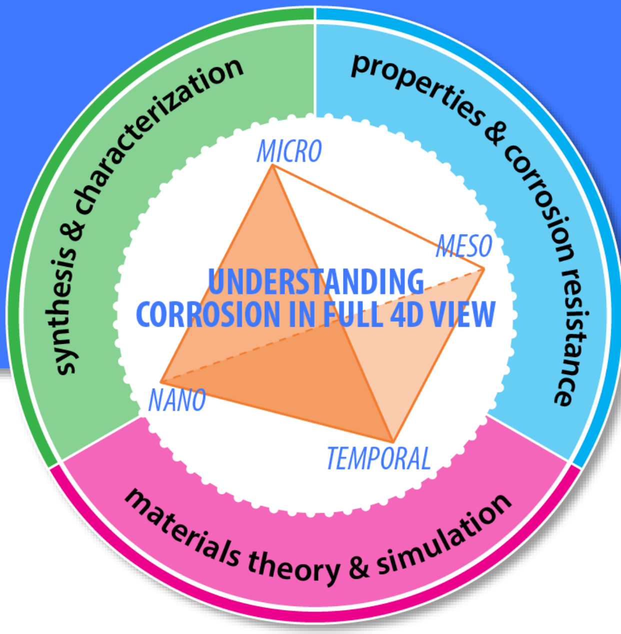
Understanding Atomic Scale Structure in Four Dimensions to Design and Control Corrosion Resistant Alloys



Laurence Marks, James Rondinelli, and Peter Voorhees
Northwestern University

Hendrik Heinz
University of Akron

John Miao
University of California, Los Angeles

Petra Reinke and John Scully
University of Virginia

John Perepezko
University of Wisconsin, Madison

Motivation

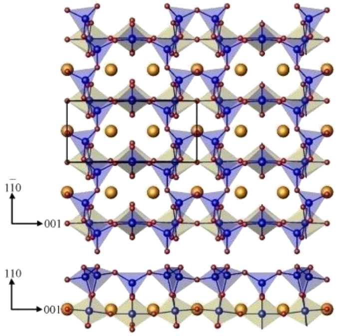
- Corrosion affects the longevity in applications ranging from gas transmission pipelines to DoD/ONR warfighters and warships. The total cost of corrosion in the United States was $276 Billion in 1998, about 3.15% of GDP, and in 2010, the Department of Defense (DOD) estimated that corrosion costs the department over $23 billion annually and an October 2009 study estimated that corrosion is responsible for up to 16 percent of the unavailability of the equipment reviewed.

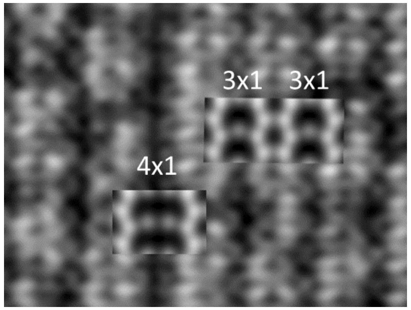
Rusted Deck and Ventilation Equipment
Source: www.corrdefense.org

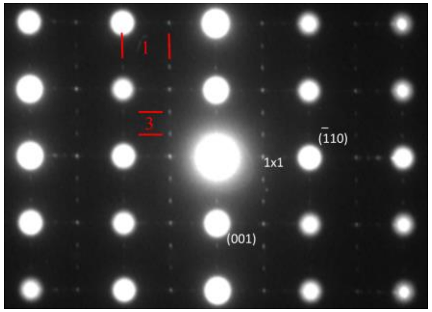
The Opportunity

- There has been an explosion of tools to image materials at the atomic scale and accurately calculate their behavior. Not only can single atoms be imaged, their chemical state can be measured. Modern ab-initio methods such as density functional theory are now starting to be able to handle materials such as transition metal oxides. Our intent is to bring the full power of these new tools to bear on corrosion at the atomic scale *on the same systems*.

TEAM 1.0 Electron microscope, NCEM





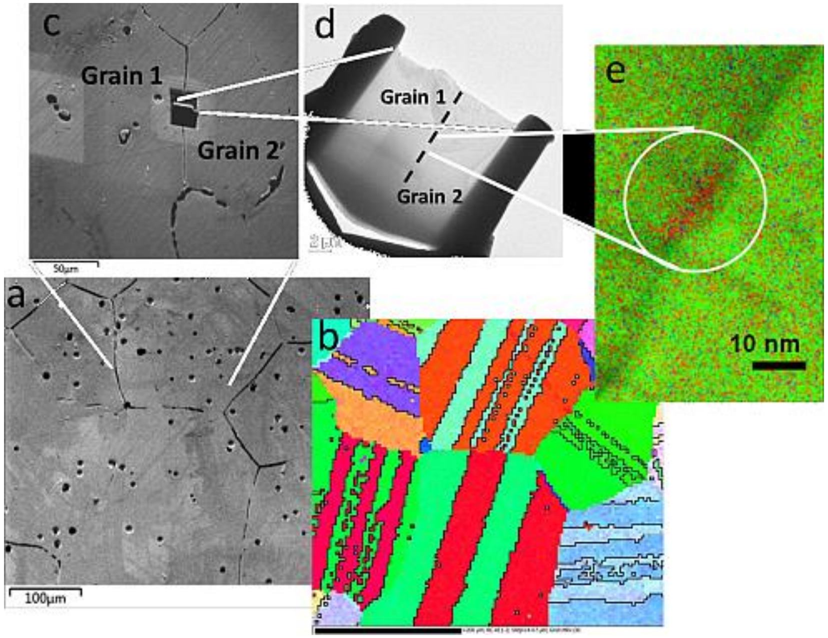


Combining advanced TEM, DFT & STM to solve complex surface structures: Enterkin et. al., Nature Materials, 2010

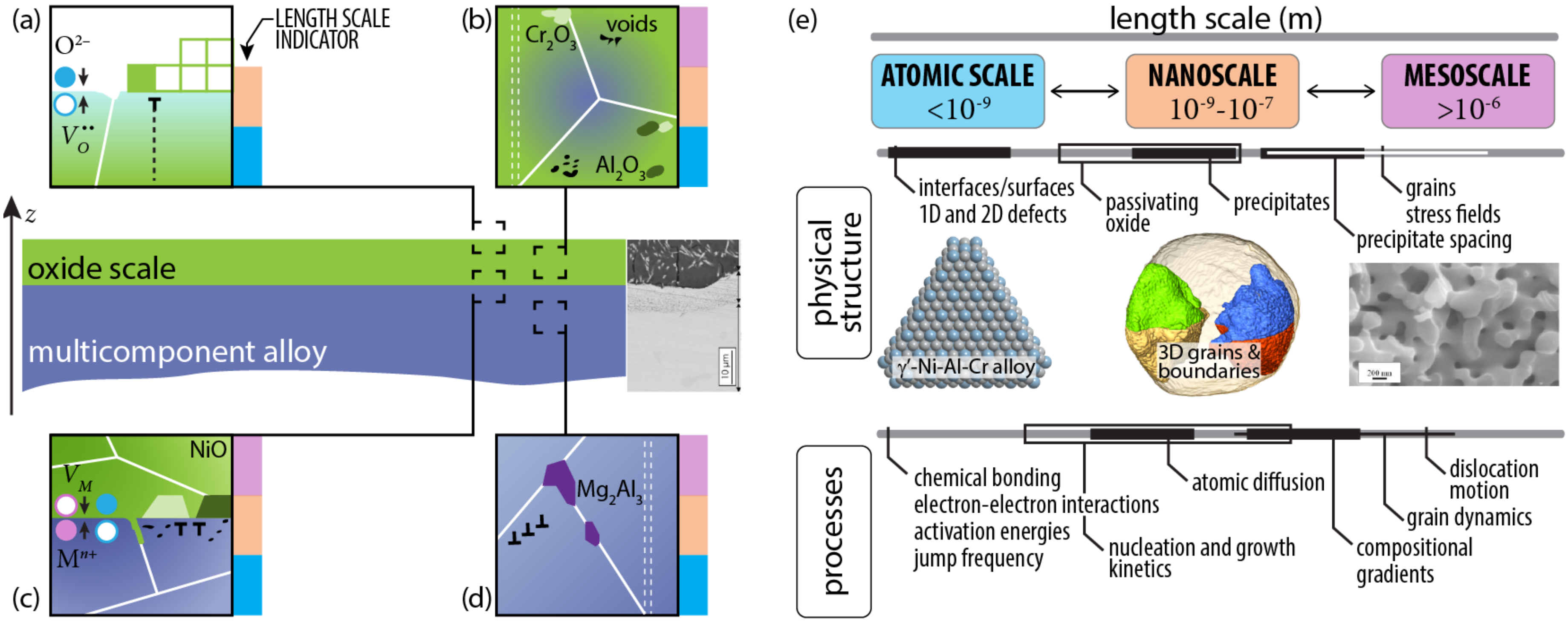
Towards a new Paradigm

- Our target to understand in detail the early-stage oxidation and aqueous corrosion in three selected model systems. We believe that a comprehensive experimental and theoretical attack will enable us to understand what matters, what does not, and lay the basis for a paradigm shift in improvements of corrosion-resistant materials.

Multiscale analysis of a corroded Co-Cr-Mo alloy

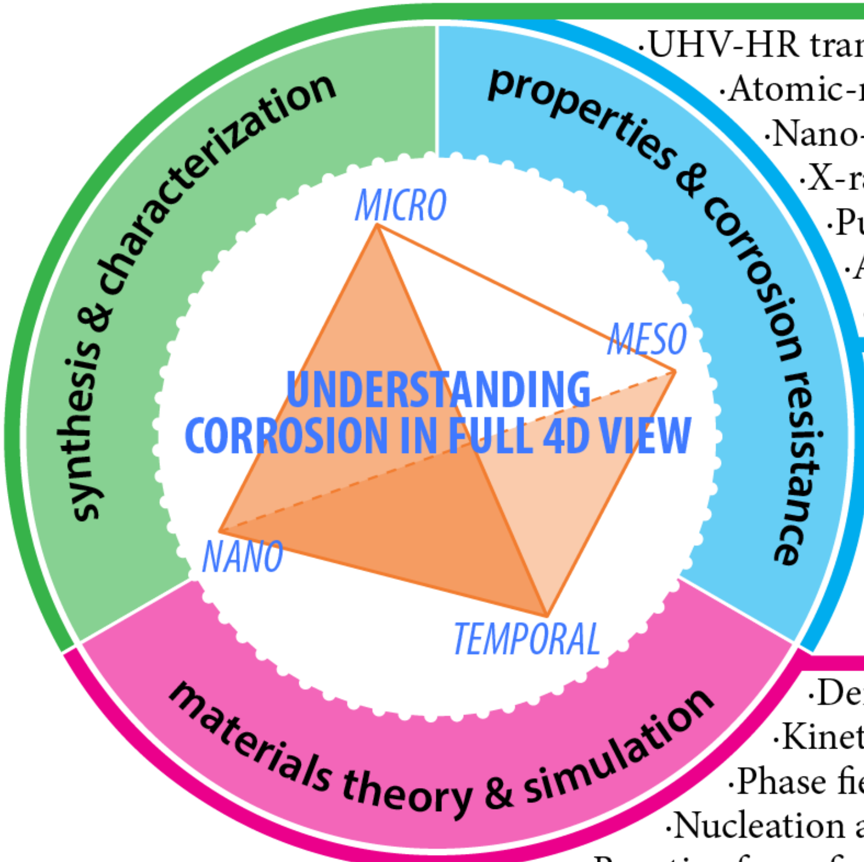


A Multiscale Problem

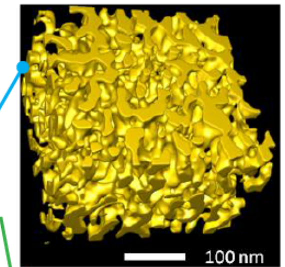


Multiple processes occurring over wide spatial and temporal scales control the nucleation, stability, and utility of oxide scales. An integrated multiscale modeling combined with real and reciprocal space experimental characterization tools is required to fully understand and predict corrosion processes.

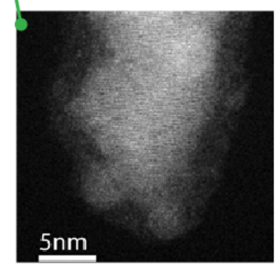
Exploit a range of tools to tackle key science issue



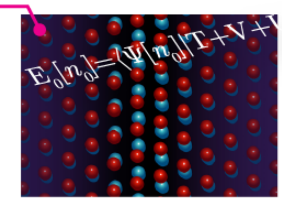
- UHV-HR transmission electron microscopy
- Atomic-resolution electron tomography
- Nano-focused *in situ* X-ray diffraction
- X-ray tomography
- Pulse oxidation
- Abberation-corrected microscopy
- Atom probe tomography



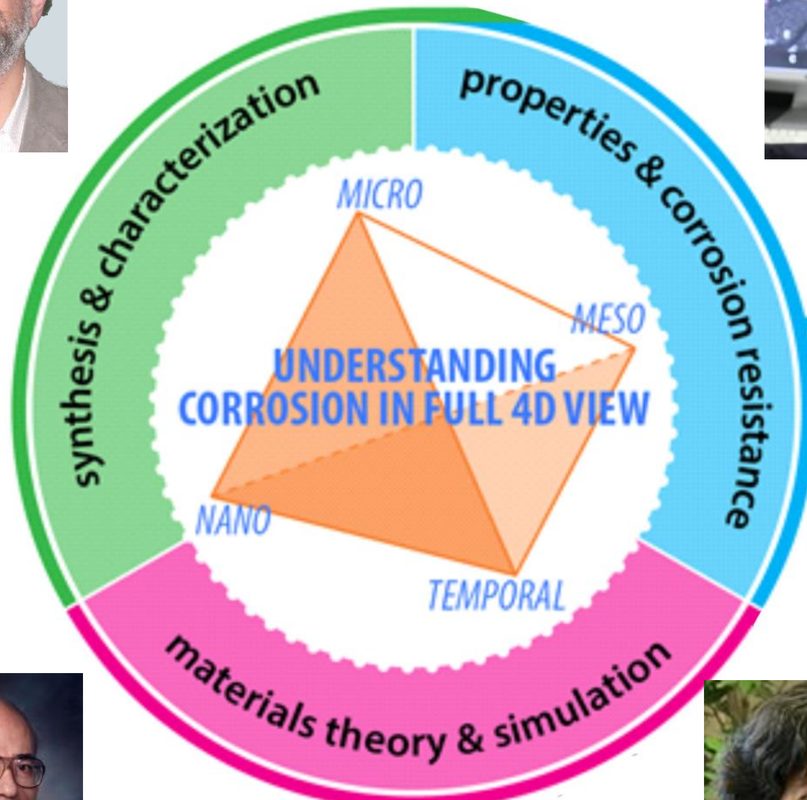
- *How*, *when*, *where* of oxidation?
- Grain-boundary sensitization
- Protective oxide layers
- Defect specific Pourbaix diagrams

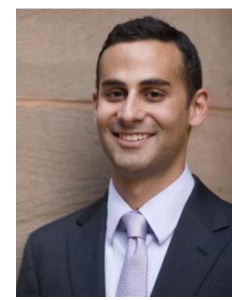


- Density functional theory (DFT)
- Kinetic Monte Carlo (KMC)
- Phase field simulations
- Nucleation and growth theory
- Reactive force-field molecular dynamics (MD)



Team: PIs work in multiple elements of the science





Facilities: National and International

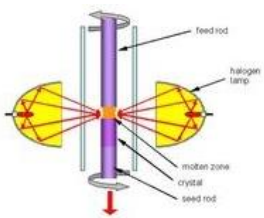
Electron Microscopy

ANL
NCEM
UIC
UWM

Synchotron

APS
BNL
ESRF

Single Xtals

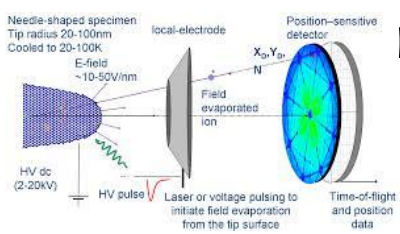


NU
UWM

Computation

Quest, NU
XSEDE, NSF
DSRCs, DOD
OSC
AF-HPC

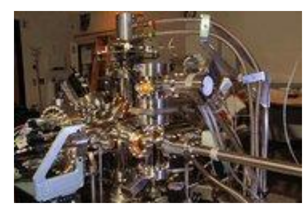
Atom Probe



NU

Surface Science

UVA



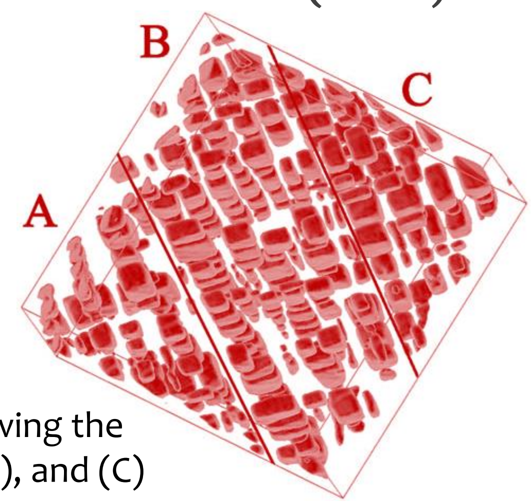
NU

Strategy:

- Instrumentation and Computers are no longer limiting, samples and physical models are
  - KISS & GIGO must control research design
- Well controlled samples/physical models for accurate comparisons by multiple methods
  - DFT → Force Field → Phase Field
  - ACHREM + AREELS + APT + STM + ARET + …
  - Single Crystals bulk samples, wires or large grain epitaxial films
  - Sharing of samples among the experimental groups
    - Single Crystal oriented Wires examined by APT & TEM (LDM), ET (JM), pulse oxidation (JP) and electrochemical methods (JS)
  - Examine single crystal AlNi in-situ (LDM & PR) with surface structures modelled accurately (LDM & JMR) extending to selvedge region below surface monolayer (JMR, HH, PWV)

Task I: Ni-Cr-Al Superalloys

- The Problem/Challenge we pose is: ***When**, **where**, and **how** does oxidation initiate in these materials and what atomistic scale features facilitate the (early stage) growth of the oxide?*
- Combine
  - Targeted materials, AlNi (γ') & AlNiCr (γ) single crystals (LDM, JP)
  - In-situ pulsed oxidation studies (LDM, PR)
  - Pulsed oxidation thermodynamics & Kinetics (JP)
  - Point defects (JMR) → Collective oxidation (HH) → Phase Fields (PWV)
  - Surface structure (LDM, PR)
  - Match experiments to models
  - Progress to multiphase materials

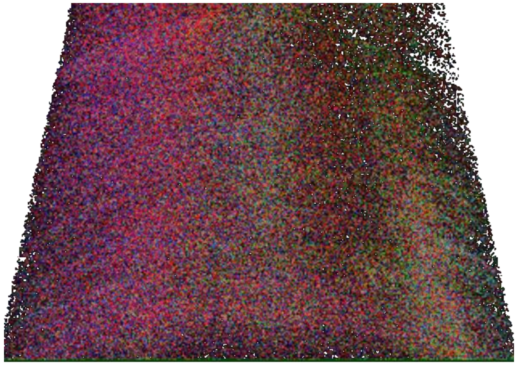


Three-dimensional reconstruction of a γ-γ'structure in Ni-Al, showing the alignment of cuboidal precipitates into three rafts labeled (A), (B), and (C)

Task II: Mo-Si-B Oxidation Resistant Material

- The challenge we pose is ***how do the nanoscale oxide structures develop, and what are the kinetics of oxidation at different stages that bridges the meso and nanoscales.***
  - Develop controlled calibrants (JP)
  - Understand the base single phase alloys (JM, LDM, JP)
  - Understand transient oxidation by experiments (JP, LDM, PH, PR) coupled with theory (JMR, HH)
  - Understand the 4D oxide network development by tomography experiments (JM, PWV) and connect to larger scale modelling (HH, PWV)

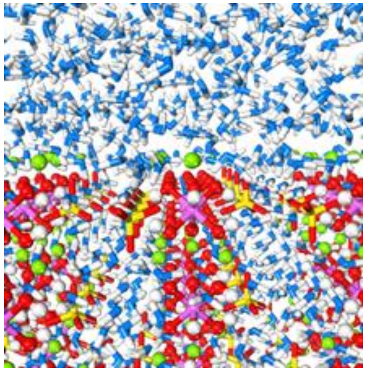
3D APT image of MoSiB base alloy with Mo in red, B blue and Si grey



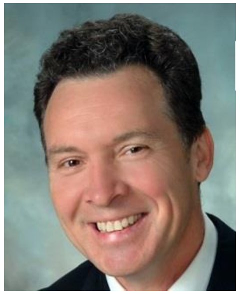
Task III: Aqueous Corrosion of Ni-Cr-Mo Alloys

- The challenge we pose is ***which characteristics of the metal oxide bilayer control aqueous passivation and passive film breakdown?***
  - Develop improved models for point defect thermodynamics and kinetics including more complex phenomena such as screened image charges (JMR, PWV, HH, LDM)
  - Develop designed samples to shed light on the key science issues (PR, JP, LDM)
  - Detailed atomic characterization of well defined surface oxides in 3D by a range of methods (PR, JM)
  - Develop elemental as well as interface specific Pourbaix Diagrams (JMR, JS)
  - Evolve the research from simpler systems towards more complex engineering materials and alloys (JP, JS, PWV)

Perspective atomistic view onto the surface of a hydrated alumina phase in contact with water



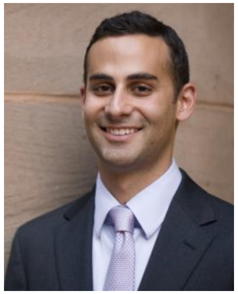
PI's working on multiple tasks



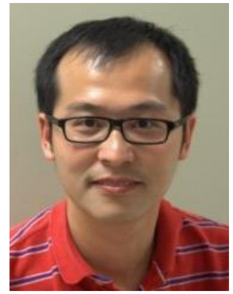
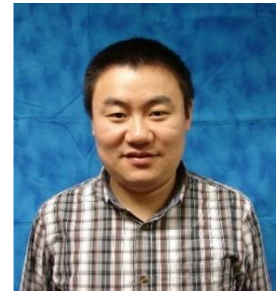
Task I: Ni-Cr-Al

Task II: Mo-Si-B

Task III: Aqueous



Graduate Students, Postdocs, RAP joining effort









Administration Centered at Northwestern

Yifeng Liao

Emily Hoffman

Molli Connell

Maura Cleffi

Industrial Liason

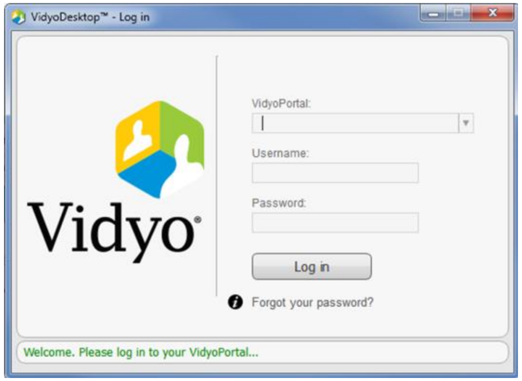
Giorgio Bortolotto

Sarah Stein

Internal Collaborations

- Co-supervised graduate students
- Monthly student organized video conference where students/postdocs will present results and discuss the science
- Monthly PI video conference calls
- Annual Meetings involving PI's as well as collaborators, scientists from DoD laboratories, industry, as well as other academic institutions

Northwestern Video Conference Software

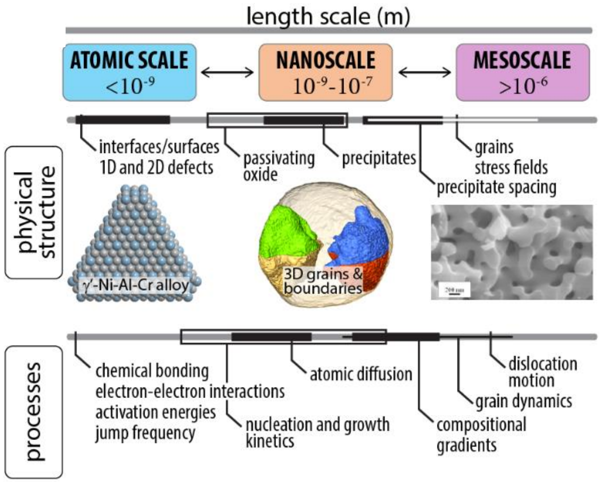


External Collaborators

- Network Of External Collaborators, Expanding

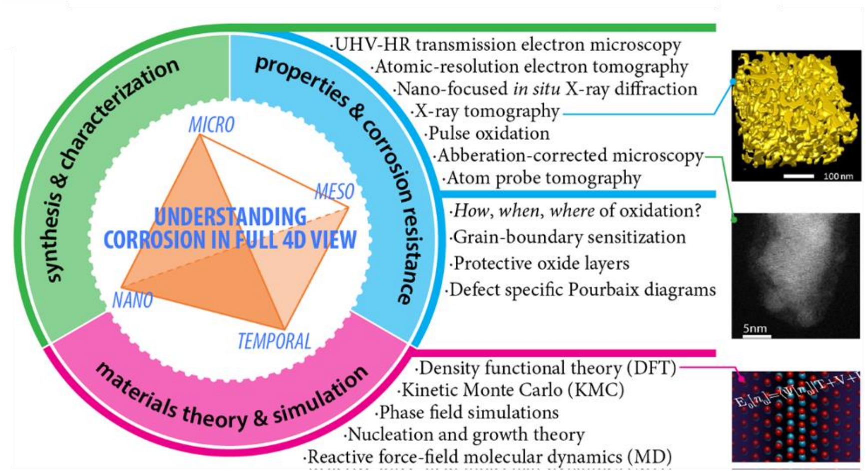
- Collaborations Established
- Discussion Ongoing

The Challenge



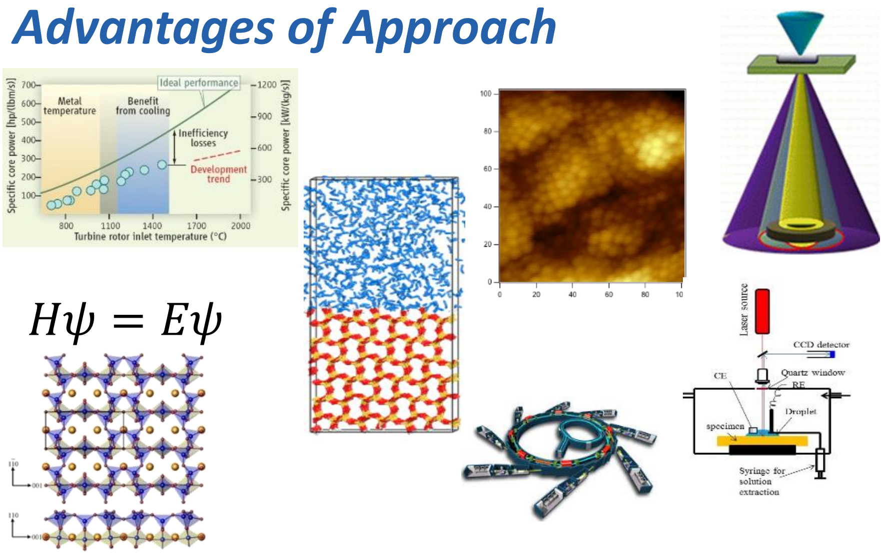
Complex multiscale corrosion

The Approach



Multi-PI and Method Team Approach

Advantages of Approach



$$H\psi = E\psi$$

No single approach adequate

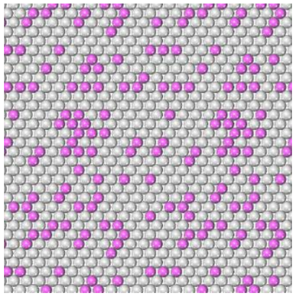
What is Learned

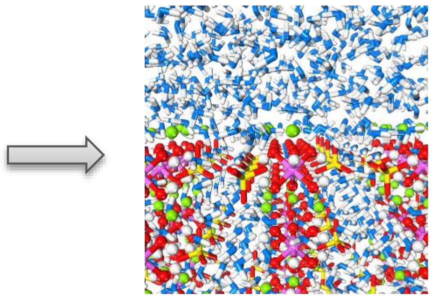
A comprehensive experimental and theoretical understanding of what matters, what does not, to lay the basis for a paradigm shift in improvements of corrosion-resistant materials

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

MULTIDISCIPLINARY UNIVERSITY RESEARCH INITIATIVE

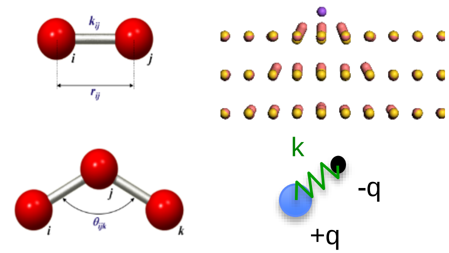
The Challenge





Understand phase changes upon heating, oxidation, and aqueous corrosion

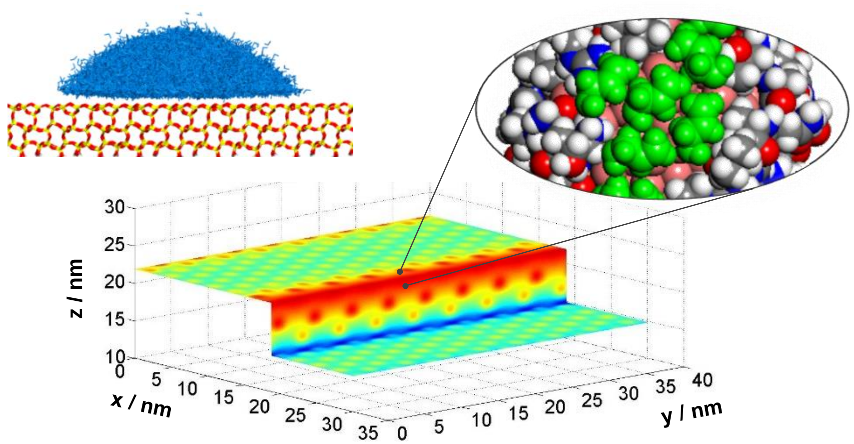
The Approach



$$E_{pot}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \underbrace{E_{bonds} + E_{angles} + E_{torsions} \, (+ E_{out\text{-}of\text{-}plane})}_{\text{bond}} + \underbrace{E_{Coulomb} + E_{vdW}}_{\text{non-bond}}$$

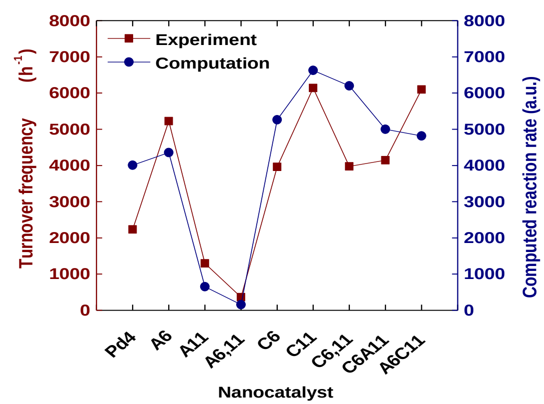
Atomistic simulation guided by experiment (MD, kinetic MC, and FF development)

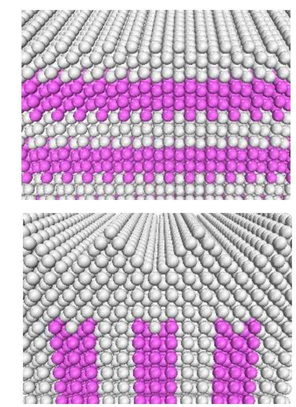
Advantages of Approach



Chemical accuracy at the 1 to 100 nm scale

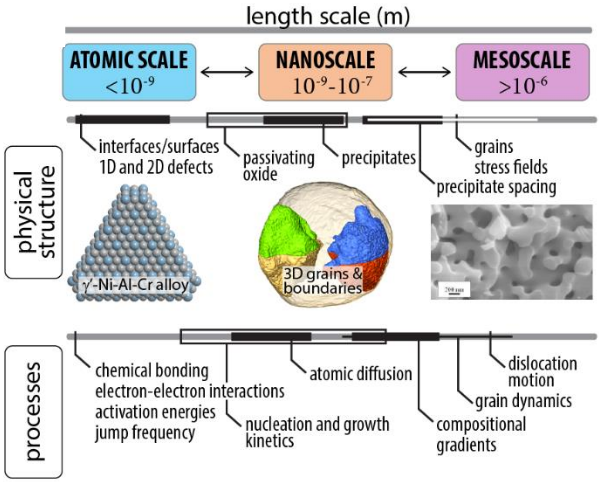
What is Learned





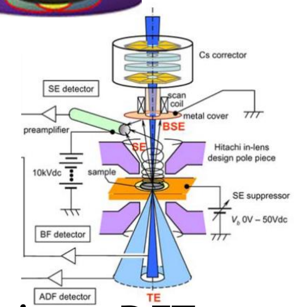
Controls for reactivity and degradation resistance

The Challenge



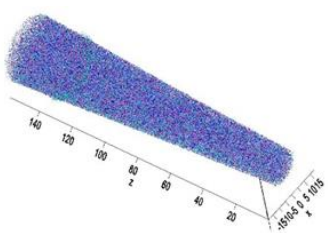
Link the size and time scales

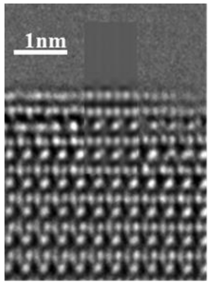
The Approach

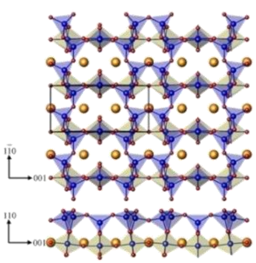


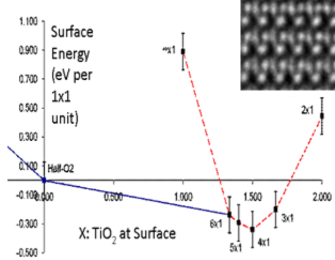
Multiple Microscopies + DFT of controlled samples

Advantages of Approach





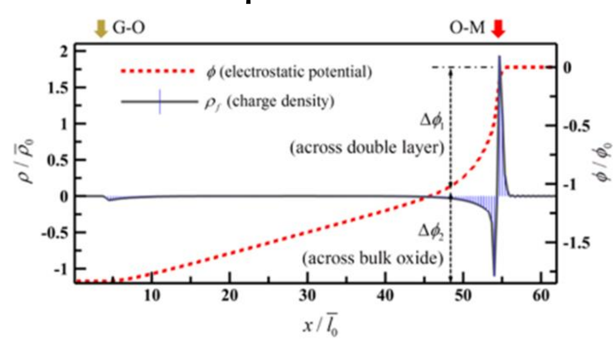




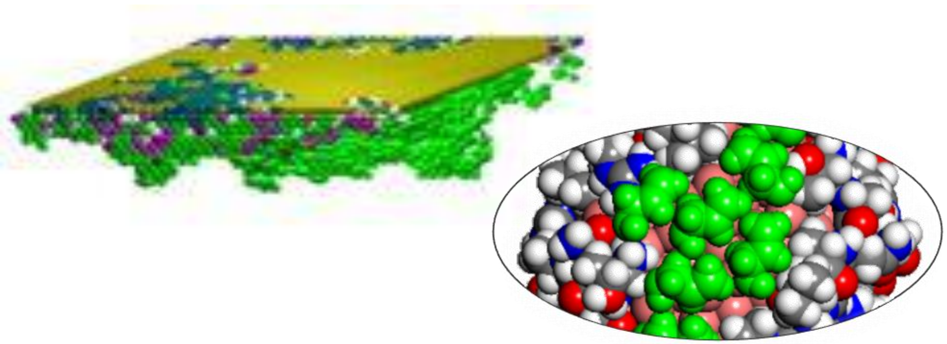
No single tool solves everything

What is Learned

Hard details to define what matters, what does not, the proper models at the atomic scale upwards



The Challenge



4D characterization of oxidation and corrosion at atomic resolution

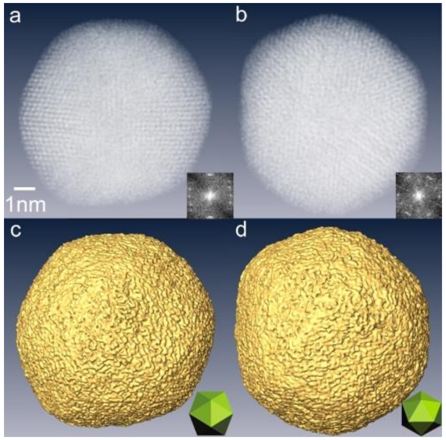
The Approach

TEAM I @ NCEM

Advanced Synchrotron

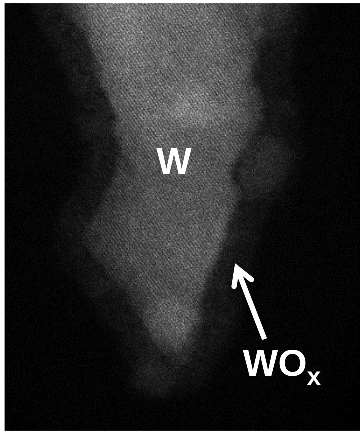
Atomic resolution electron tomography and in situ X-ray nanodiffraction

Advantages of Approach



Achieving electron tomography at atomic resolution [*Nature* **483**, 444-447 (2012)].

What is Learned

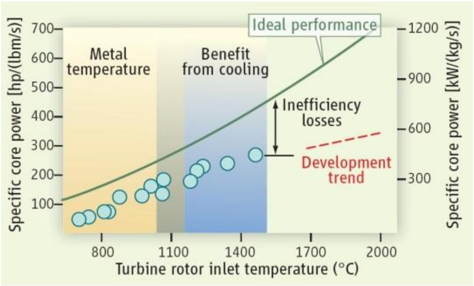


3D imaging of crystal defects in materials at atomic resolution.

New information at the atomic scale

The Challenge

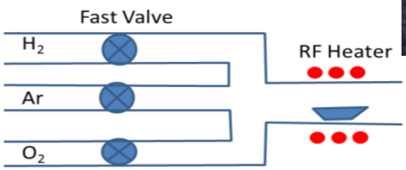
Higher temperatures yield more power and efficiency, but a more aggressive environment.



Performance requires oxide scales that are adherent and protective against attack

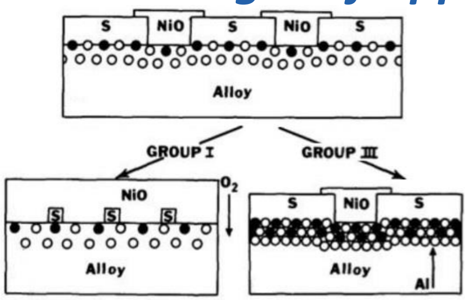
The Approach

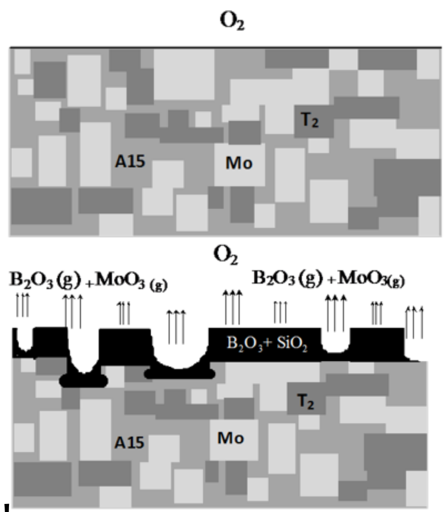
The initial reaction sets the stage for scale evolution.



Limited attention in past for multiphase multicomponent systems.
Pulse oxidation and atomic scale characterization to reveal critical details

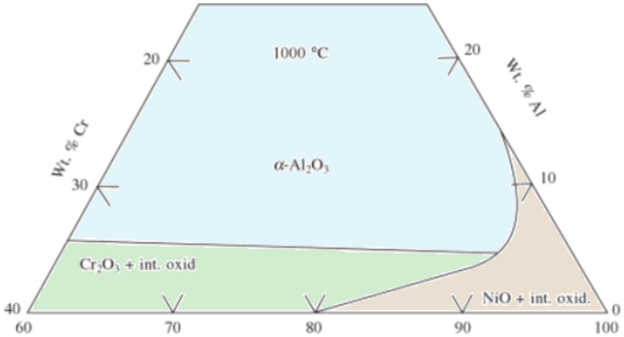
Advantages of Approach





Local Structure initiates reaction
Track oxide evolution over multiple length scales

What is Learned



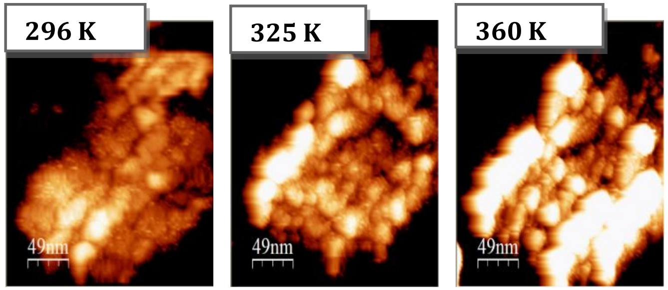
What controls oxide nucleation / phase selection?
How to control initiation site?
How to predict oxide evolution to yield oxidation maps and alloy design guidance?

The Challenge

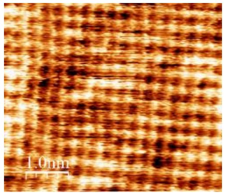
- Unravel initial reaction steps for oxidation of alloys with relevance to naval applications
- Link initial steps in oxidation/corrosion and performance of oxide
- Impact of minor alloying elements on oxide

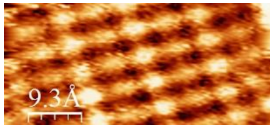
VO_2 insulator-to-metal transition at 350 K

[JAP **109** 024311]



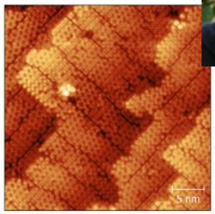
The Approach





Cu(100) grain in pc-substrate

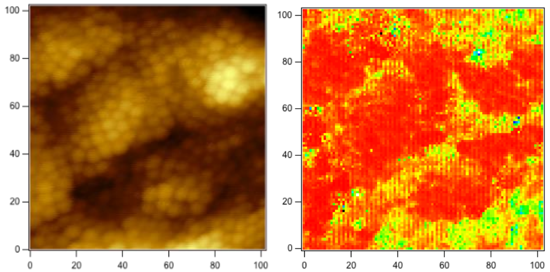
W(110) – thin film on MgO



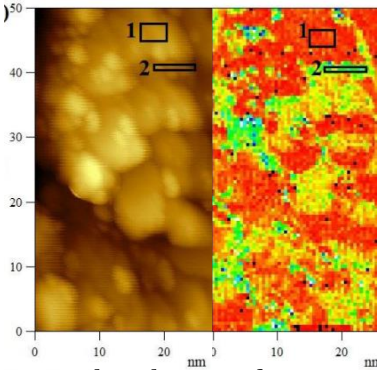
Ge (100) wetting layer on Si

Identify atomic level reaction sites (defects, terraces…) to mesoscale observation of oxide nucleation/growth in composition- p(O_2) – T parameter space. Combine with structural analysis of alloy and oxide, EC of identical material and theory/simulation.

Advantages of Approach



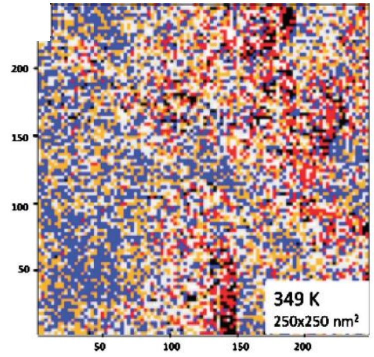
STM (L) and STS (R) map
Metal (red) and nearly metallic (yellow) W-C nanospheres (25^2 nm^2)



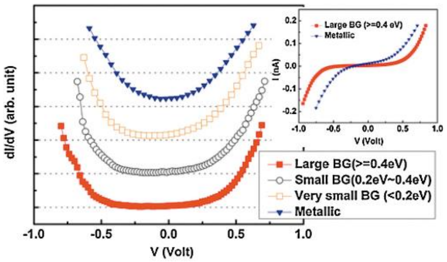
Oxidized W-surface
WO_2 and oxy-carbide
1 nm=1 pixel

Nano- to mesoscale information on geometric and electronic structure of alloy and oxide

What is Learned



Bandgap map and STS on hot VO_2 surface

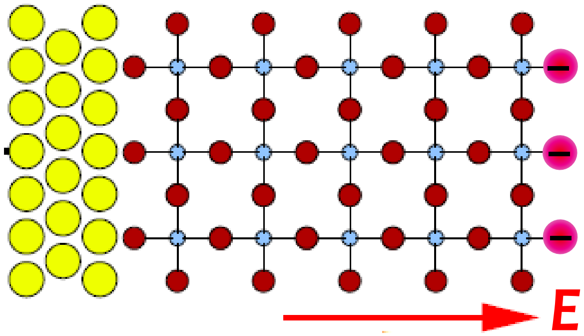


Understanding of fundamental processes in oxidation has the potential to lead to new strategies in the design/control of oxides and corrosion mitigation.

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

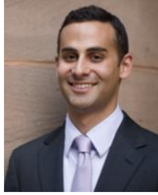
MULTIDISCIPLINARY UNIVERSITY RESEARCH INITIATIVE

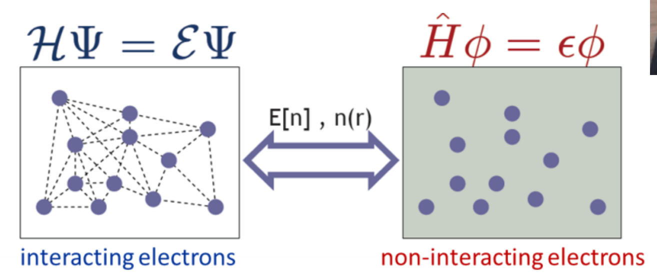
The Challenge



Identify microscopic mechanisms and driving forces for oxide formation to design the interfacial structure to limit growth

The Approach

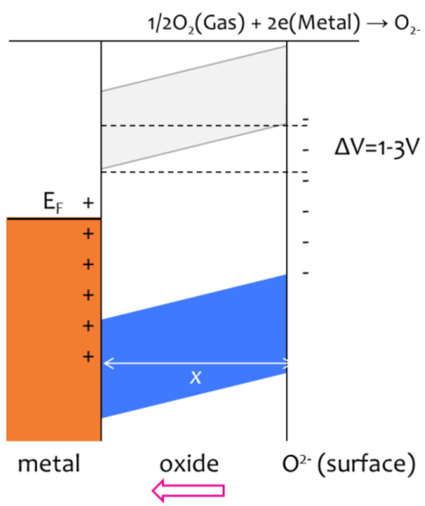




$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

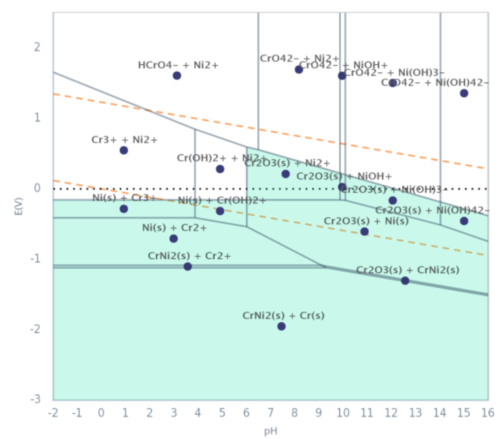
Ab initio electronic structure methods to evaluate phase equilibria, thermochemistry, and activation barriers for defect migration

Advantages of Approach



(In)Validate proposed models, formulate new theories, and create design guidelines for experimental exploration

What is Learned

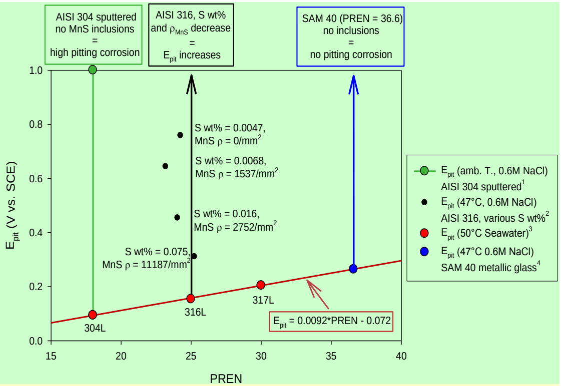


New routes to control oxidation at the nanoscale in various environments

The Challenge

Alloy design for corrosion based on empirical rules and trial and error approaches

Corrosion is multi-factorial and multi-length and time scale

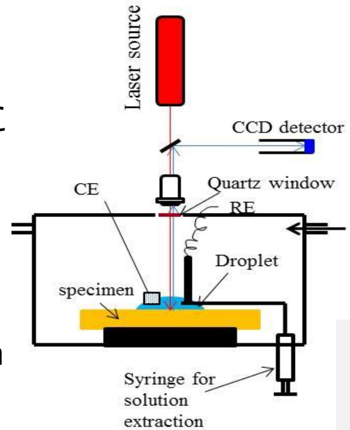


PRE' = wt%Cr + 3.3 (wt%Mo + wt%W) + 30 wt%N

Isolated and incomplete connections between atomic scale phenomena and engineering scale properties

The Approach

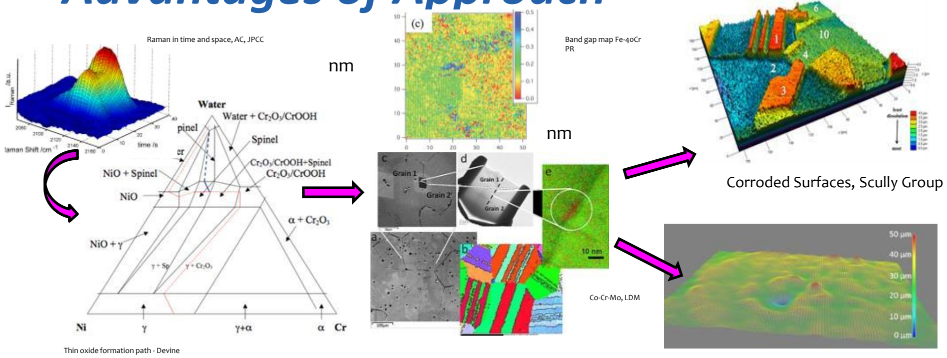
Simultaneous AC and DC electrochemistry, solution and surface mapping in real time on model material with know crystal orientation



SERS, TERS
Also SKP
SECM

Needs and Gaps: Lack of exp. information in 4 or 5 dimensions, nor in real time across multi- length and time scales

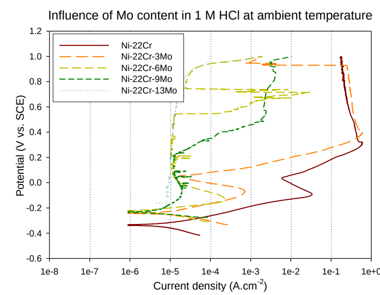
Advantages of Approach

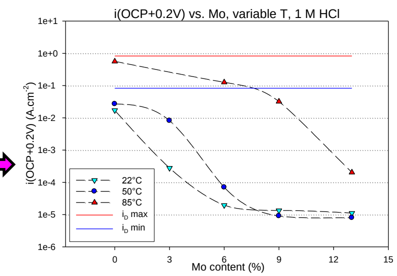


Track evolution of metal/oxide/solution interface and fate of alloying elements controlling corrosion with spatial resolution over multiple length scales

Identify controlling unit processes in passivity/breakdown

What is Learned





How metal/oxide structure, composition, LDOS, defect density affect global ETR and corrosion reaction rates

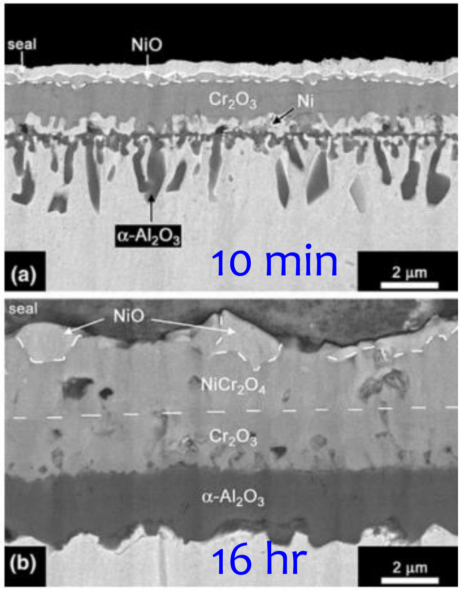
Modeled unit processes in passivity and local breakdown can be exercised to gain atomistic understanding to enable alloy design for corrosion

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

MULTIDISCIPLINARY UNIVERSITY RESEARCH INITIATIVE

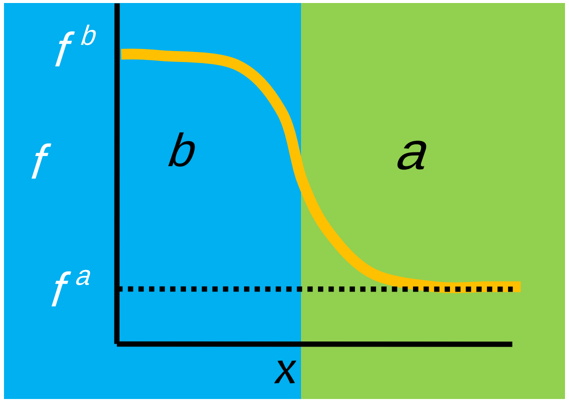
The Challenge

Model the morphology and growth of oxide films from the onset of oxidation



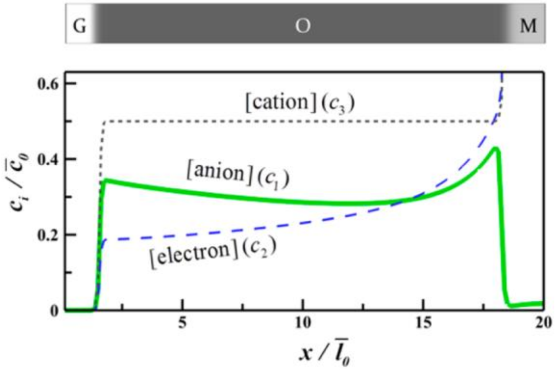
From Nijdam, T. J., Jeurgens, L. P. H., & Sloof, W. G. *Acta Materialia*, 2005. **53**(6), 1643

The Approach



Continuum and phase field methods.

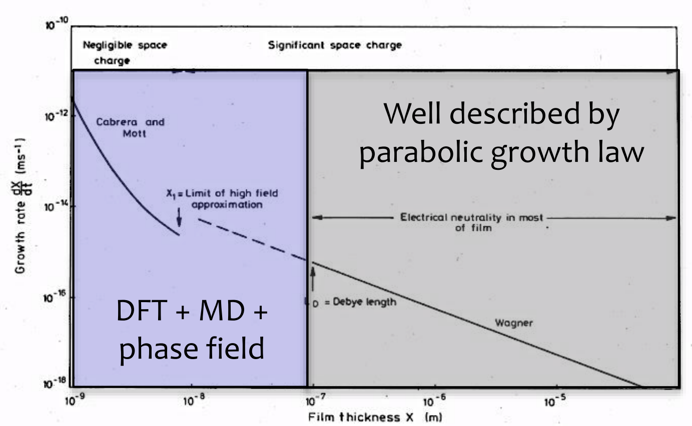
Advantages of Approach



From Chen, Wen, & Hawk. *J. Phys. Chem. C.* 2014, **118**, 1269

Can follow the evolution of morphologically complex oxide domains and their compositions.

What is Learned



From Atkinson, A. *Reviews of Modern Physics* 1985, **57**, 2, 437–470

A multi-scale model for oxide growth using data from smaller scale methods and experiment

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

MULTIDISCIPLINARY UNIVERSITY RESEARCH INITIATIVE

Summary

- Multi-PI, Multi-University to attack key issues in the fundamentals of oxidative and aqueous corrosion
- Heavily collaborative, interactions and joint theory/experimental work
- Follow the science, not the technique or computer code
- Exploit national and international facilities to expand capabilities
- Towards a paradigm shift in our understanding