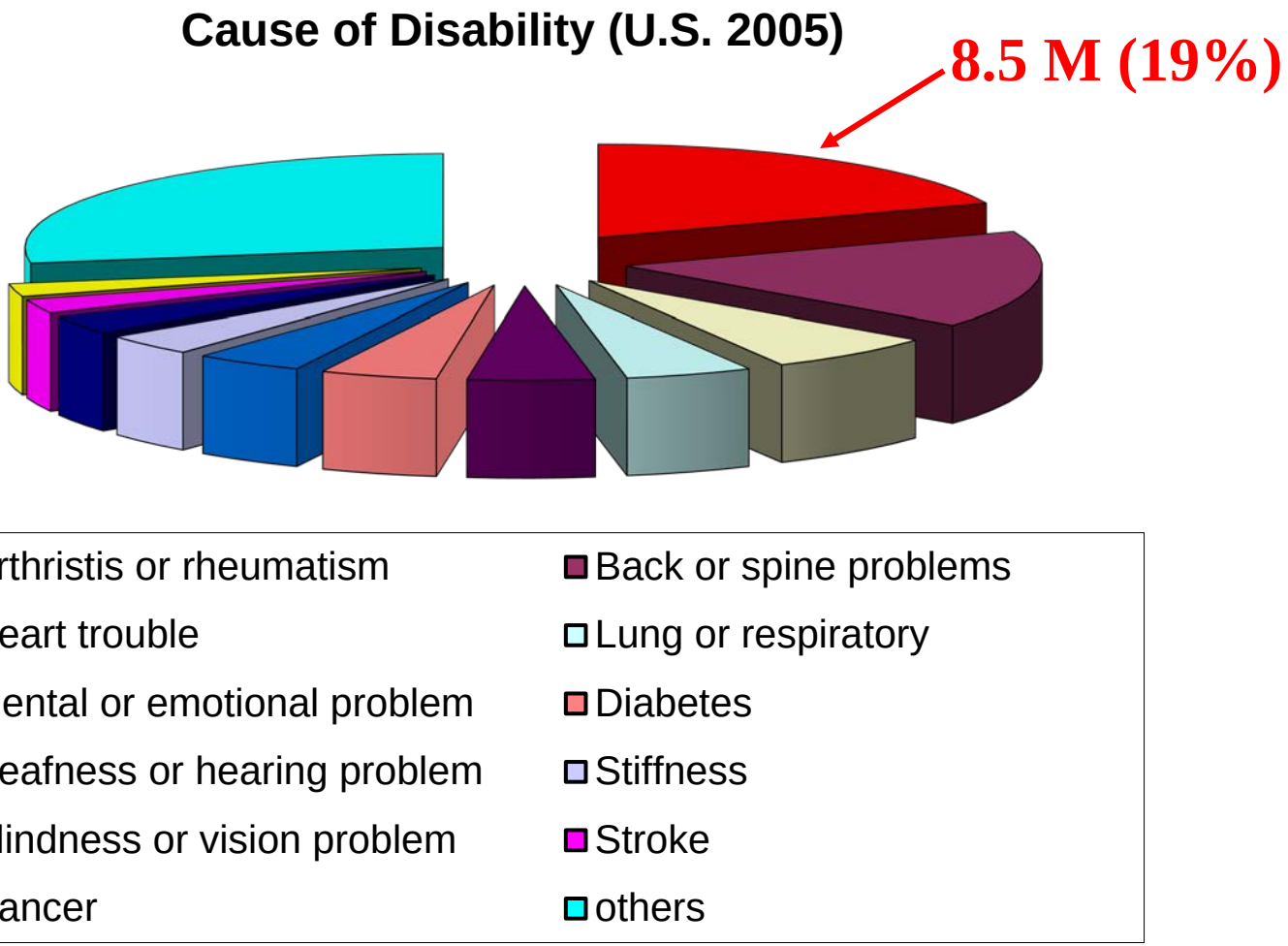
~ $1 Trillion/year

Nanoparticles

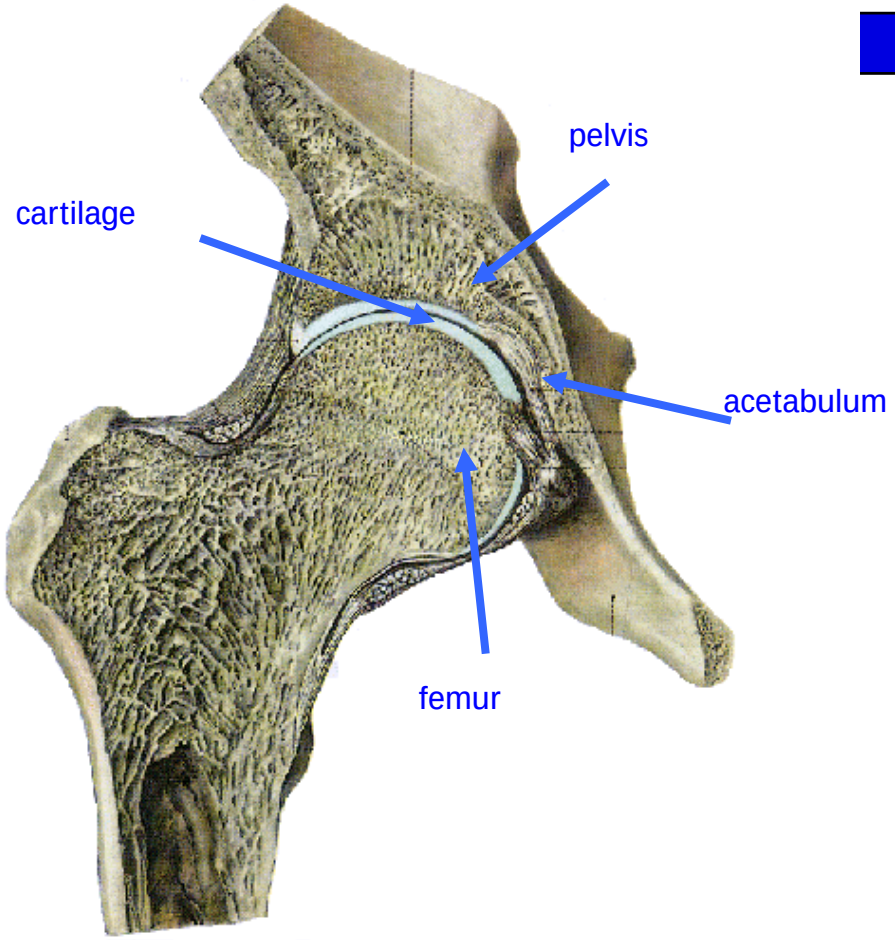
$20-70 Billion/year

Corrosion effects many materials

Arthritis and Hip Replacement

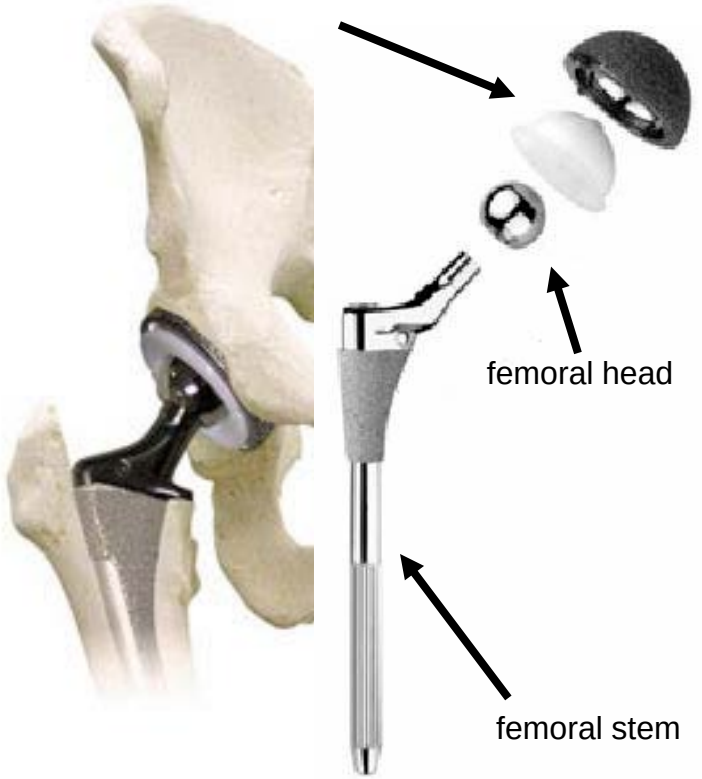


Hip Joint



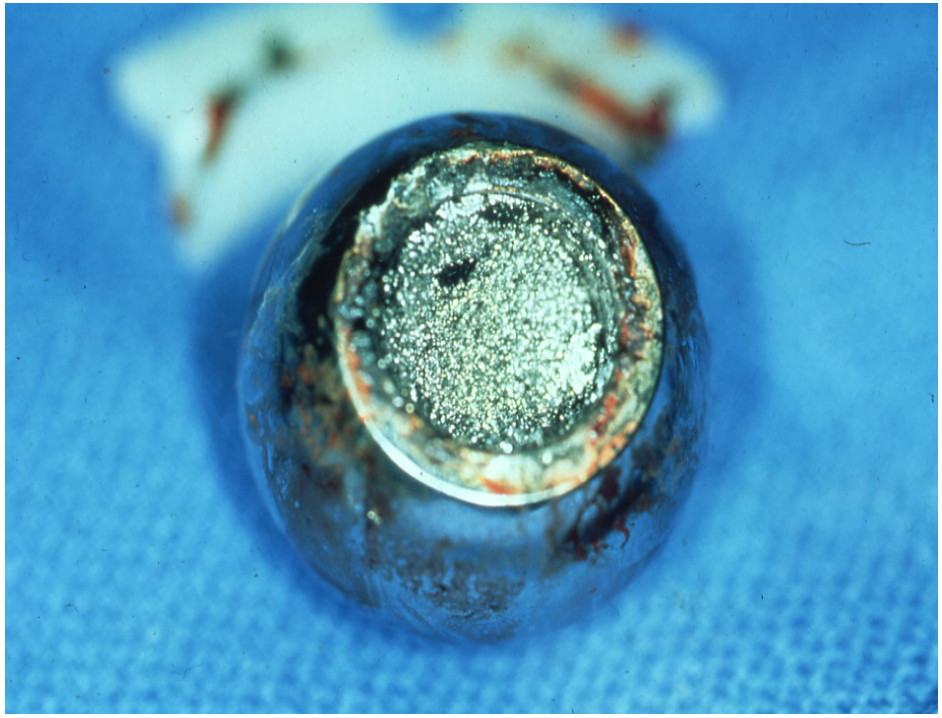
Rauber/Kopsch: Anatomie des Menschen (1998)

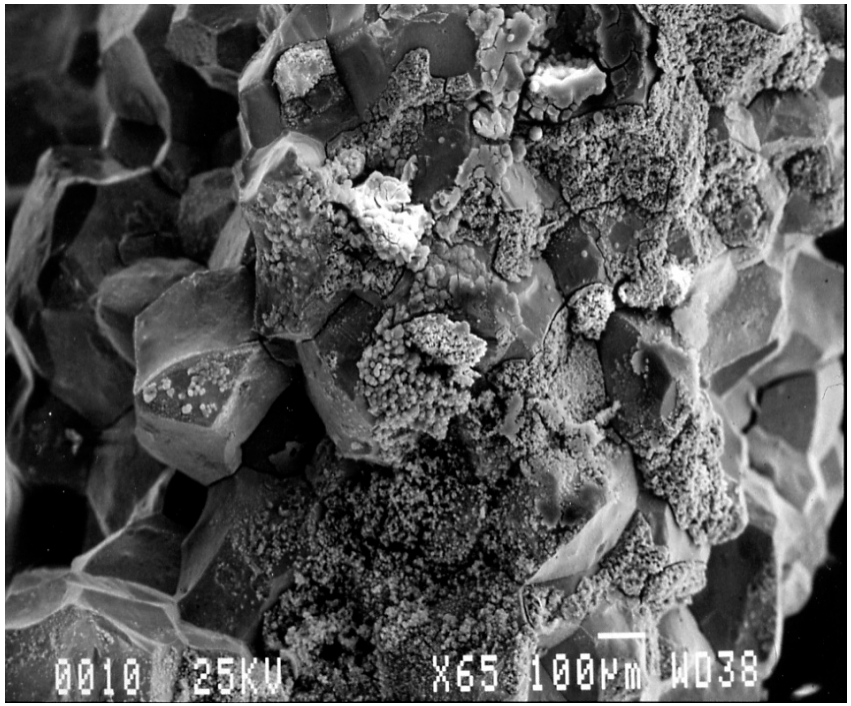
acetabulum cup



www.zimmer.com

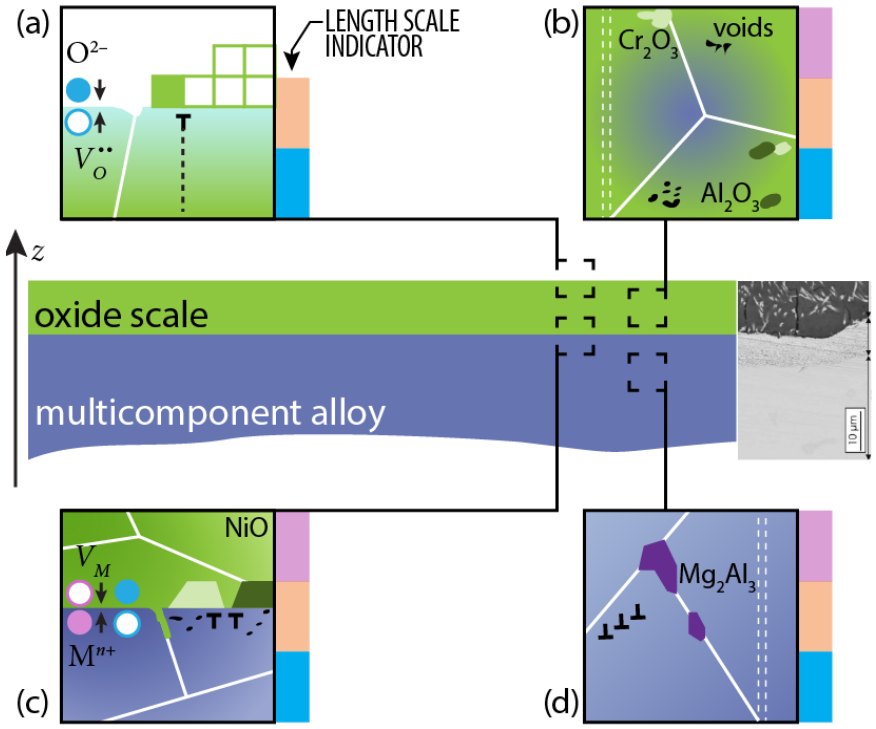
Intergranular Corrosion of CoCrMo implants

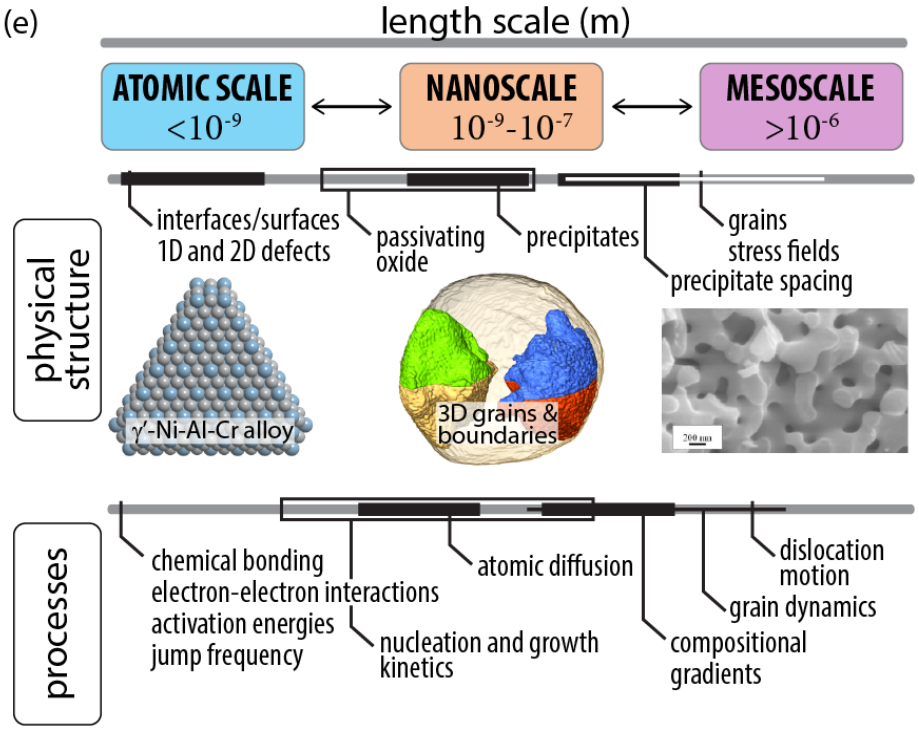




Images curtesy of J. Jacobs, Rush

Corrosion: A Multiscale Problem





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

Many corrosion studies

Atoms

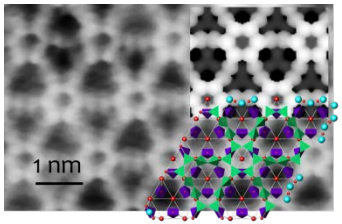
Atom Clusters

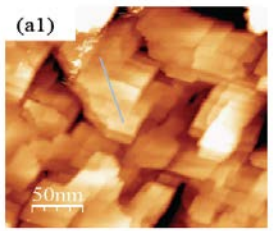
Nanometer scale defects

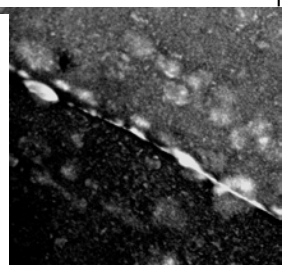
Micrometer scale defects

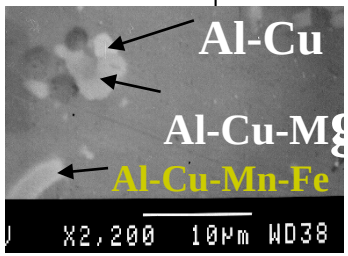
Mesoscale defects

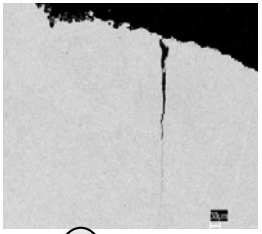
0.1 nm 1 nm 10 nm 100 nm 1 μm 10 μm 100 μm





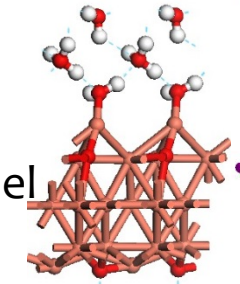


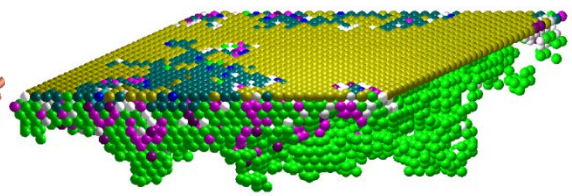


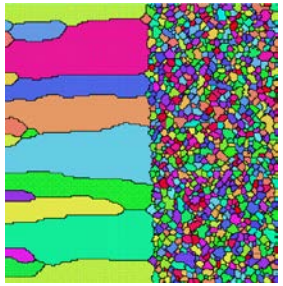


Exp

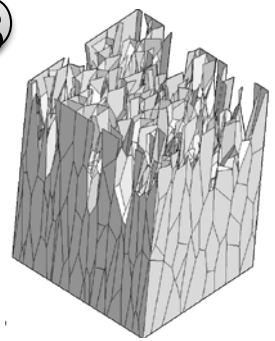
Model





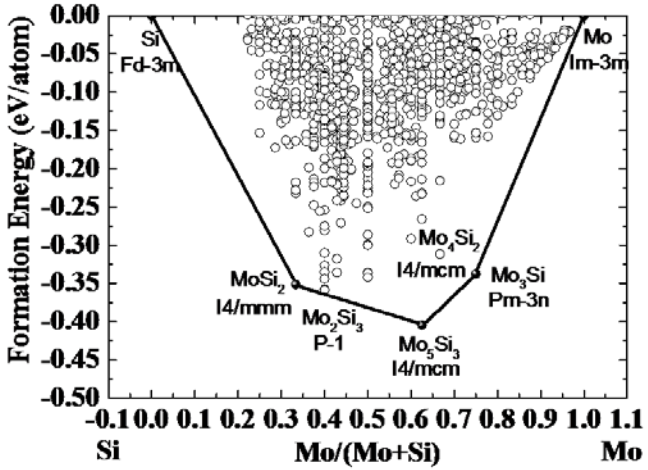


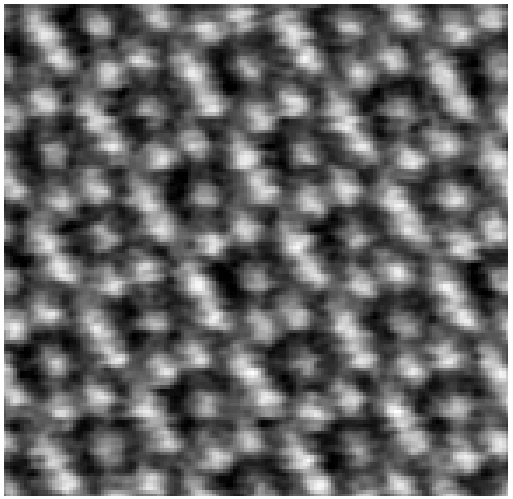
3



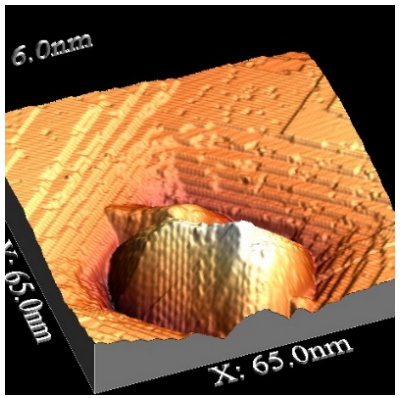
The Opportunity

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





Oxford ARM



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

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

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)

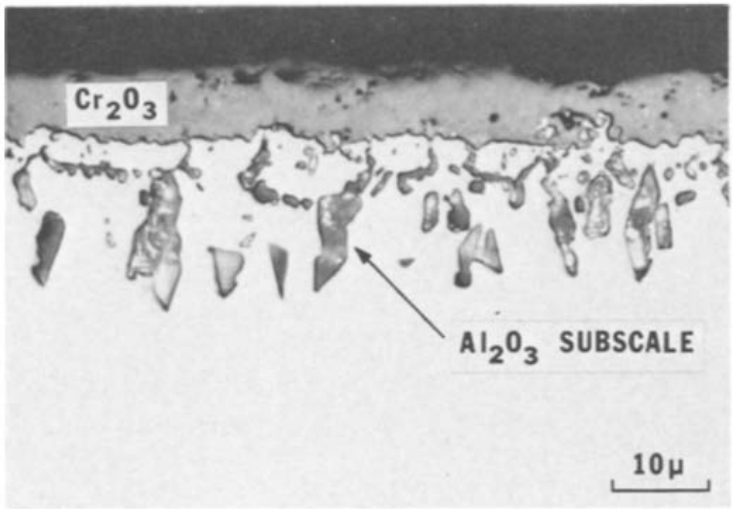
Rusted Deck and Ventilation Equipment
Source: www.corrdefense.org

Basic Chemical Components

- Oxidation of a metal by the environment – typically O_2 either at high temperatures or in aqueous environment

$$M + 1/2O_2 \rightarrow M^{2+} + O^{2-} \rightarrow MO \text{ thin film}$$

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

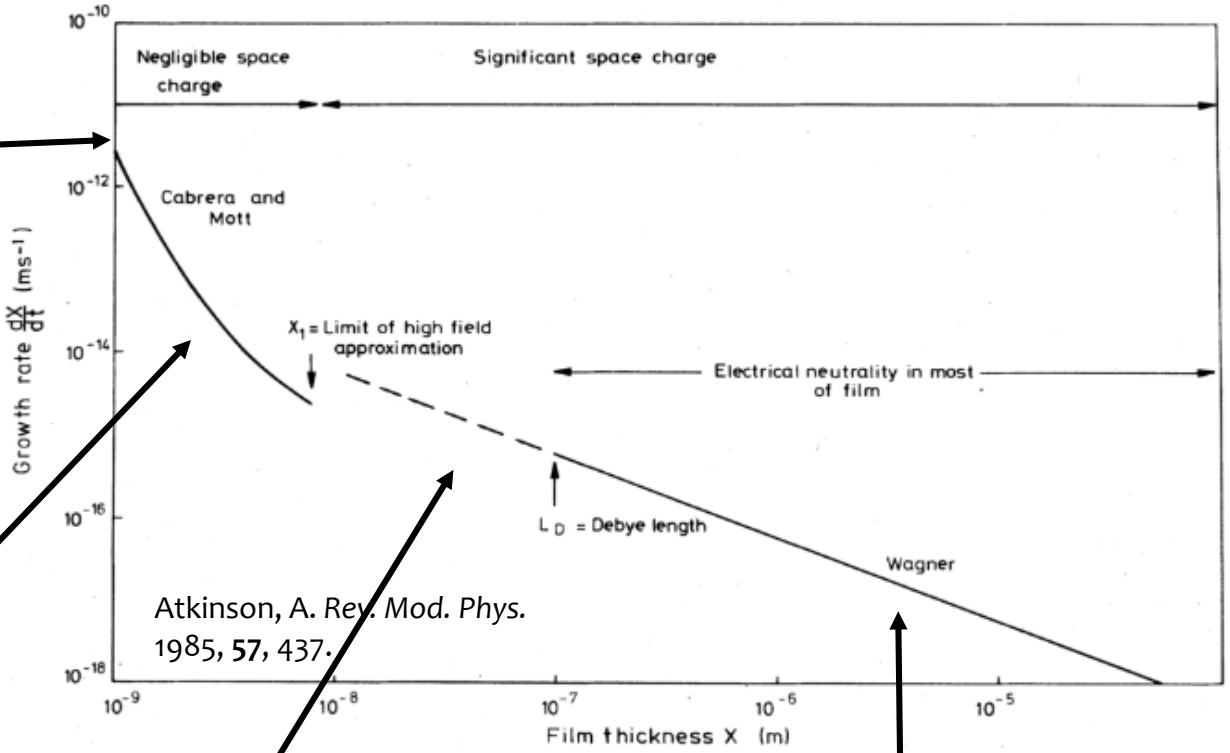


Typical protective Cr_2O_3 layer on NiCrAl superalloys

Oxide growth

Nucleation (~1nm)
Surface Chemistry and Structure matter

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



Atkinson, A. *Rev. Mod. Phys.* 1985, **57**, 437.

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]

[1]Wagner. *Phys. Chem. B* 1933, **21**, 25
[2]Cheng, Wen, & Hawk. *J. Phys. Chem. C.* 2014, **118**, 1269
[3]Xu., Rosso, & Bruemmer. *PCCP.* 2012, **14**(42), 14534–9.
[4]Cabrera 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)

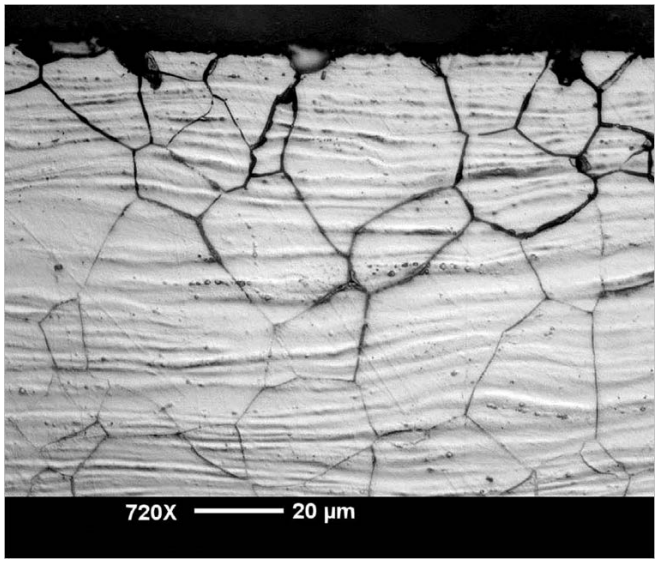
$M^+(aq) + H_2O \rightarrow MOH + H^+$

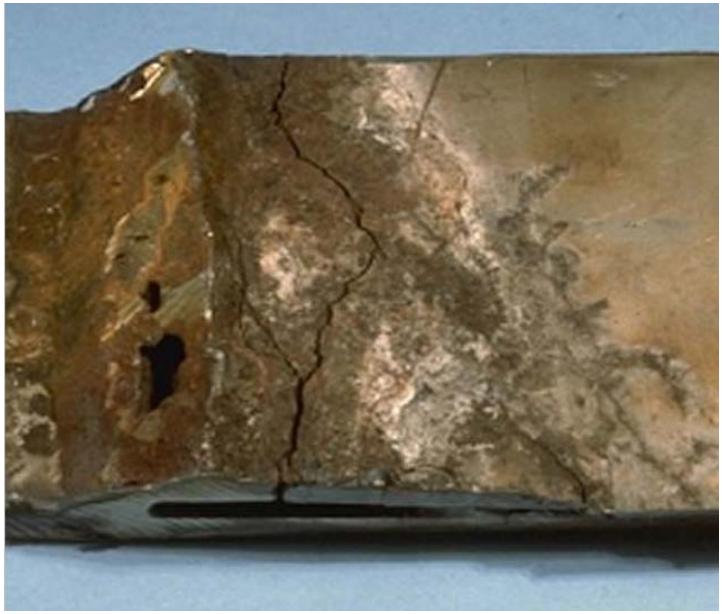
Typical Failure Mechanisms

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

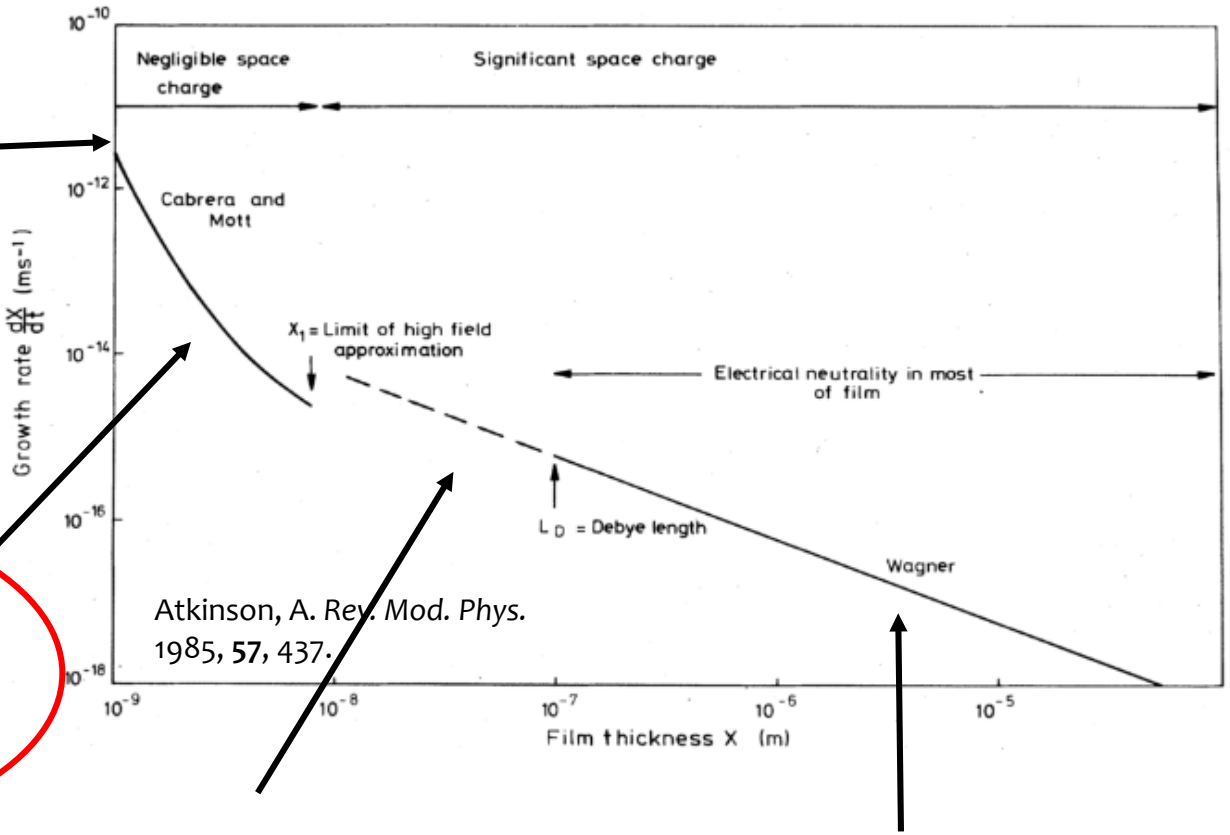
Combination of normal corrosion + stress, sometimes due to hydrogen incorporation but can be more complex

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

Oxide growth

Nucleation (~1nm)
Surface Chemistry and Structure matter



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

Atkinson, A. *Rev. Mod. Phys.* 1985, **57**, 437.

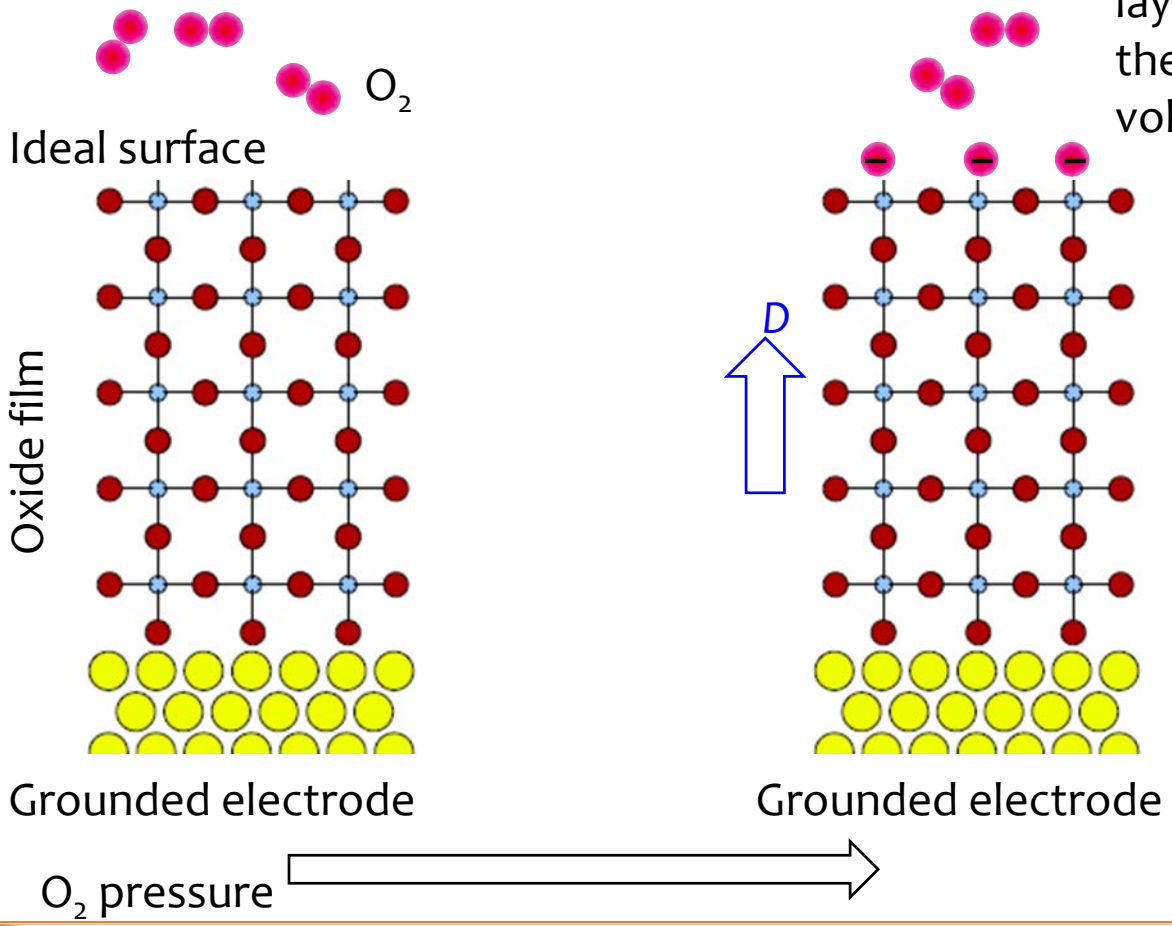
Intermediate
Complex region, not as yet well understood in detail

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

[1]Wagner. *Phys. Chem. B* 1933, **21**, 25
[2]Cheng, Wen, & Hawk. *J. Phys. Chem. C.* 2014, **118**, 1269
[3]Xu., Rosso, & Bruemmer. *PCCP.* 2012, **14**(42), 14534–9.
[4]Cabrera and Mott, *Rep. Prog. Phys.* **12**, 163

The Cabrera-Mott Model

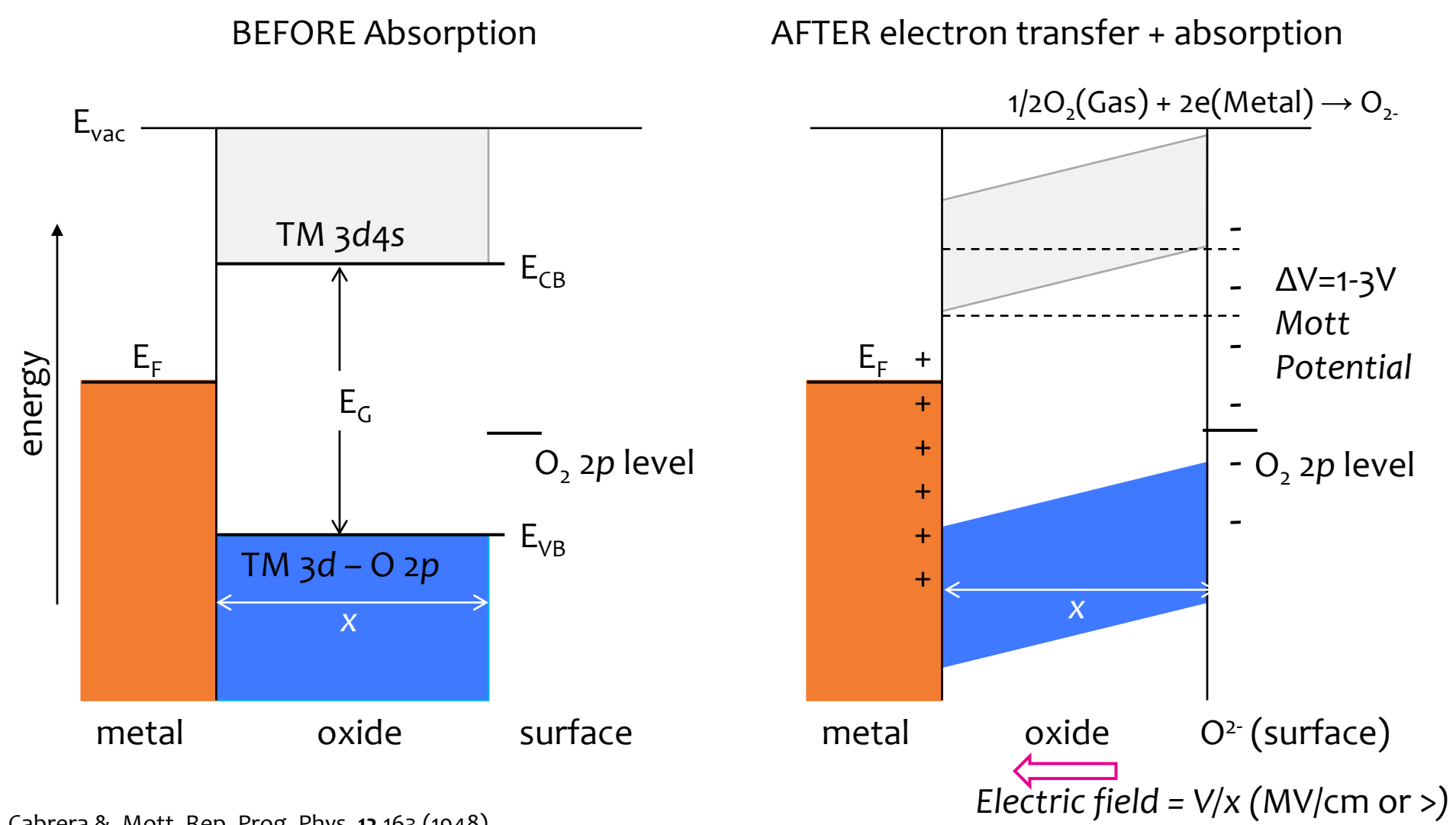
- Electrons pass freely from the metal to the oxide surface to ionize oxygen
  - Creates a ***uniform*** field within the oxide, which leads to a shift in the Fermi level of the oxide



layer of adsorbed ions provides the surface charge and the voltage across the oxide

$$D = \frac{(\text{coverage})\,(\text{charge})}{\text{surface}}$$

Band structure evolution



Cabrera &. Mott, Rep. Prog. Phys. **12** 163 (1948)

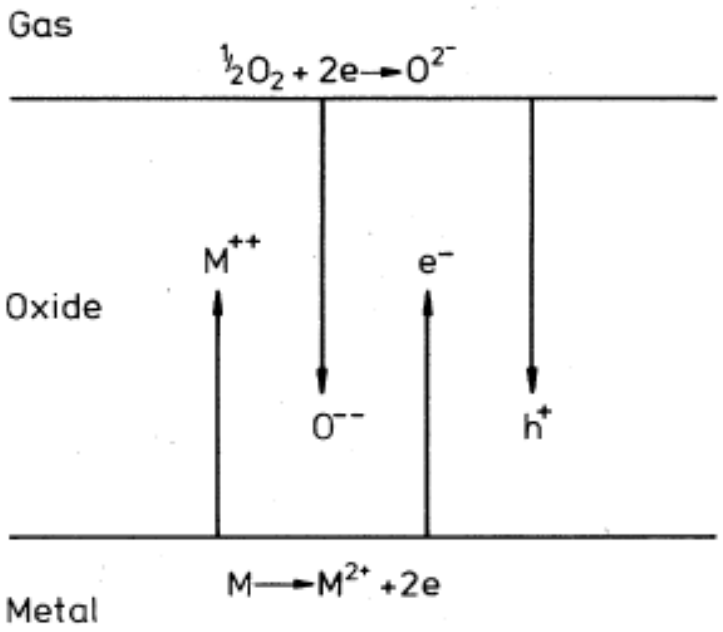
Microscopic mechanisms

- 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

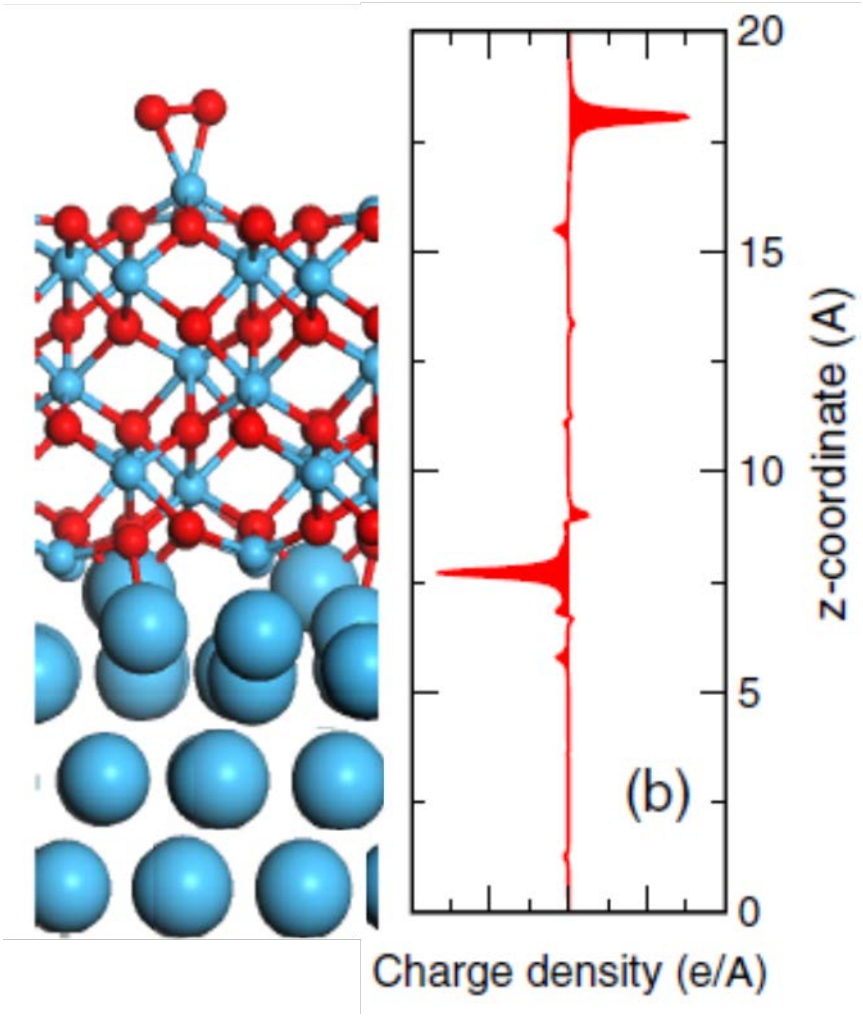
Oxygen interstitials (into oxide)
Oxygen vacancies (out)

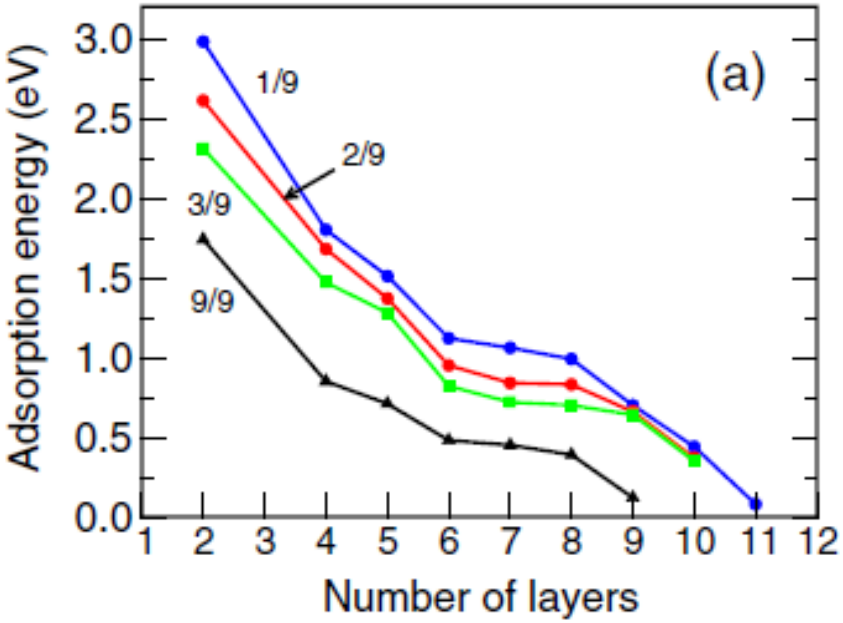
Metal interstitials (into oxide)
Metal vacancies (out)

Electron (hole) transport across the film



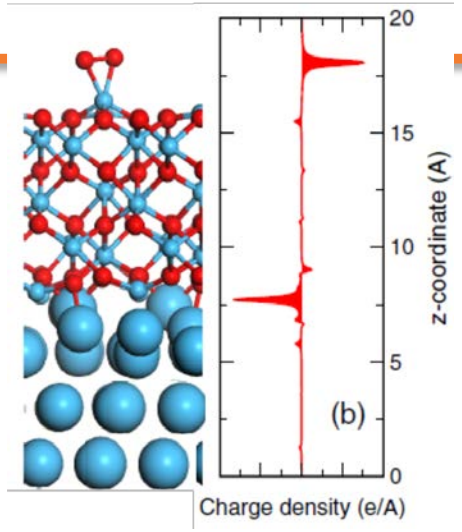
Cabrera-Mott model





Baran *et al.*, Phys. Rev. Lett. **112** 146103 (2014)

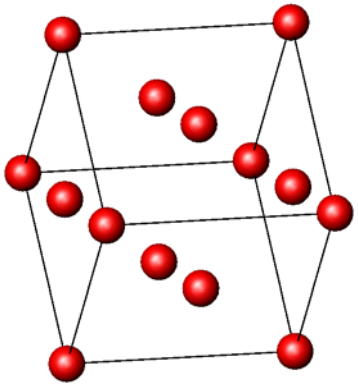
Issues



- Is this general?
  - Other oxides?
  - Other structures, surfaces?
- Does is matter which oxide is used?
  - Al2O3 has Al^{3+} -- which has no available electrons
  - Most relevant oxides involve transition metals, with partially filled d-bands

Consider a more complex model

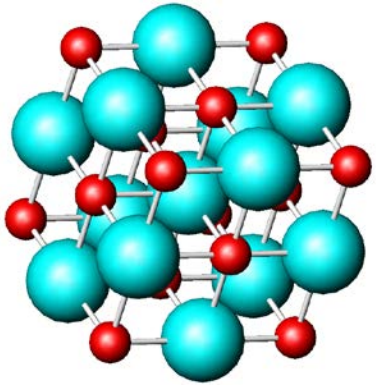
- KISS (Keep it Simple Stupid) model
- Base metal, Al, fcc



4.0494 Å

- NiO – simple cubic, albeit slightly complex electronic structure

4.178 Å



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

GGA-PBE+*U*

E_g = 5.3 eV

Models

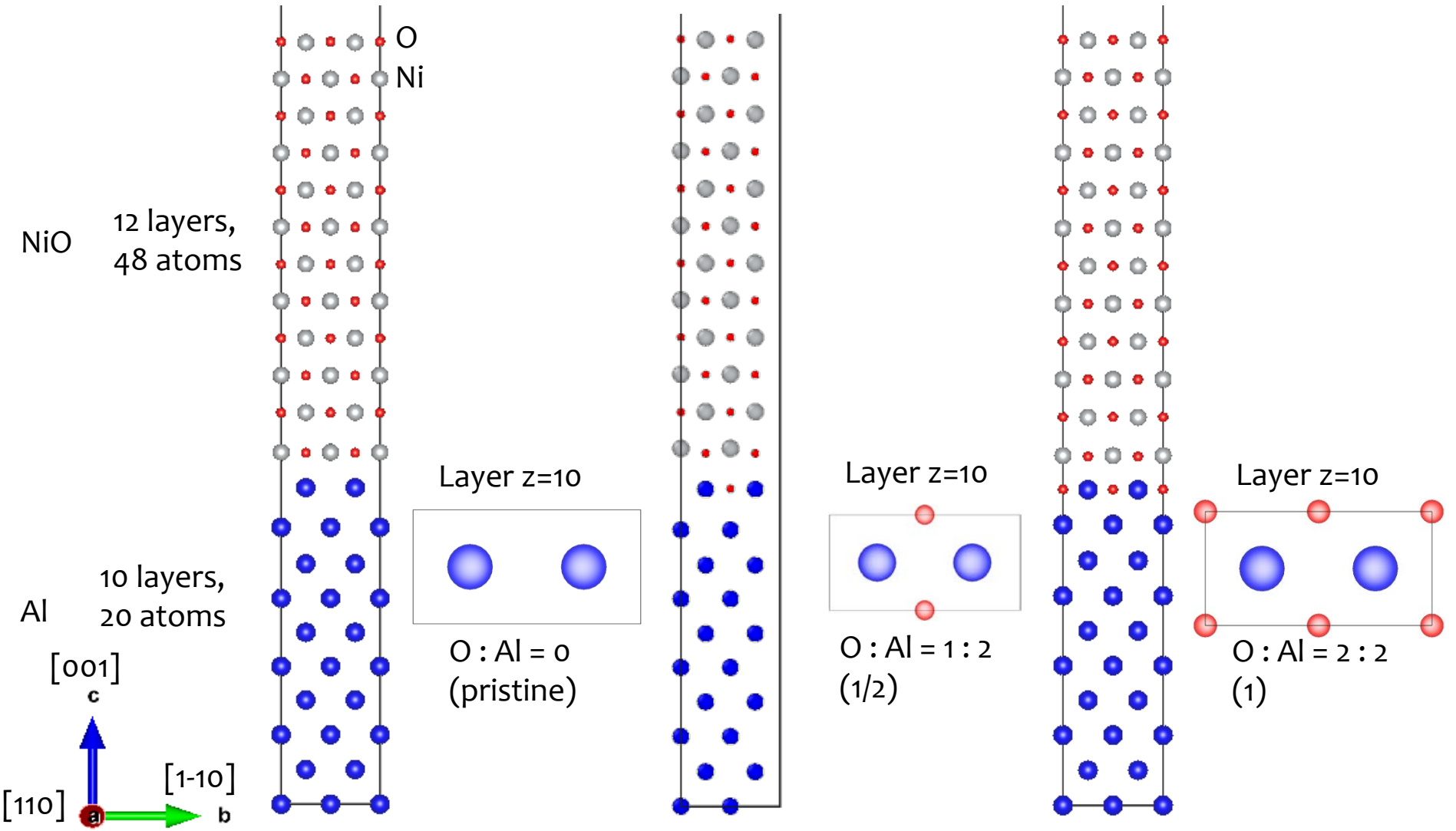
Slab models (150+ atoms) with varying interfacial O compositions

NiO

12 layers,
48 atoms

Al

10 layers,
20 atoms

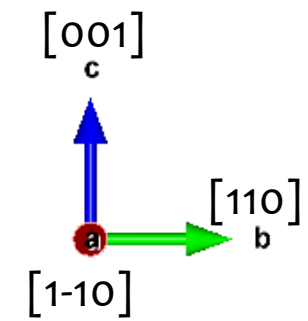


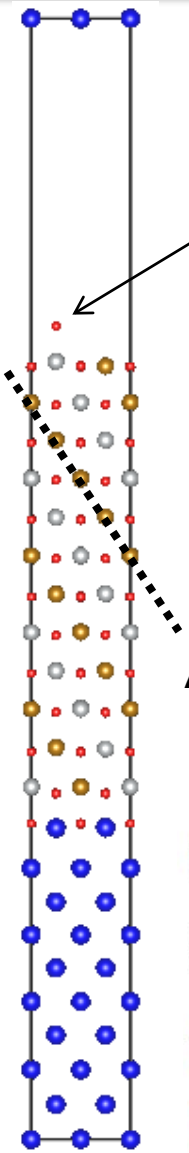
Monomolecular O_2 adsorption on the surface

Initial Model

NiO 1~12 layers

Al 10 layers, 40 atoms

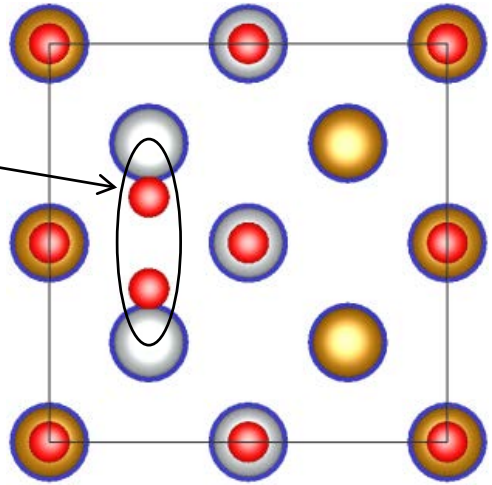




O_2

AFM

(11-1)



Ni hollow

The spin-parallel Ni atoms underneath

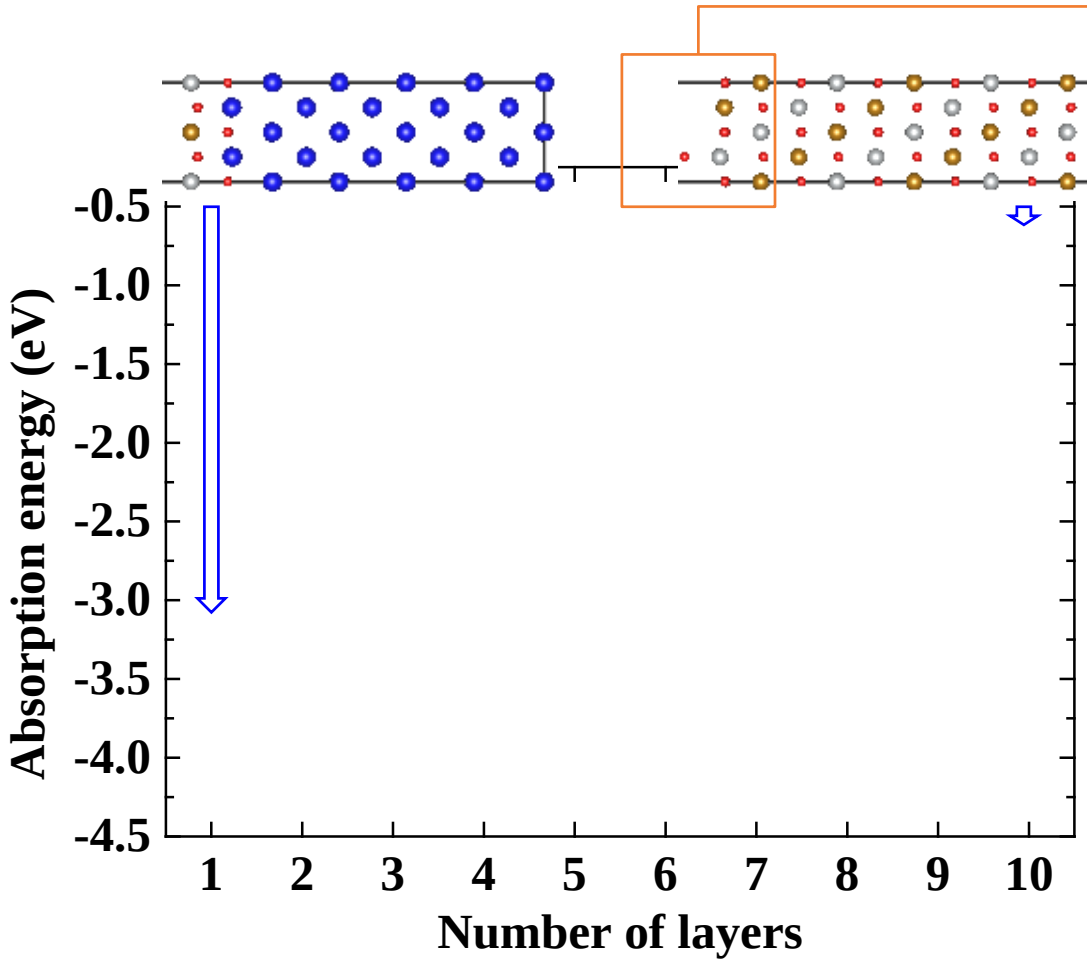
Spin-down Ni

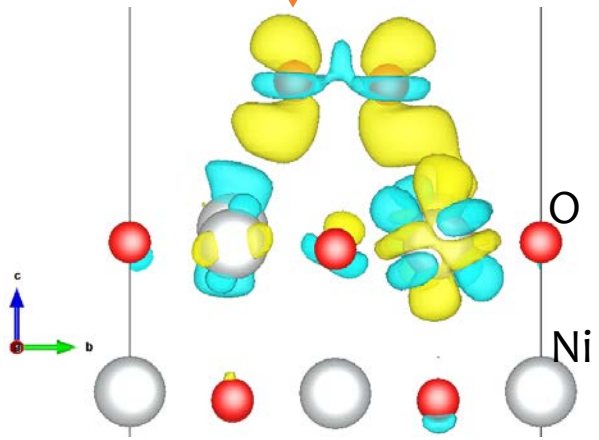
Spin-up Ni

Al

O

Monomolecular O2 absorption energies





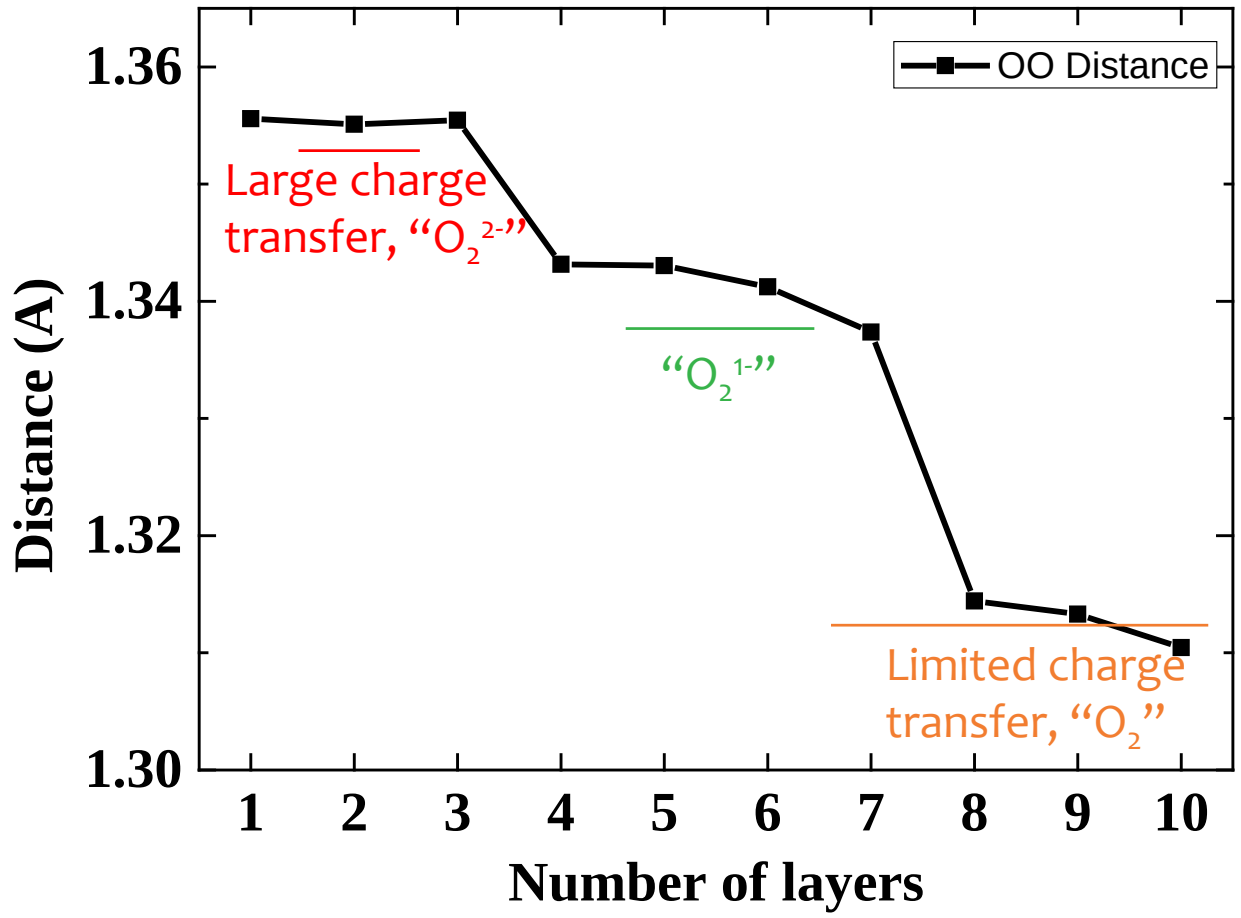
The charge density differential after O_2 molecule adsorption

$$E^{O_2}_{absorption} = E_{surface\ with\ O_2} - E_{clean\ surface} - E^{molecule}_{O_2}$$

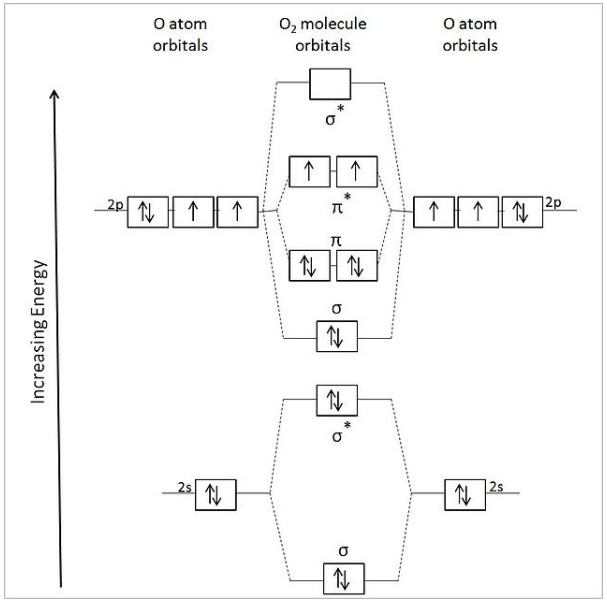
The absorption energy increases (becomes unfavorable) as the thickness of NiO increases

O-O bond distance of the adsorbed molecule

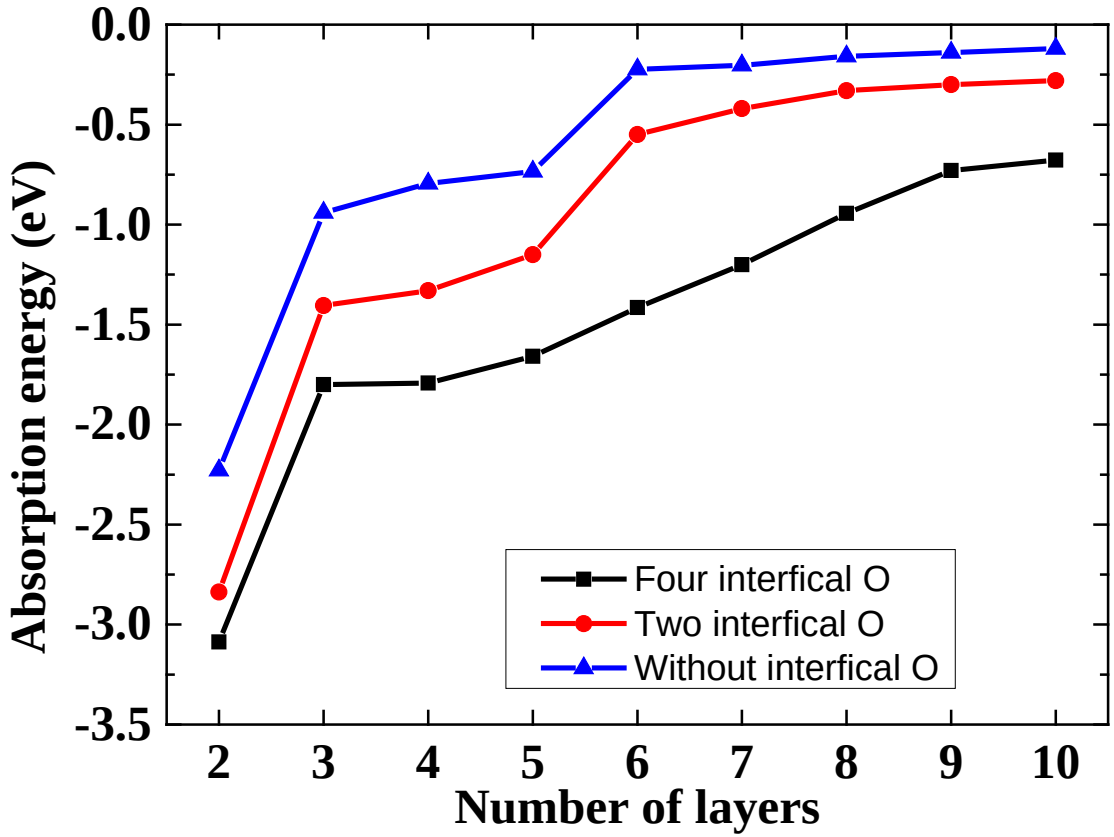
The O-O distance of adsorbed O_2 molecule decreases as the thickness of NiO increases

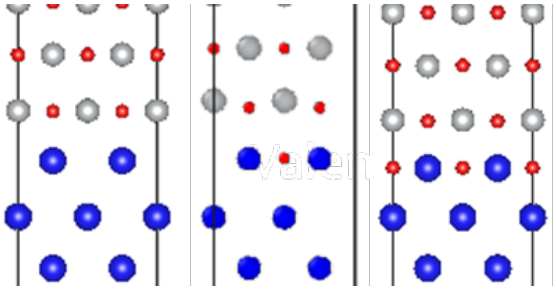


Bond length for molecular oxygen 1.24 Å



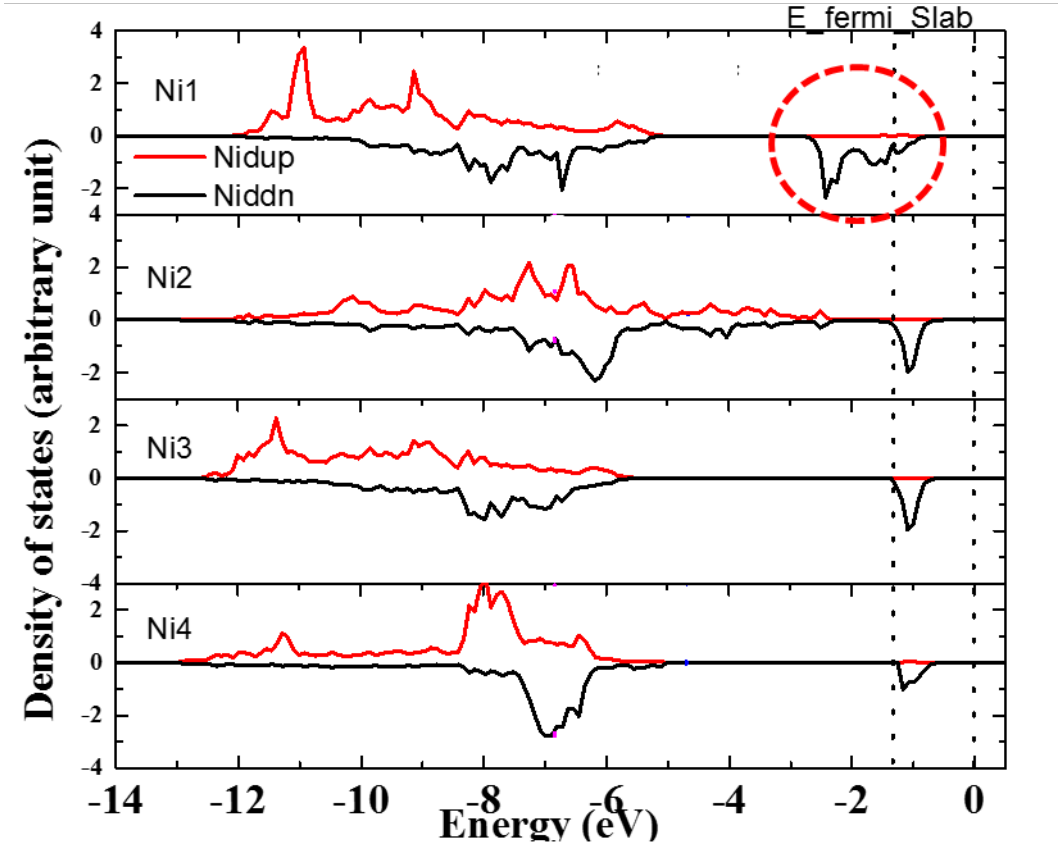
But….

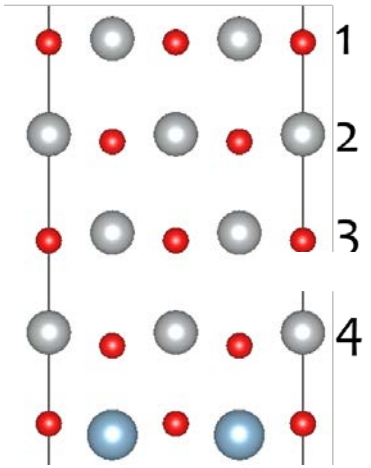

0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
Absorption energy (eV)
2
3
4
5
6
7
8
9
10
Number of layers
Four interfical O
Two interfical O
Without interfical O



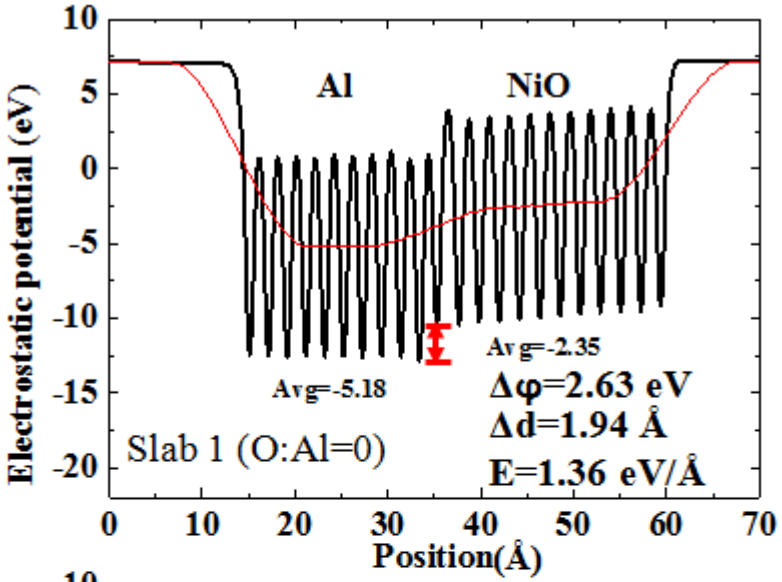
0 2 4

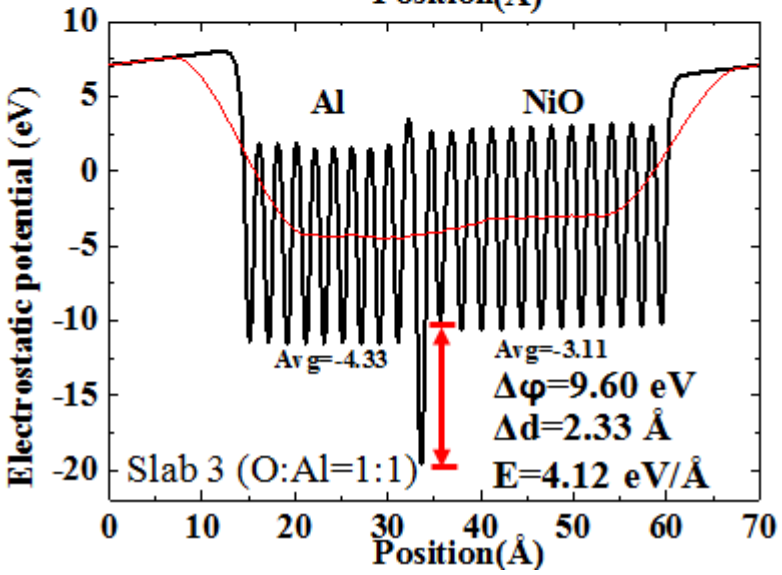
Transfer of charge from Al to surface Ni

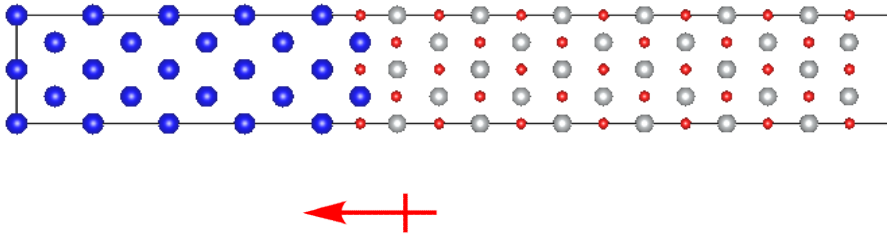




Interfacial Dipole Leads to Band Bending

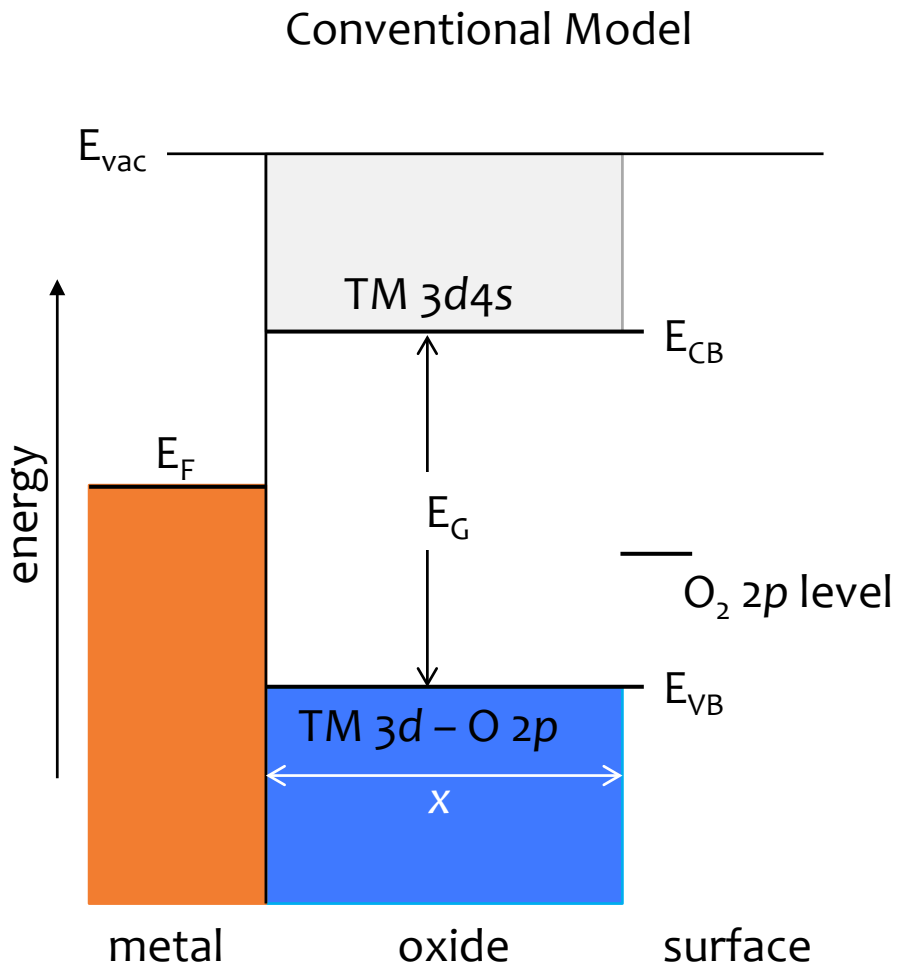


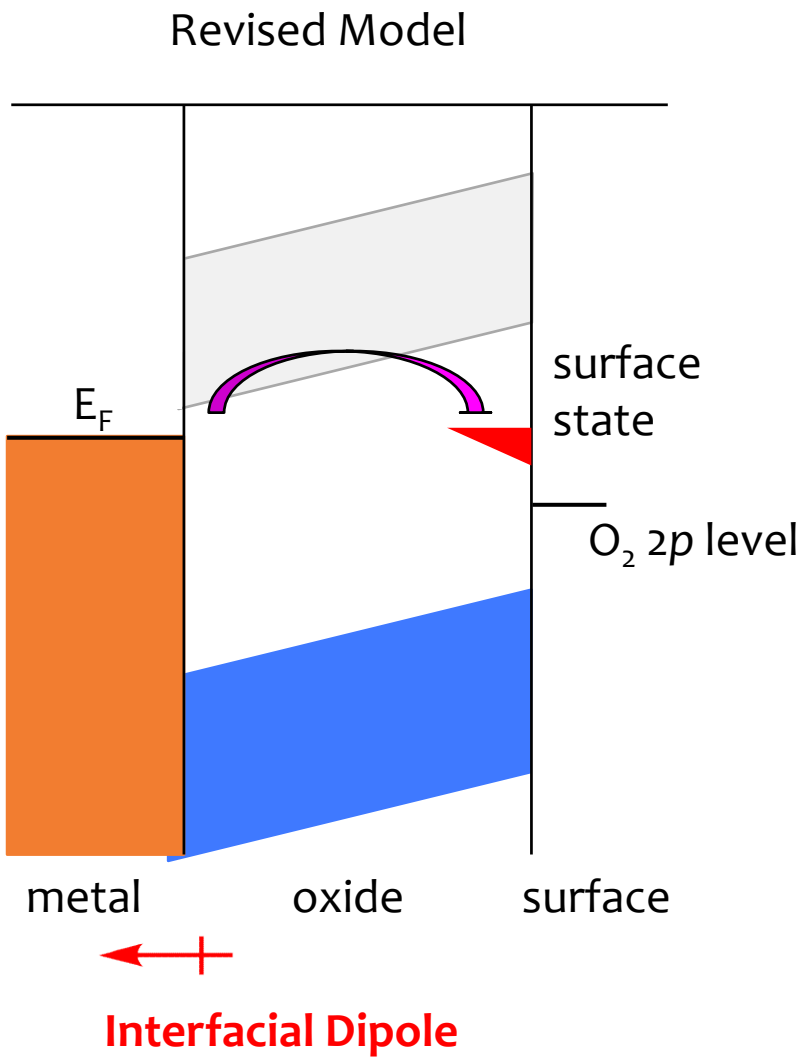




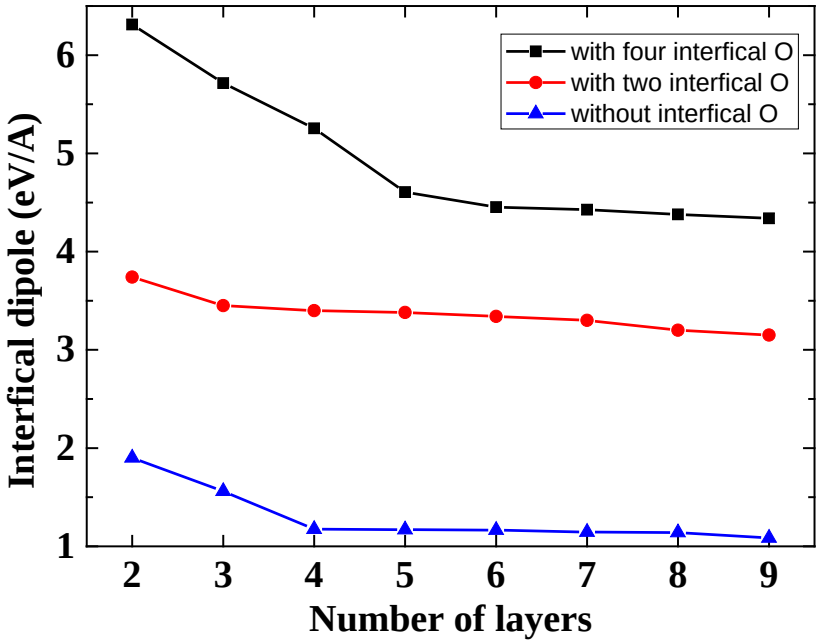
Interface dipole at buried interface is positive towards external NiO surface, hence a larger bonding of O_2^{n-} – reduces the Mott Potential

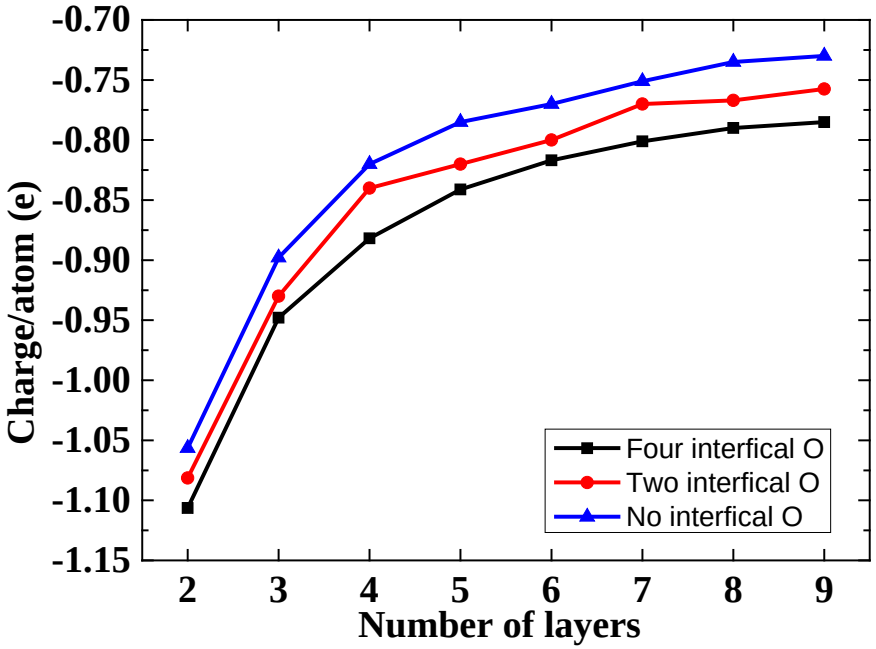
Band structure evolution





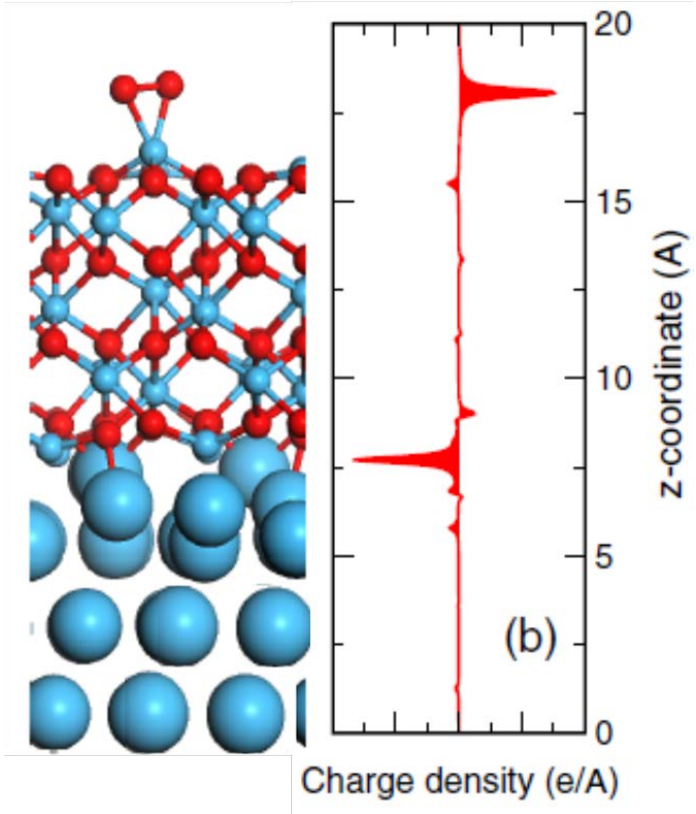
Interfacial Dipole and Surface Charge

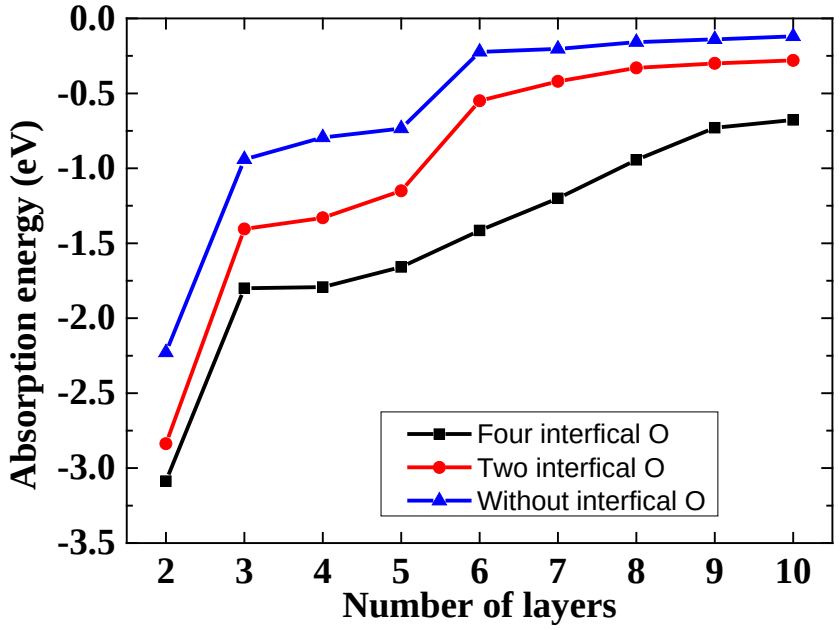


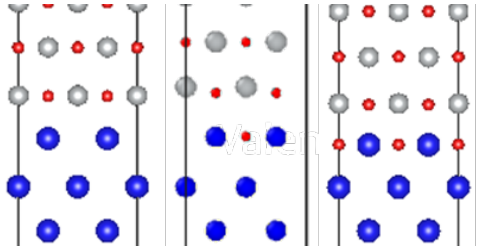


Take Home message

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







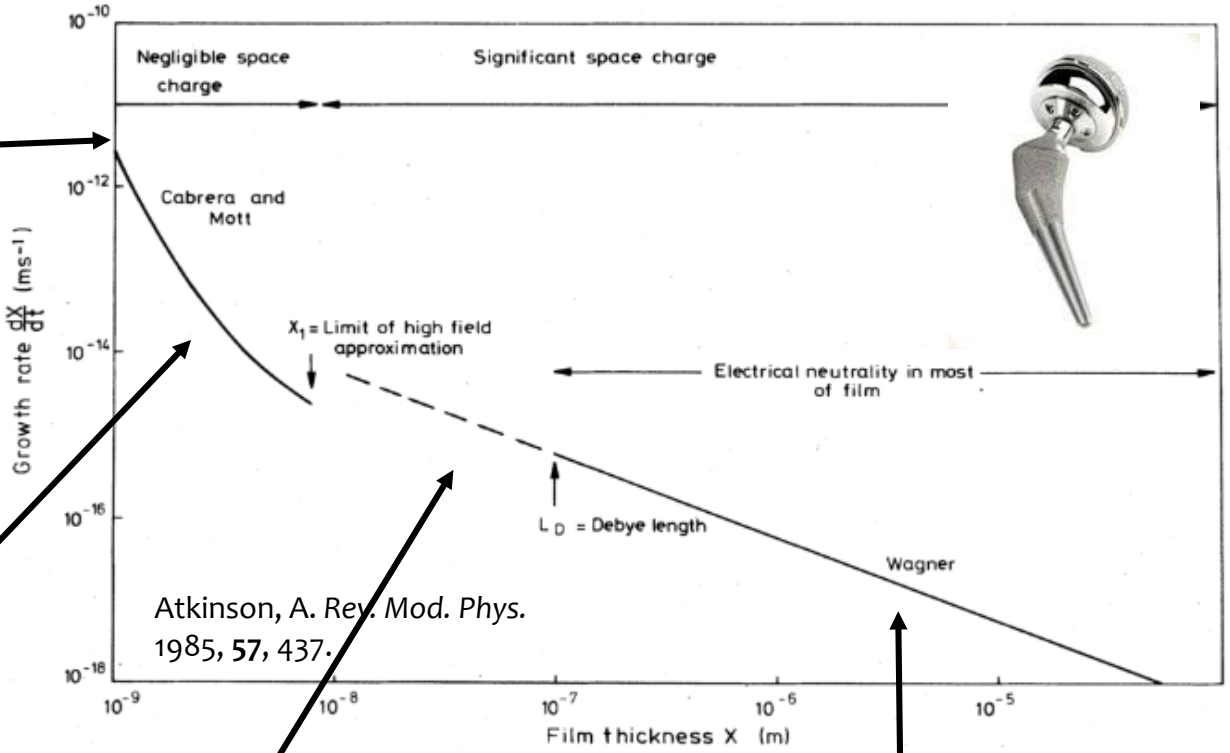
Overview: Three Topics

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

Oxide growth

Nucleation (~1nm)
Surface Chemistry and Structure matter

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



Atkinson, A. *Rev. Mod. Phys.* 1985, **57**, 437.

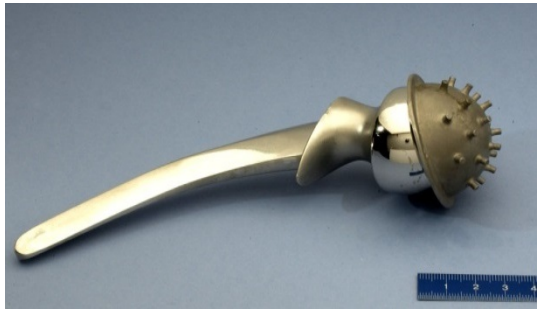
Intermediate
Complex region, not as yet well understood in detail

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

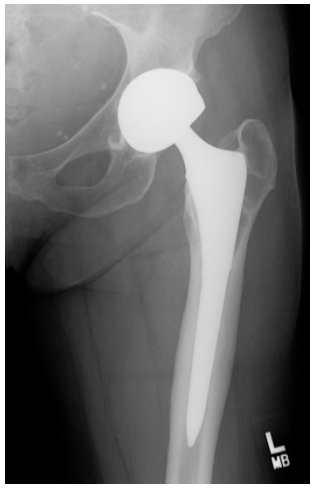
[1]Wagner. *Phys. Chem. B* 1933, **21**, 25
[2]Cheng, Wen, & Hawk. *J. Phys. Chem. C.* 2014, **118**, 1269
[3]Xu., Rosso, & Bruemmer. *PCCP.* 2012, **14**(42), 14534–9.
[4]Cabrera and Mott, *Rep. Prog. Phys.* **12**, 163

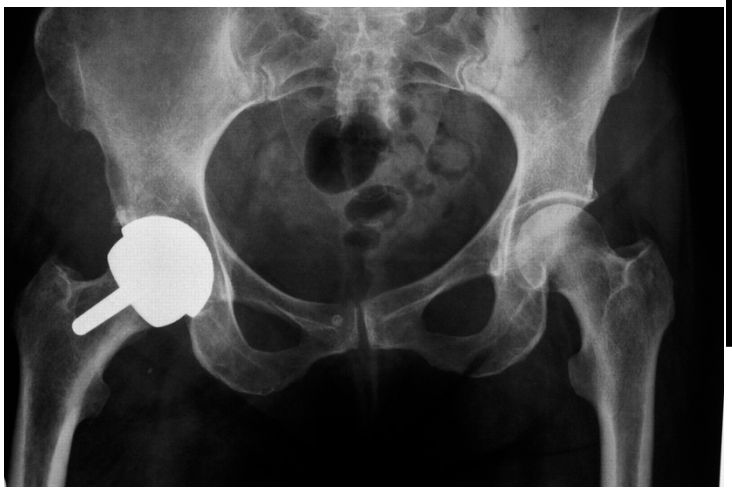
CoCrMo Alloys

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



Zimmer Inc.





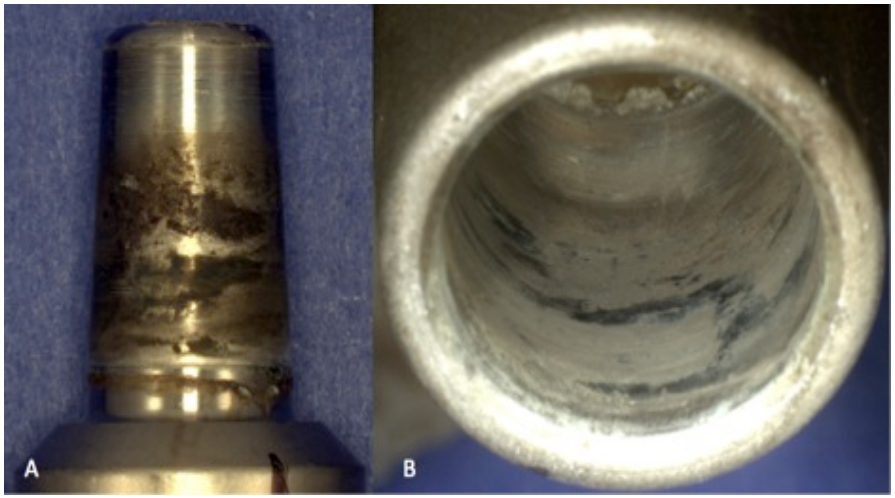
chemical composition

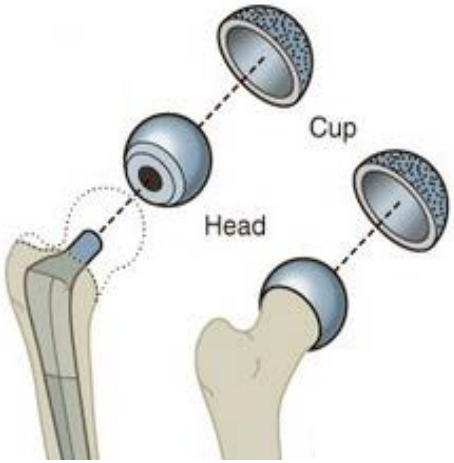
	ASTM F1547/HC	ISO 5832 / HC
Co	Balance	Balance
Cr	26-30 %	26-30 %
Mo	5-7 %	5-7 %
Mn	0-1 %	0-1 %
Si	0-1 %	0-1 %
N	0-1 %	0-1 %
C	0.15-0.35 %	0.15-0.35 %
Fe	0-0.75 %	0-0.75 %
N	0-0.25 %	0-0.25 %

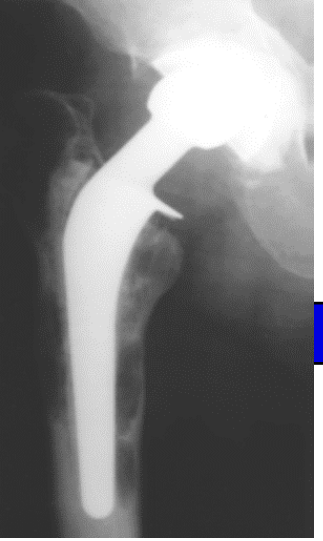
Clayton JBJS 2008;90:1988

Corrosion of Implants

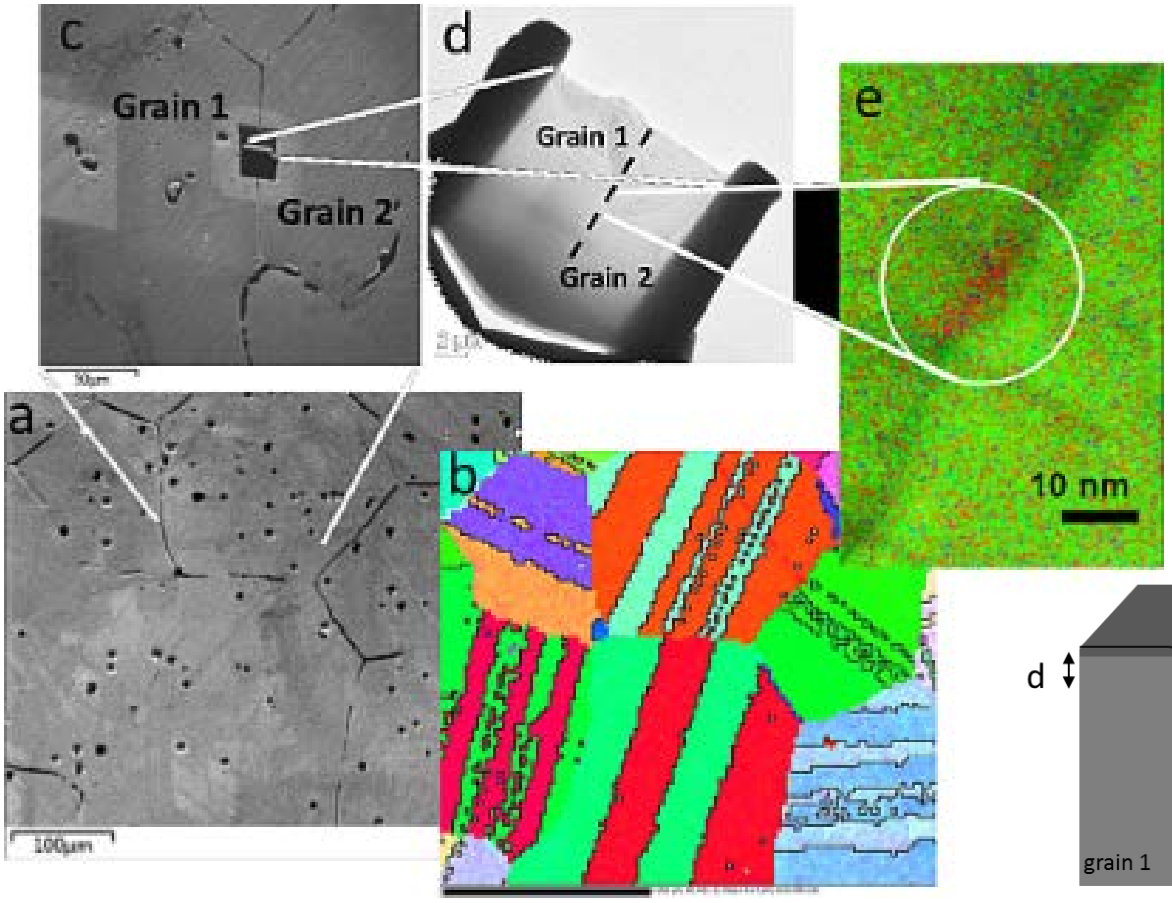
- CoCrMo implants corrode approximately 0.01 mm per year
- >350K/year total hip replacements performed in the US

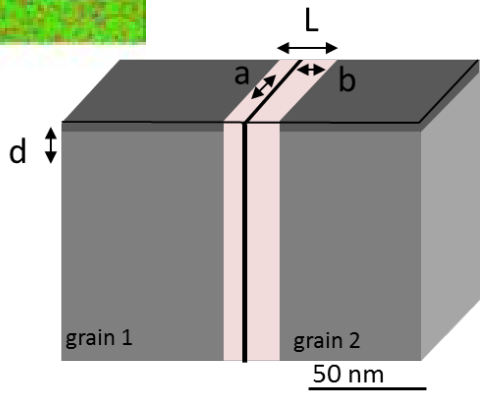




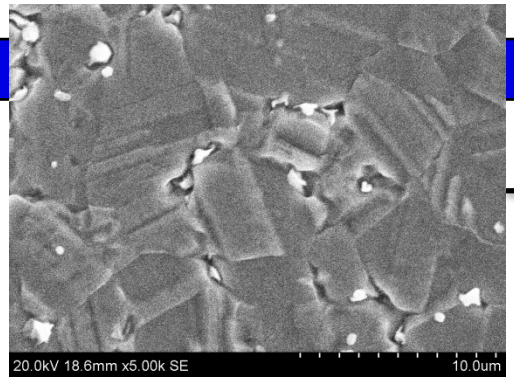


Multiscale Analysis in Practice

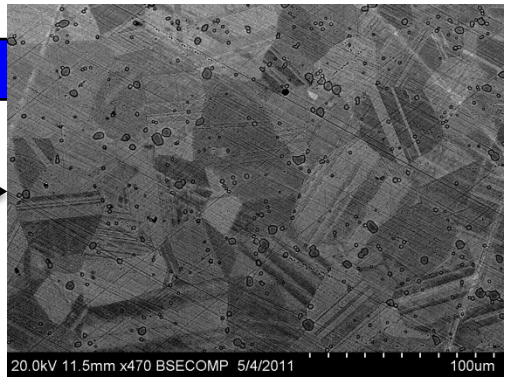




Methods



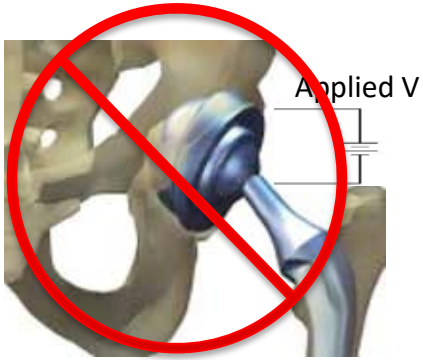
Furnace:
1150°C/2h
1150°C/24h
1230°C/2h
1230°C/24h

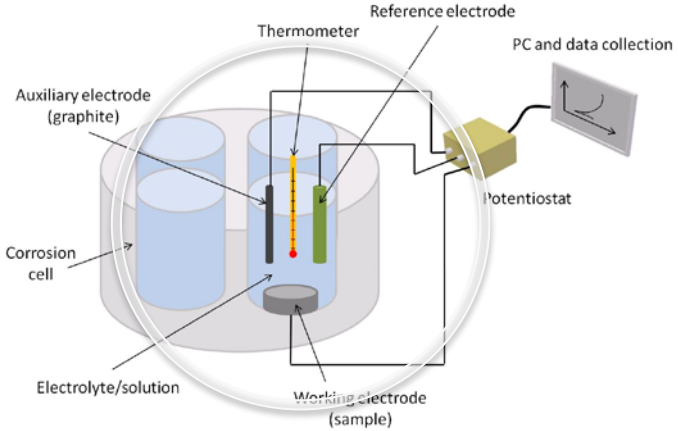


As-received, wrought
3-5 um FCC matrix grains
High number density of second phases
Heavily twinned

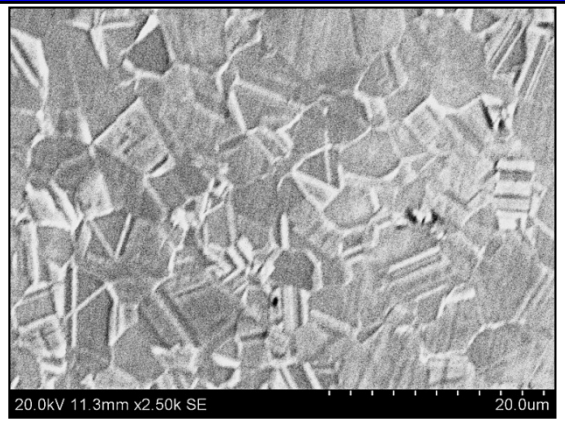
Solution annealed, same crystal structure
FCC matrix grains up to 100-300 um
Fewer second phase regions / unit area
(some carbide/intermetallic dissolution)
Heavily twinned

Accelerated electrochemical corrosion tests (in vitro)





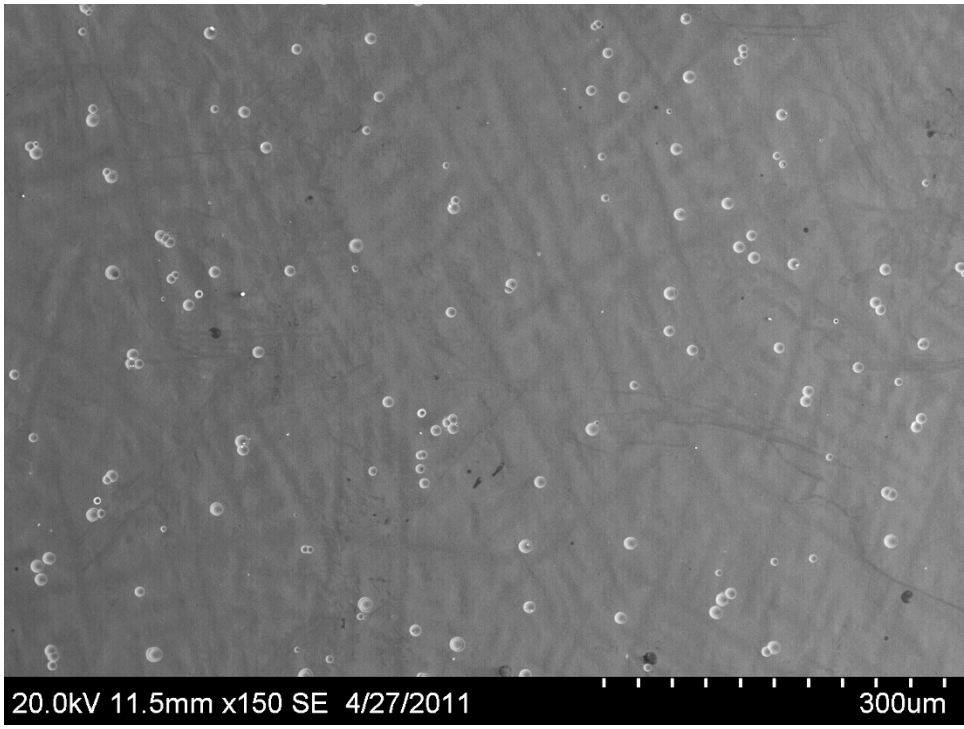
Low Carbon CoCrMo



Very few localized pits

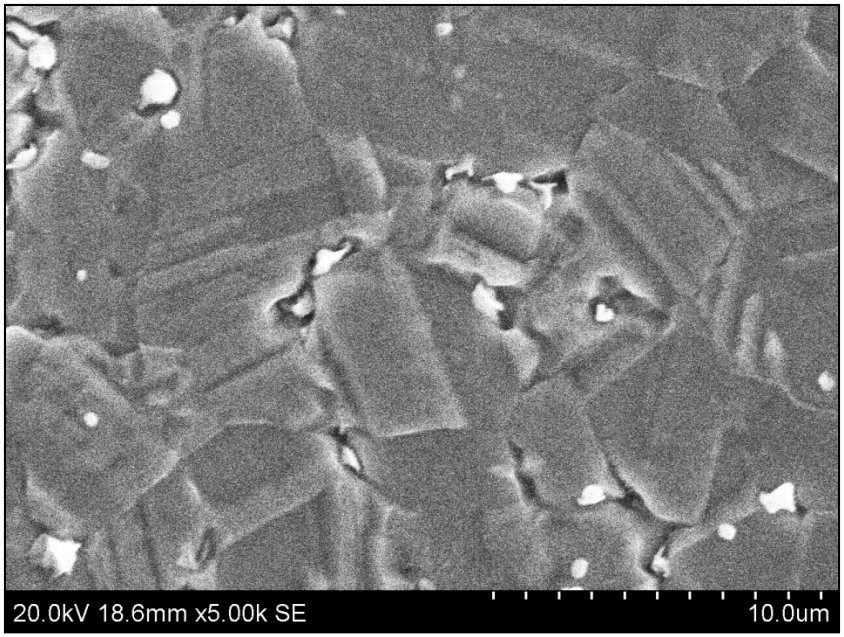
Faster overall rate of corrosion

Low-carbon alloy subject to general corrosion which attacks the entire surface

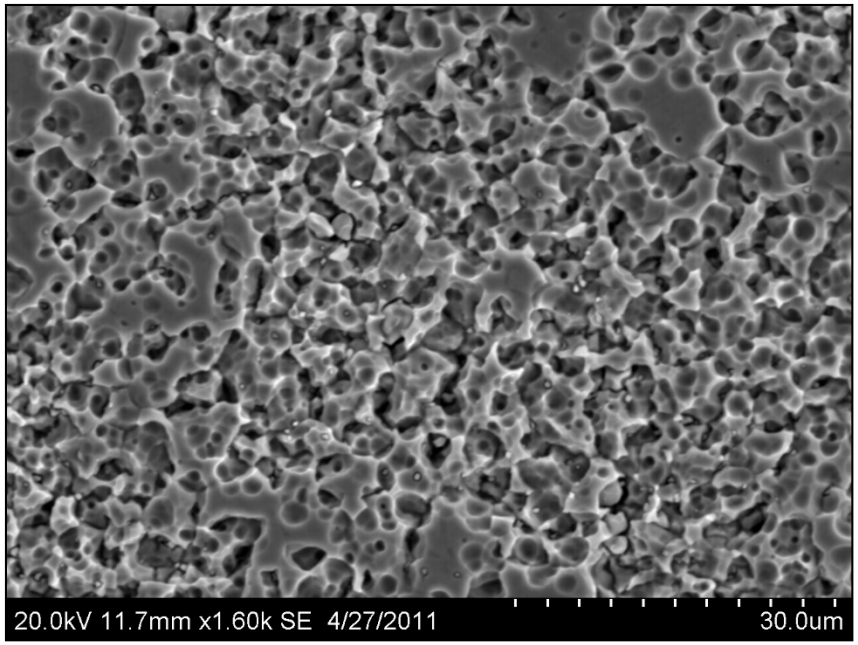


Wrought Alloy (not annealed)

Pitting corrosion everywhere



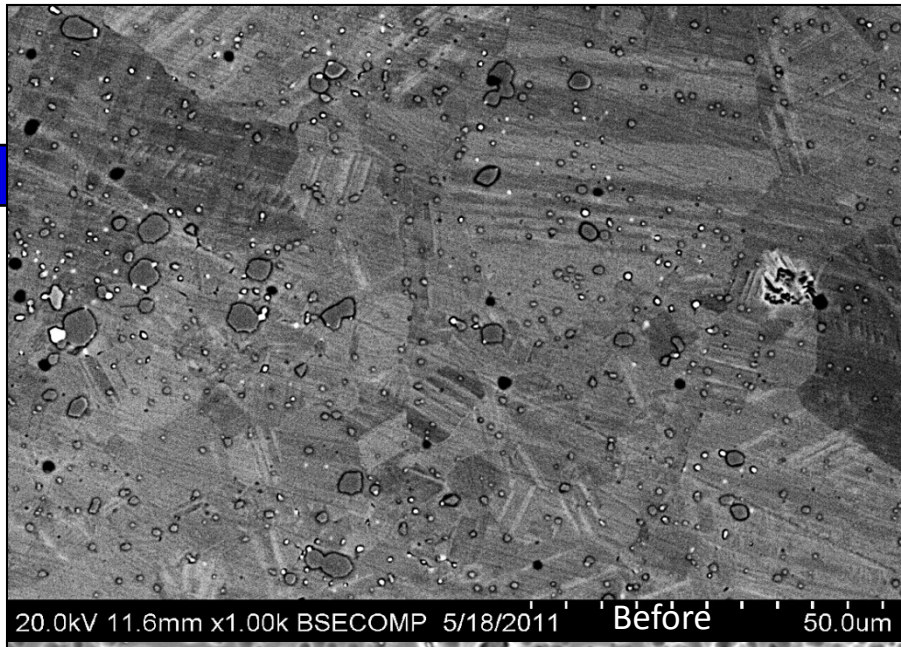
Before

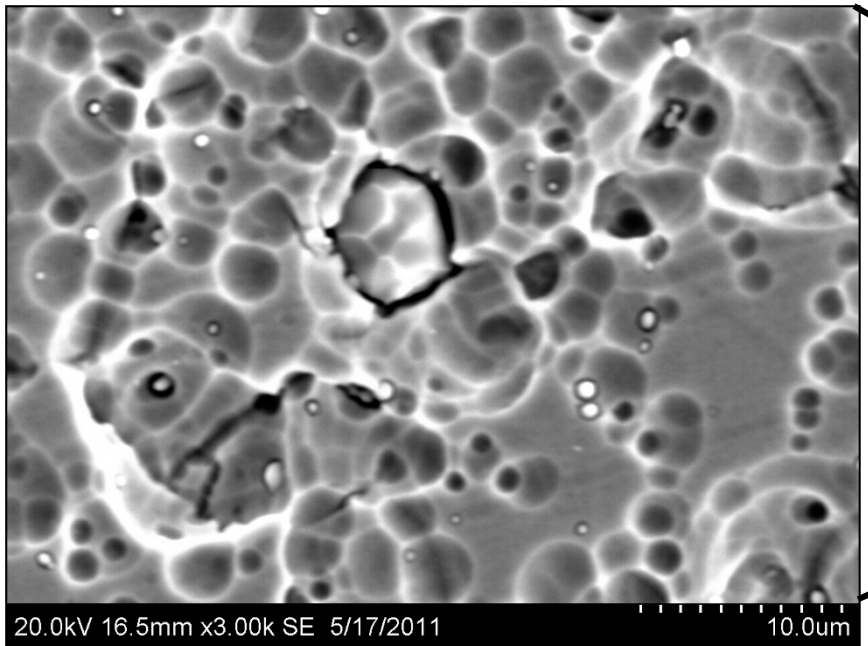


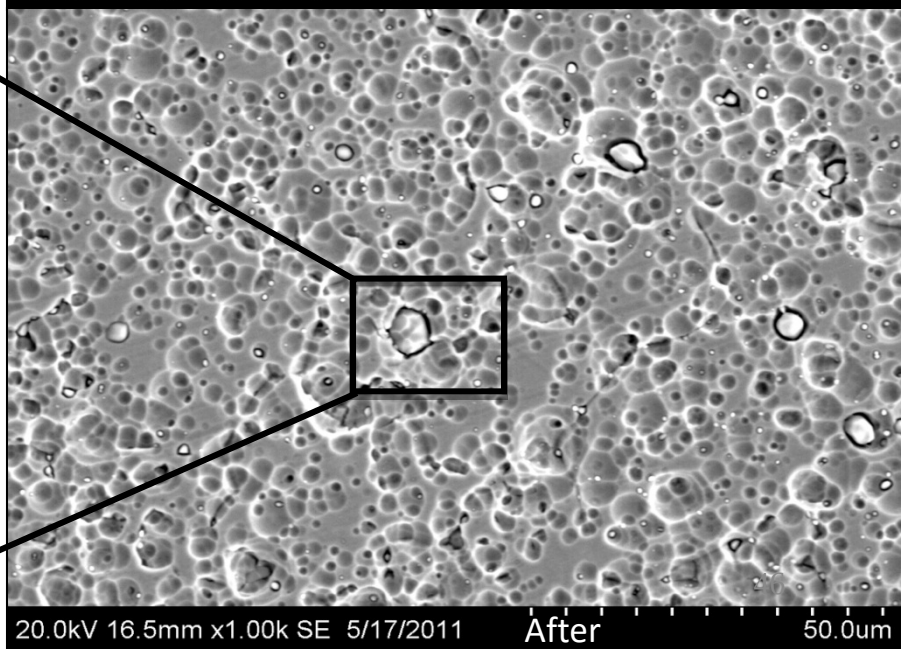
After

Annealed 1150 C/2hr

Pits have corroded *around* second phases (phase boundaries) but not the second phases themselves

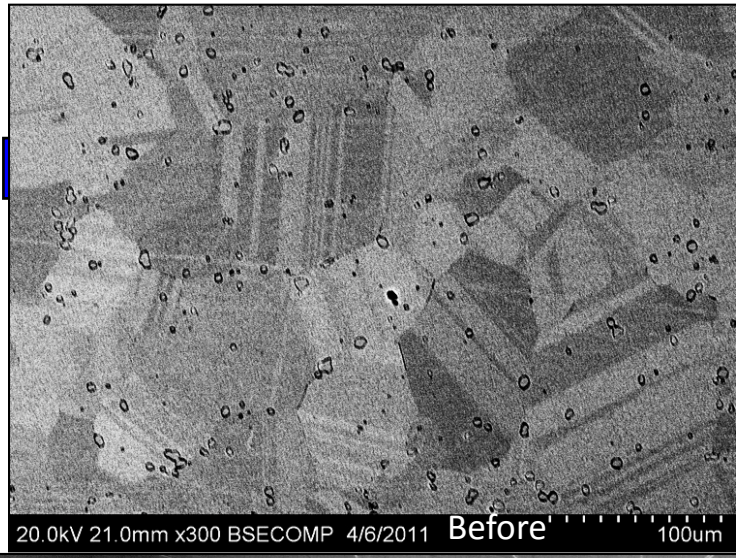


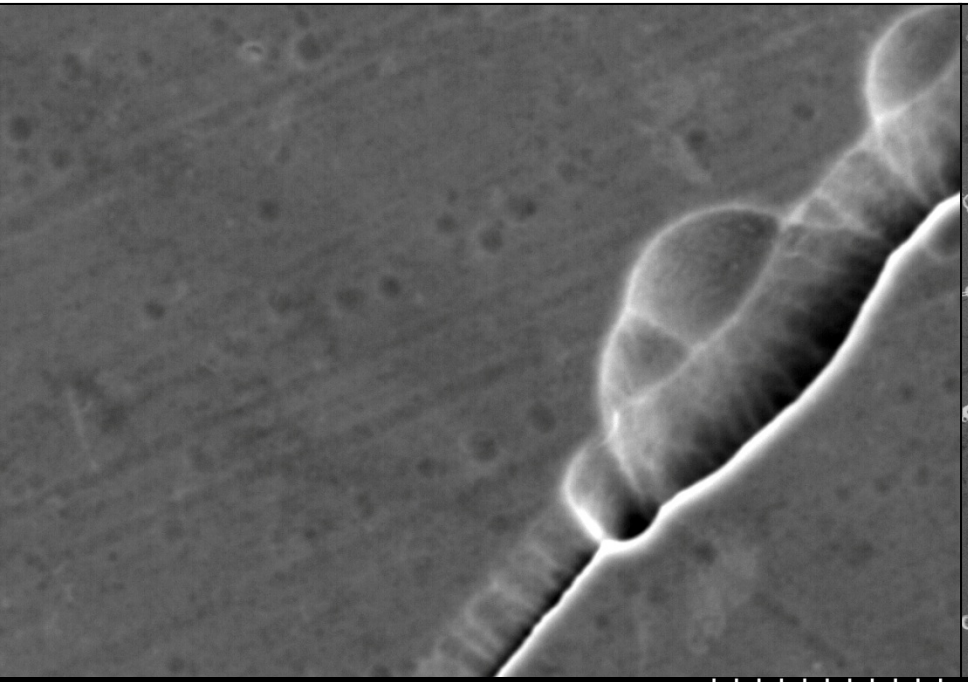


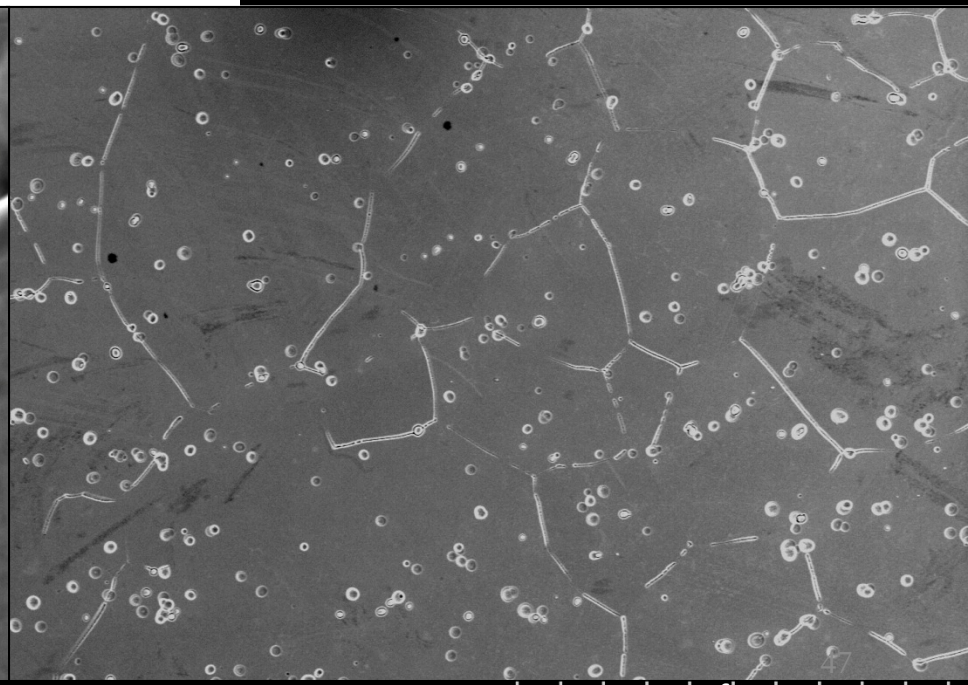


Longer Anneal (1150 C/24 hr)

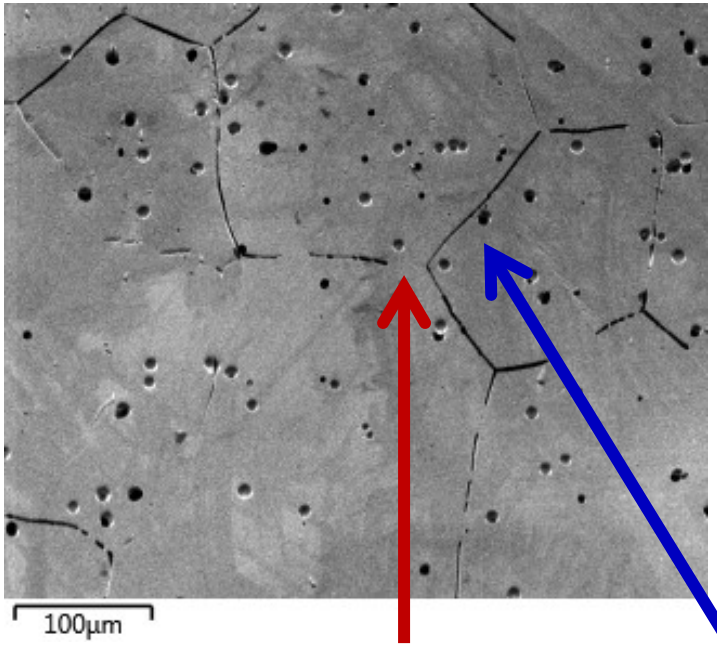
Pits localized at phase boundaries and at *some* grain boundaries



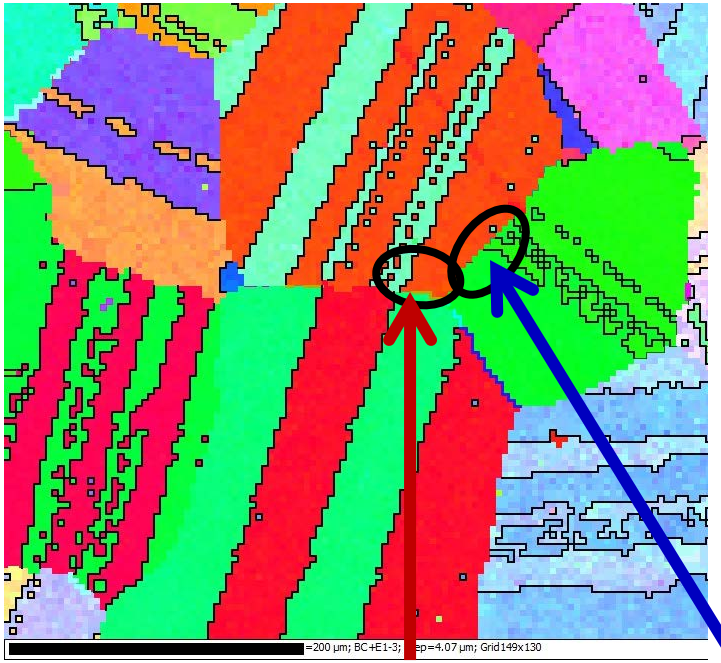




EBSD to determine orientation

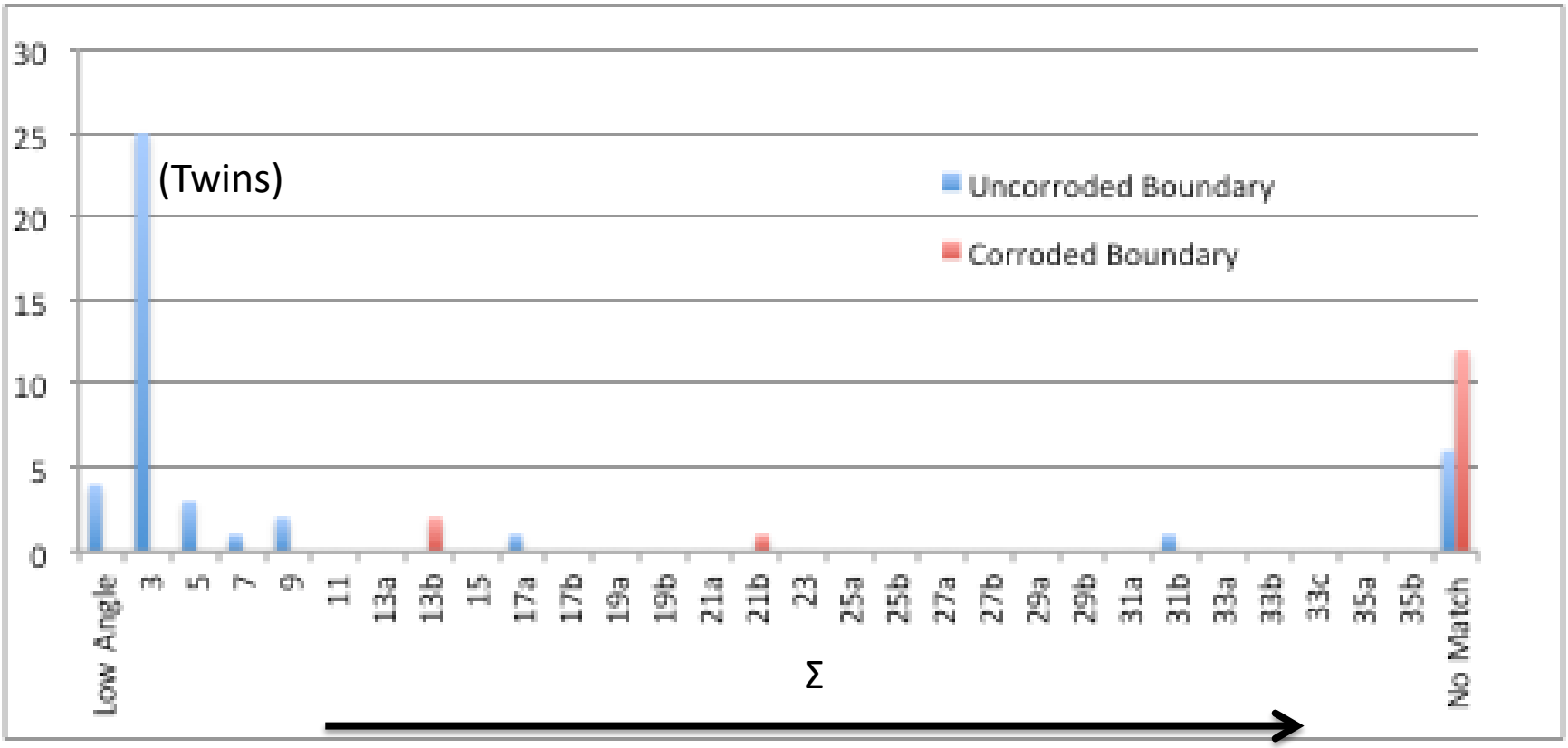


uncorroded corroded

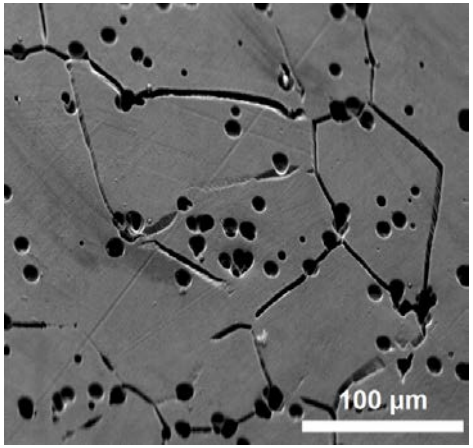


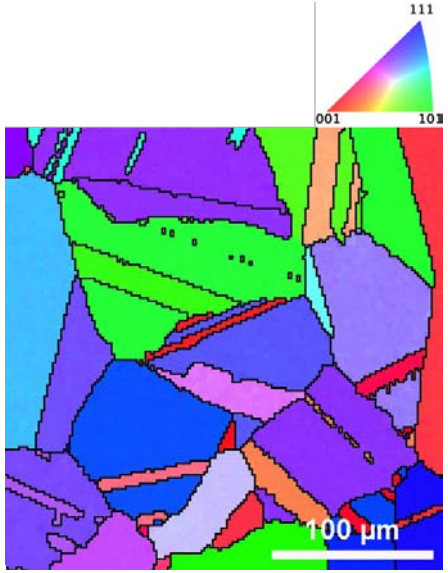
uncorroded corroded

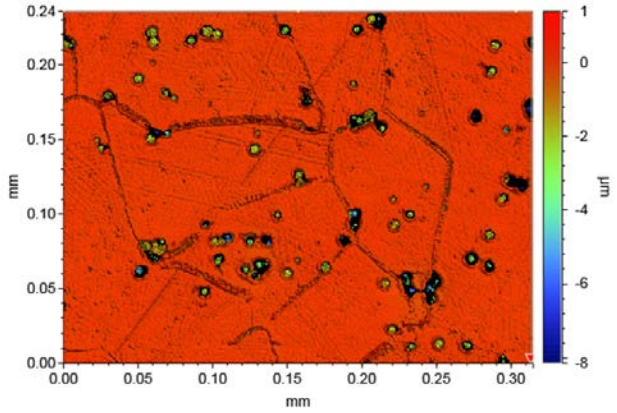
Corrosion is at high-energy boundaries

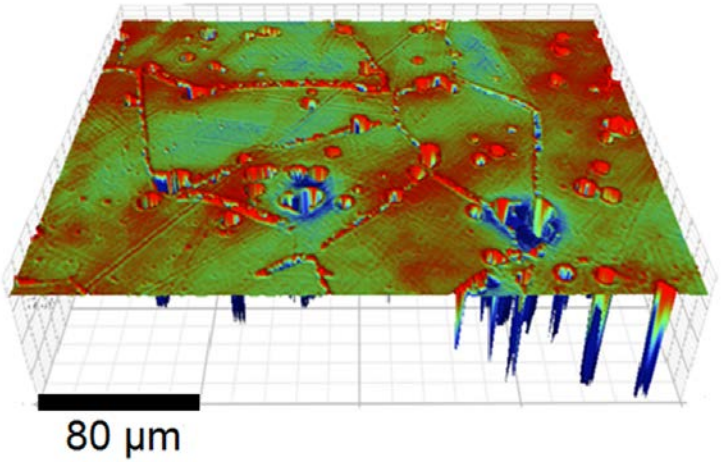


Add 3D profilometry

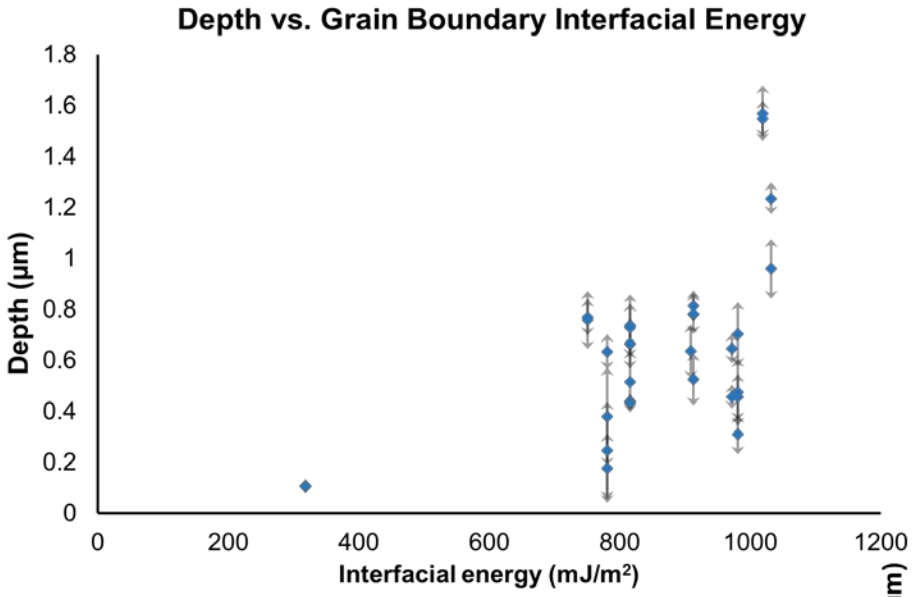


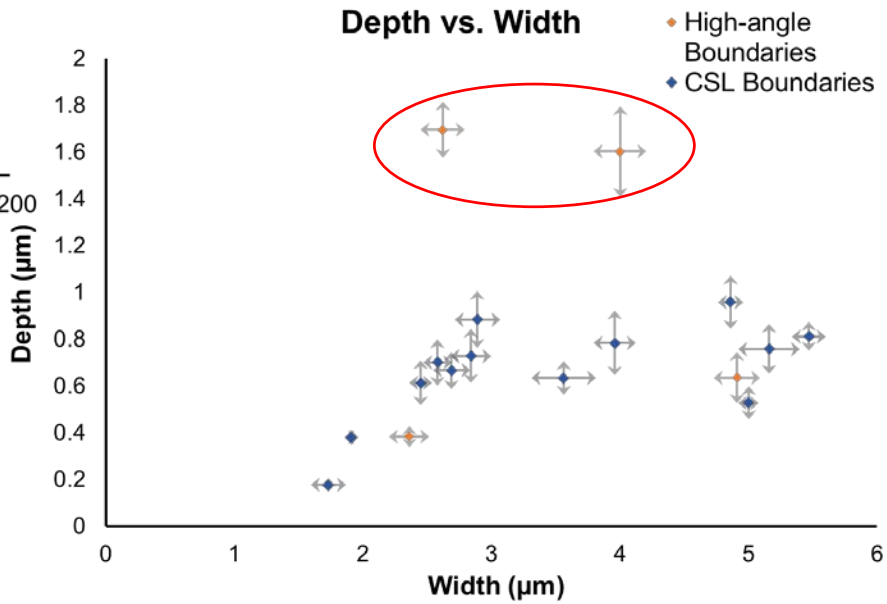




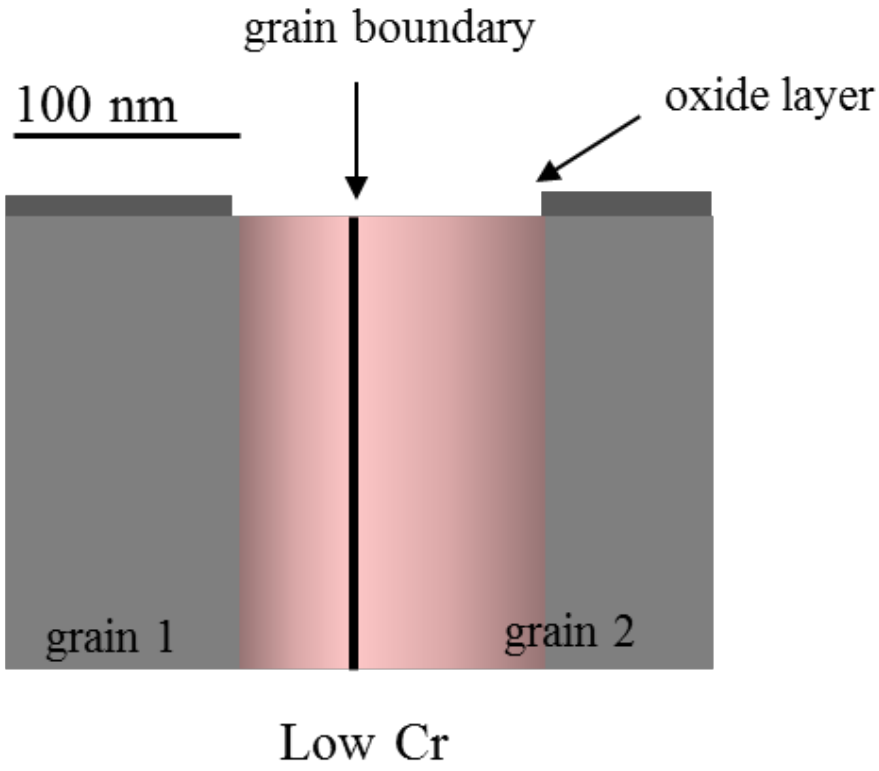


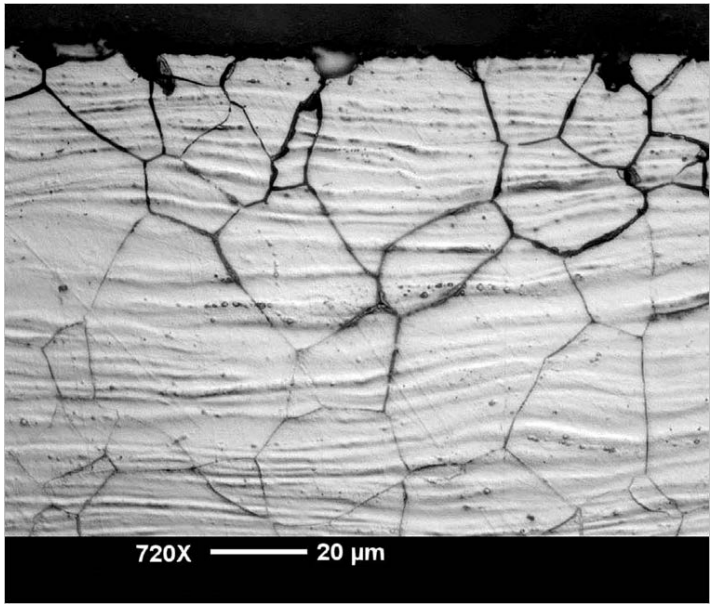
Depth Information



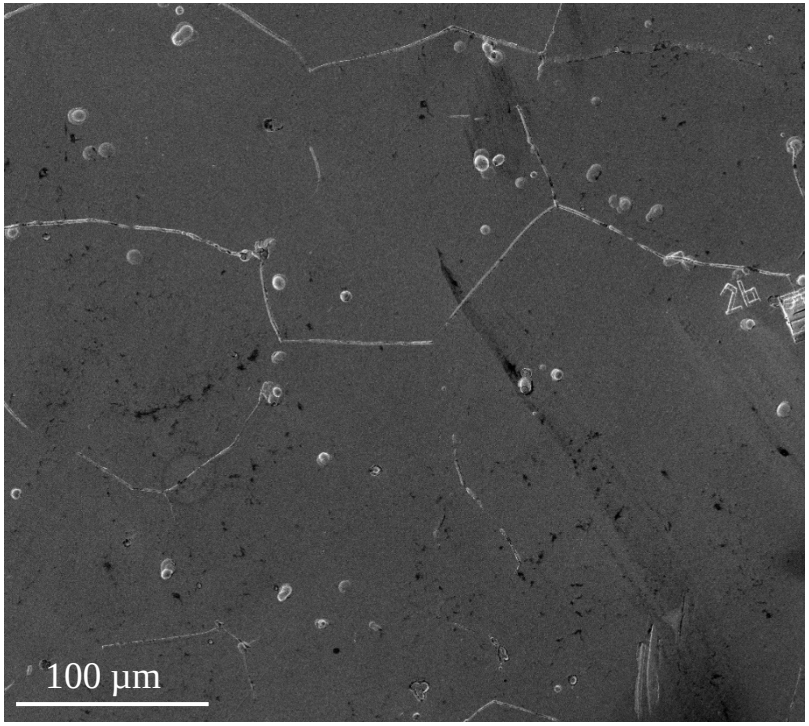


Conventional view of intergranular corrosion





What controls corrosion at a grain boundary?

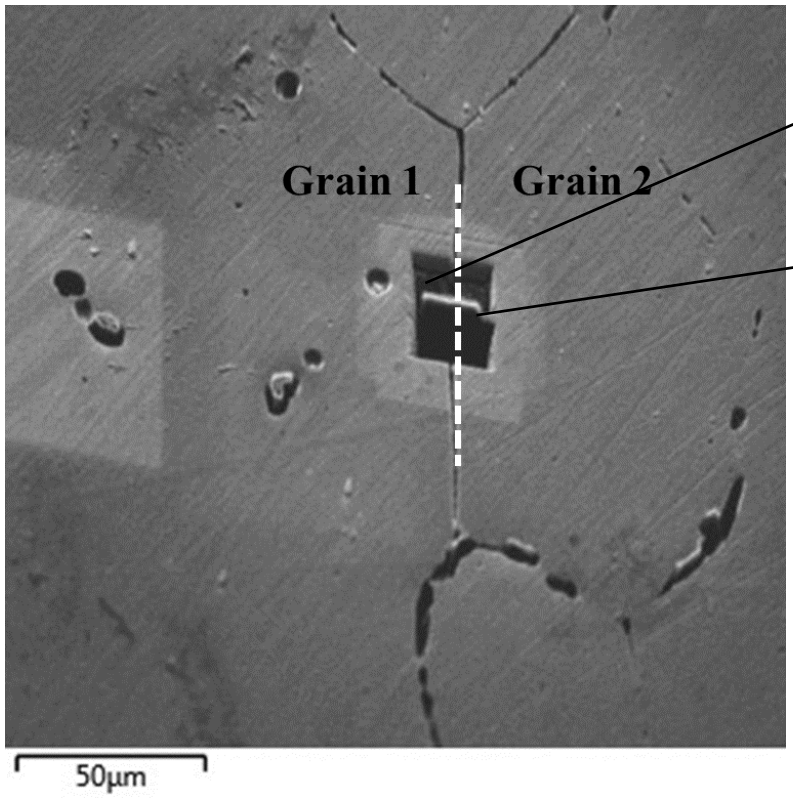


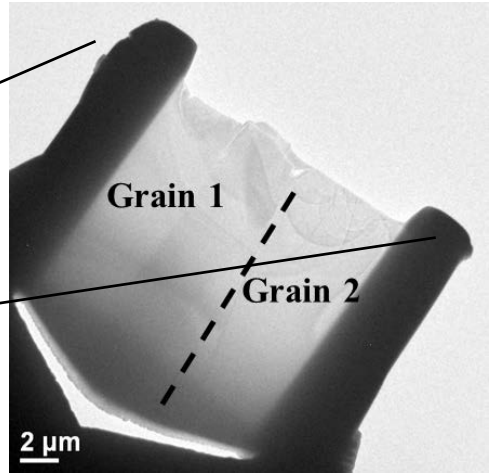
Hypotheses

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

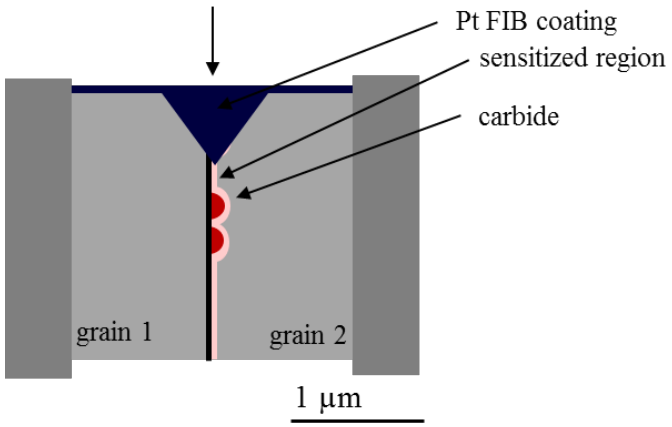
Sensitization is when the chromium of the matrix gets tied up in a carbide so the Cr_2O_3 protective layer can no longer form.

FIB TEM sample

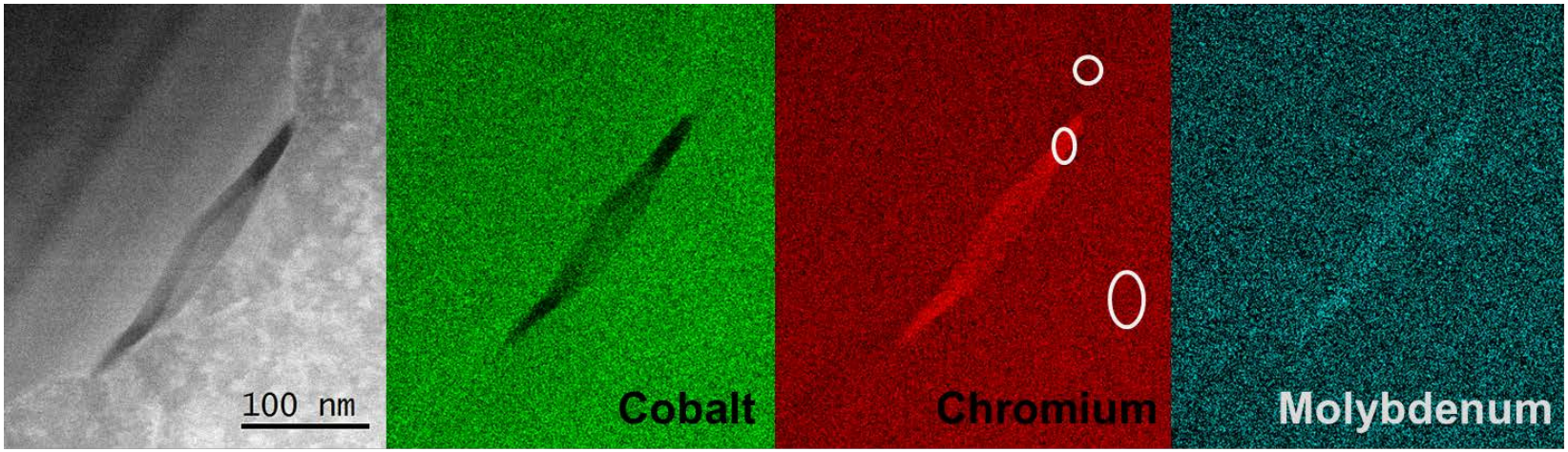




grain boundary

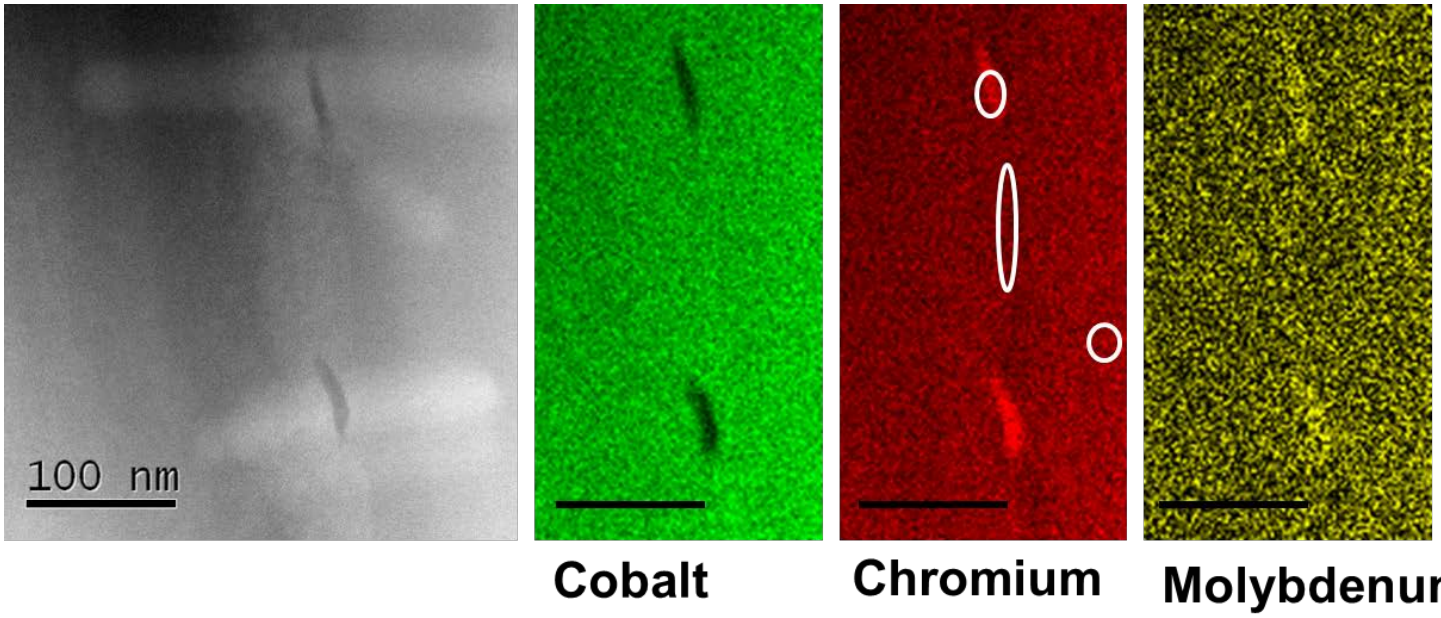


Large Precipitates: 0.68 of Cr



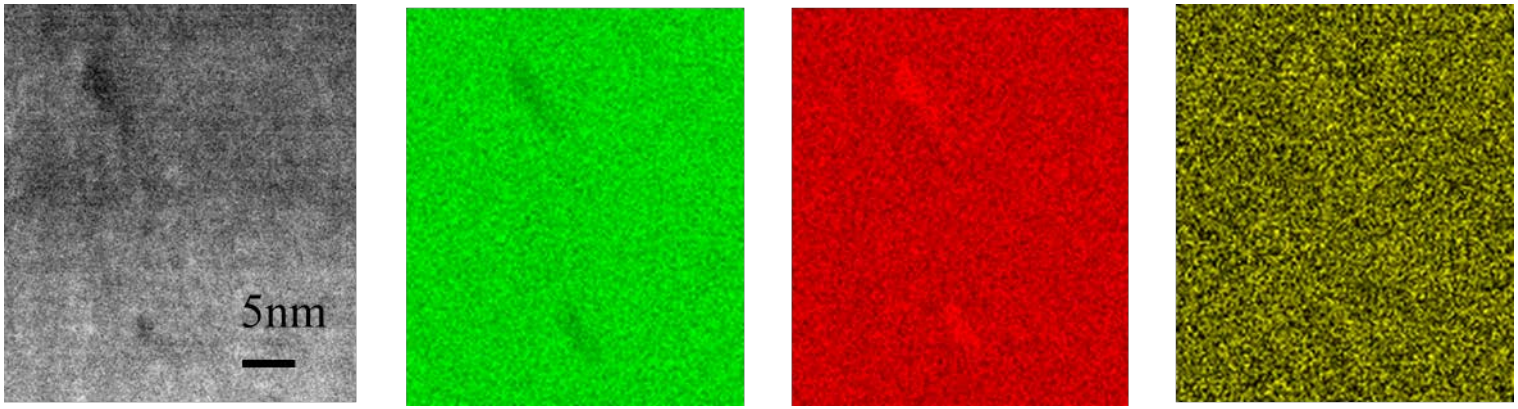
	Co (at%)	Cr (at%)	Mo (at%)
Matrix	64.48	30.62	4.9
Carbide	19.28	67.16	13.56
Sensitization	70.44	20.99	8.57

Medium Precipitates: 0.96 Cr



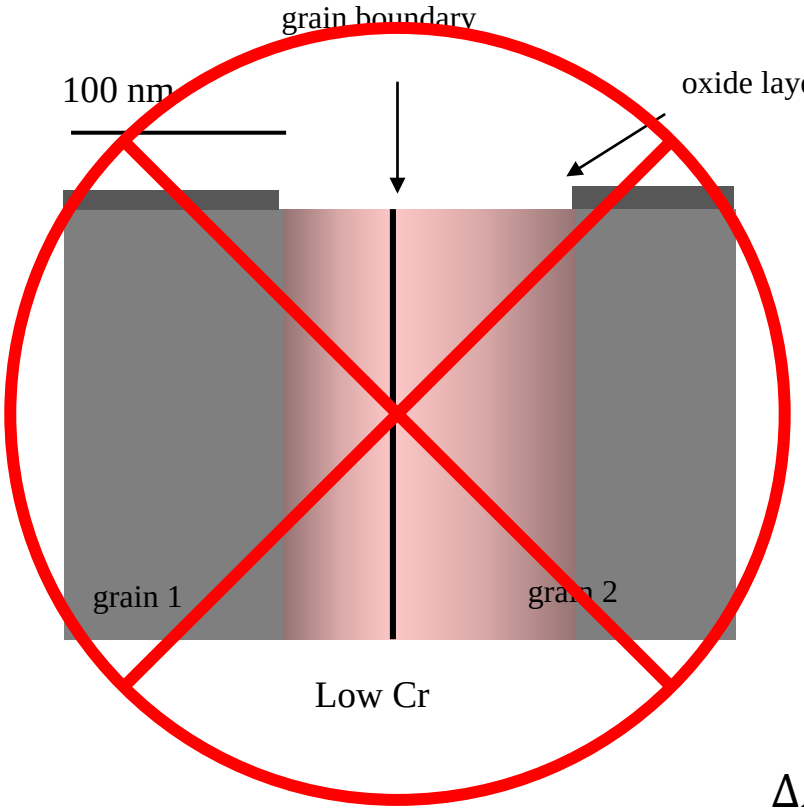
	Co (at%)	Cr (at%)	Mo (at%)
Matrix	64.52	28.31	7.17
Carbide	38.74	48.85	11.4
Sensitization	66.33	26.48	7.19

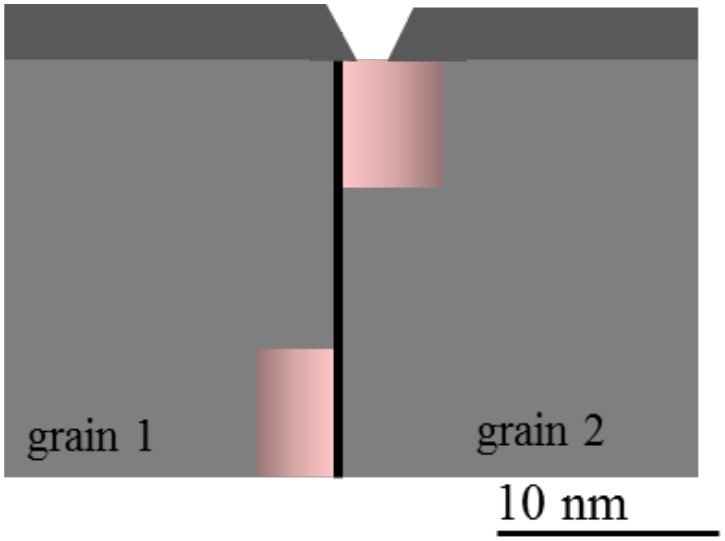
Small Precipitates: 1.0 Cr



	Co (at%)	Cr (at%)	Mo (at%)
Matrix	63.56	30.89	3.80
Carbide	59.95	33.00	4.88
Sensitized	63.56	30.89	3.80

Sensitization in Implants



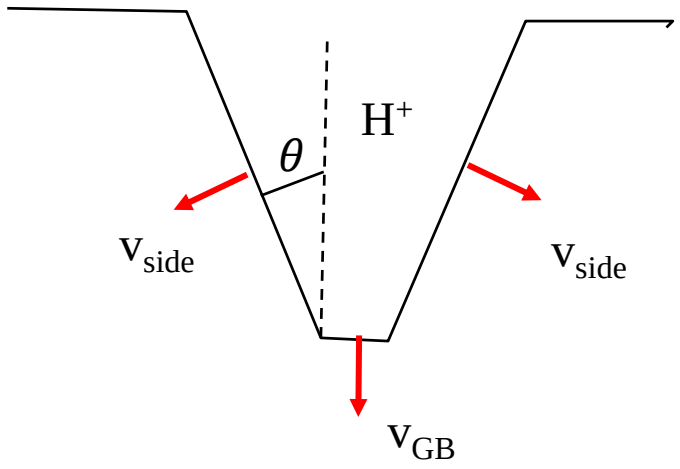


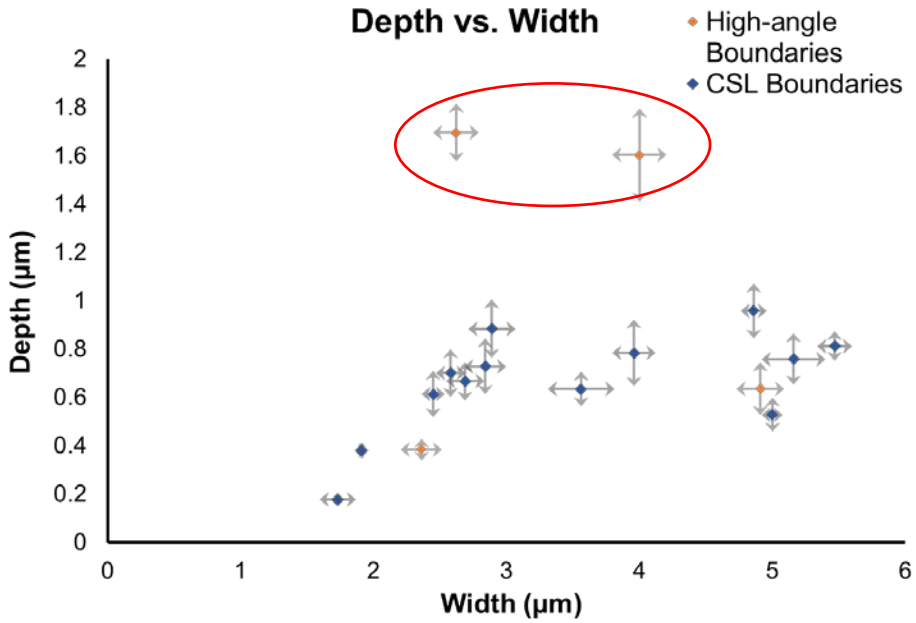
$$\Delta E_{GB} = -1.5\ to\ -5.4 \times 10^{-19}\ Jnm^{-1}$$
$$\Delta E_{Seg} = -1.8\ to\ -8.4 \times 10^{-19}\ Jnm^{-1}$$

Both grain boundaries and segregation matter

Simple Qualitative Model

- Maps to a kinetic-Wulff shape





$$\sin(\theta) = v_{side}/v_{GB} \sim \Delta\mu_{side}/\Delta\mu_{GB}$$

$$\tan(\theta) = 0.5 * Width/Depth$$

What does this mean?

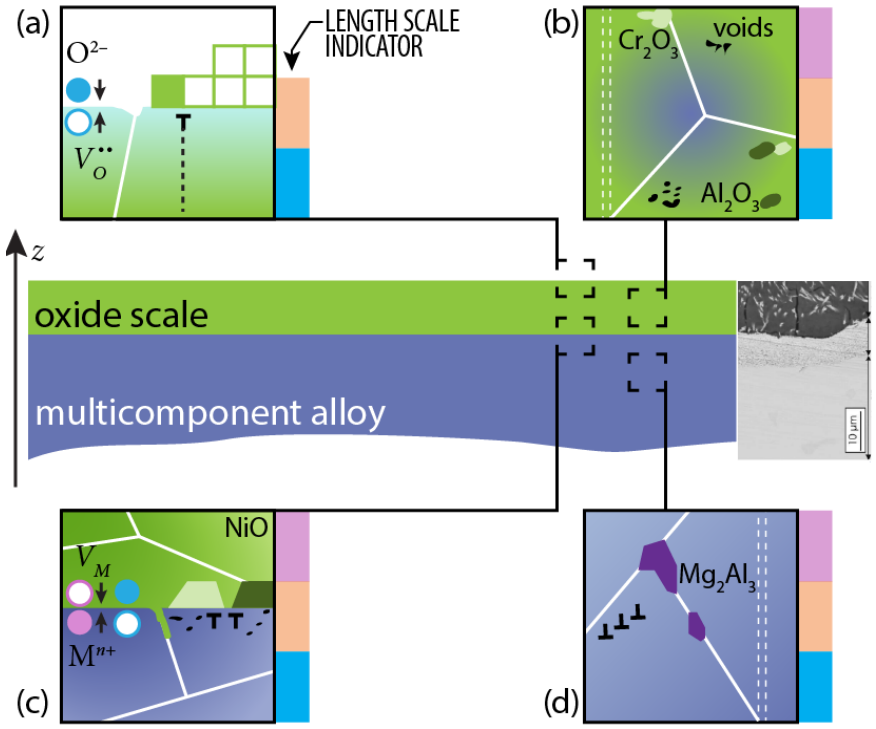
- Depletion of Cr is small – not conventional sensitization
- Grain boundary energy and chemical terms from segregation are comparable
- Cannot explain via conventional models
- Grain boundaries are only *initiators* of corrosion, then crevice corrosion

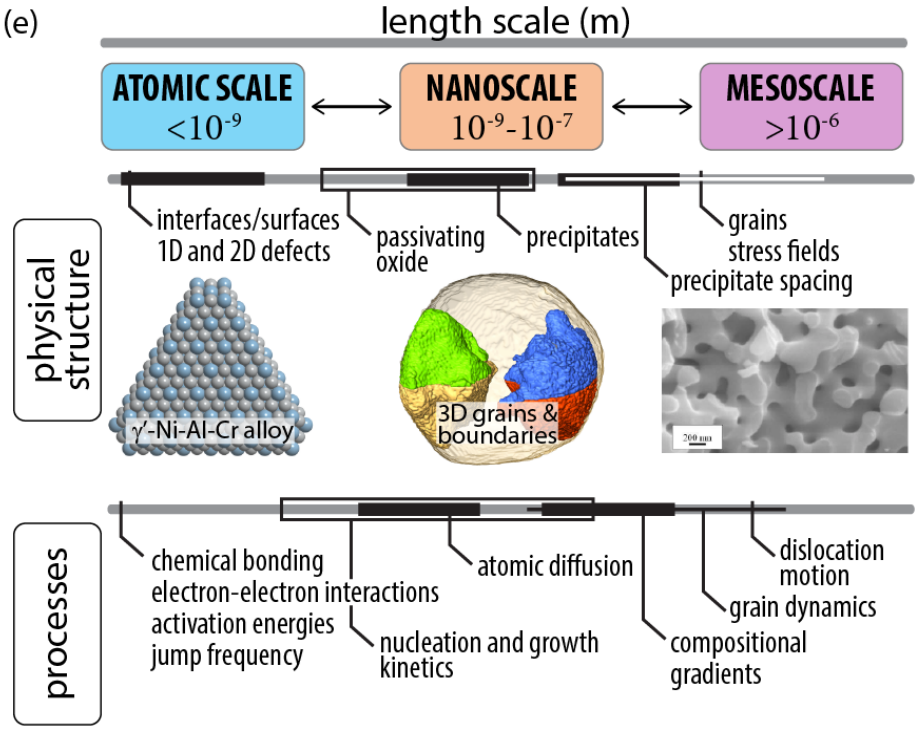
Summary

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 ?


(a)
LENGTH SCALE INDICATOR
O^{2-}
$V_O^{\bullet\bullet}$
(b)
Cr_2O_3
voids
Al_2O_3
z
oxide scale
multicomponent alloy
10 μm
(c)
NiO
V_M
M^{n+}
(d)
Mg_2Al_3


(e)
length scale (m)
ATOMIC SCALE
<10^{-9}
NANOSCALE
10^{-9}-10^{-7}
MESOSCALE
>10^{-6}
physical structure
interfaces/surfaces
1D and 2D defects
passivating oxide
precipitates
grains
stress fields
precipitate spacing
γ′-Ni-Al-Cr alloy
3D grains & boundaries
200 nm
processes
chemical bonding
electron-electron interactions
activation energies
jump frequency
nucleation and growth kinetics
atomic diffusion
compositional gradients
dislocation motion
grain dynamics