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Electrochemical Tests Supporting Long-Term Alloy Corrosion Models

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Used Fuel Disposition Working Group Meeting

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NEUP Nuclear Energy University Programs
U.S. Department of Energy

UIC UNIVERSITY OF ILLINOIS AT CHICAGO

Argonne NATIONAL LABORATORY

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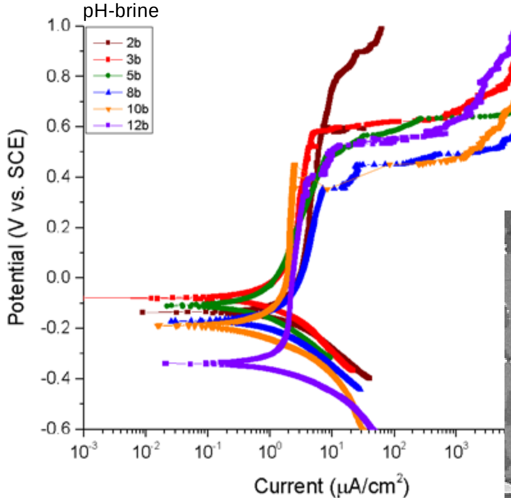
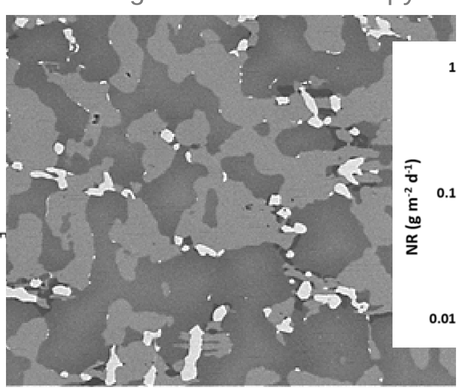
Outline

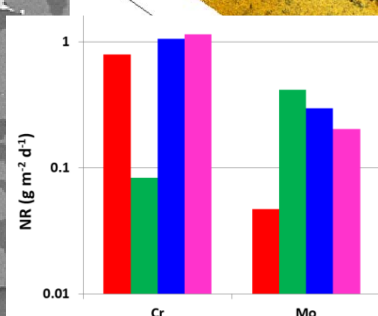
- NEUP objectives and approach
- Electrochemical model and test protocol for alloy waste forms
- Application to alloy/oxide composite waste forms
- Applications to container corrosion



Electrochemical Tests

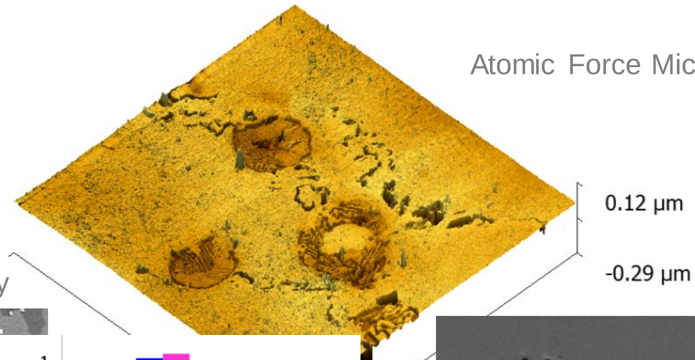
Scanning Electron Microscopy

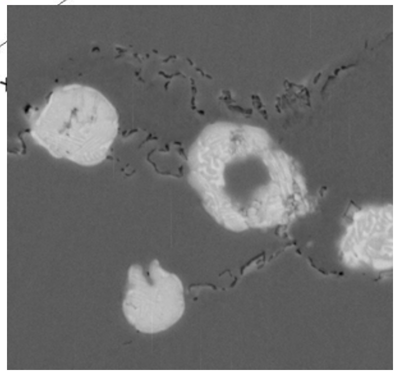




Solution Analyses

Atomic Force Microscopy





NEUP:
Alloy/Oxide Composite Waste Forms

ISSUE: Consolidating oxide and metallic wastes from electrochemical processing of spent fuel in a single waste form would reduce waste form production and disposal costs. Production of alloy/oxide composites has been demonstrated previously, but methods to **measure and model performance** of composite waste forms have not been developed.

NEUP OBJECTIVE: Demonstrate that experimental and modeling approaches developed for individual alloy and glass waste forms can be applied to alloy/oxide composite waste forms, including the effects of **phase boundaries**, **surface stabilization**, and **passivation** over long disposal times.

NEUP:
Alloy/Oxide Composite Waste Forms

BACKGROUND: A **degradation model*** has been developed for multi-phase alloy waste forms based on a two-step conceptual model of metal oxidation followed by dissolution of oxides. Electrochemical theory is used to establish credibility of long-term predictions.

A **laboratory testing protocol**** has been developed to determine environmental dependencies and measure model parameter values that represent long-term corrosion of multi-phase alloy waste forms **to provide radionuclide source terms** for performance assessment calculations.

NEUP APPROACH: Apply electrochemical testing approach to composite materials to measure effects of oxide phases on alloy behavior and distinguish chemical effects, then modify degradation model as appropriate. NEUP is coordinated with activities in Materials Recovery and Waste Form Development campaign.

*W.L. Ebert (2014). *Radionuclide Source Term Model for Metallic Waste Forms*, FCRD-SWF-2014-000244.

**W.L. Ebert and D. Kolman (2013). *Alloy Waste Form Testing Strategy Roadmap*, FCRD-SWF-2013-000226.

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Alloy Waste Form Degradation Model

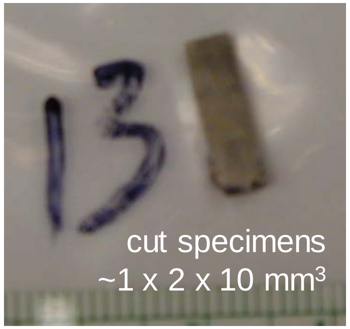
- Oxidative-Dissolution Model
  - Metallic components are **oxidized** by reaction with seepage water
  - Oxides form a surface layer or **dissolve** according to their solubilities
  - Oxidation and dissolution rates for each phase sensitive to **oxidation potential** (Eh)

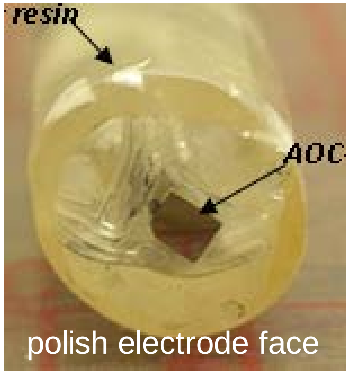
Bare surface oxidation rate in solution is moderated by passivation and dissolution affinity

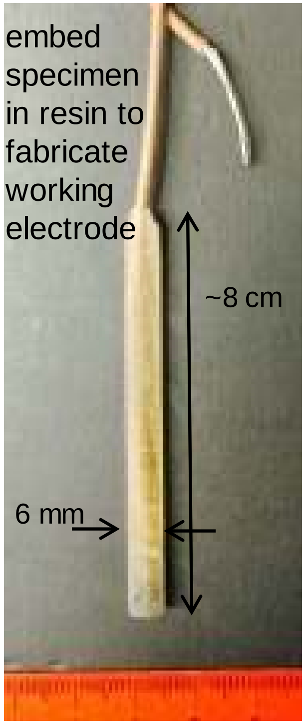
$$\underbrace{FR(RN)}_{\textit{source term}} = \underbrace{B\left(Eh, pH, T\right) \times P\left(Eh, t, Cl^{-}\right)}_{\text{electrochemical}} \times \underbrace{D\left(T, RN\right)}_{\text{chemical}}$$

- Electrochemical tests measure B term for polished surface, product of B and P terms for corroded surface, and FR term based on solution composition.
- Solutions from electrochemical tests and chemical tests at open circuit used to measure D term for oxide phases.
- Analytical expressions are being derived to quantify effects of Eh, pH, T, and key solutes on B, $B \times P$, and D terms.
- These will be used to determine over-all expression for *FR(RN)* as reduced order source term model.

Electrochemical Set Up



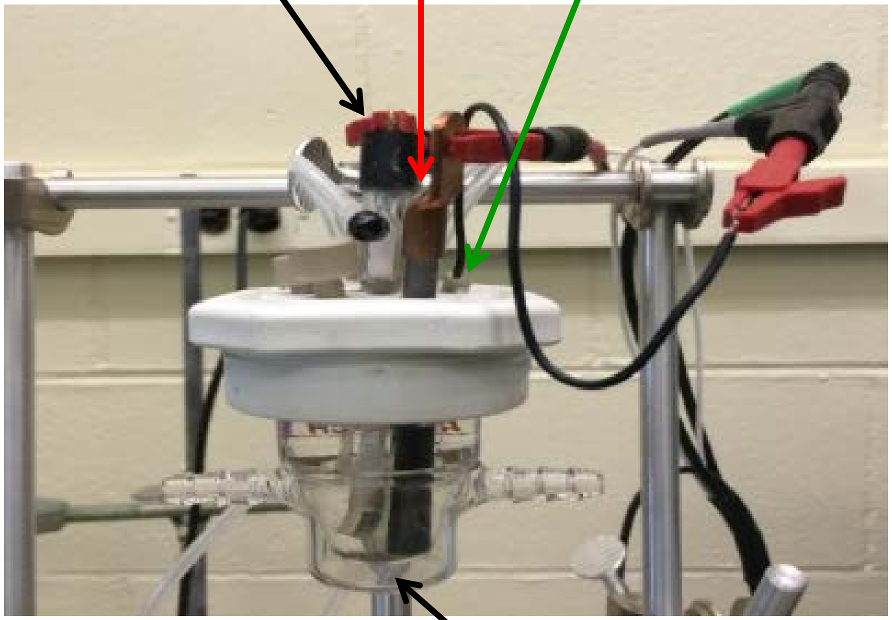




Reference electrode (SCE)

Counter electrode (graphite)

Working electrode

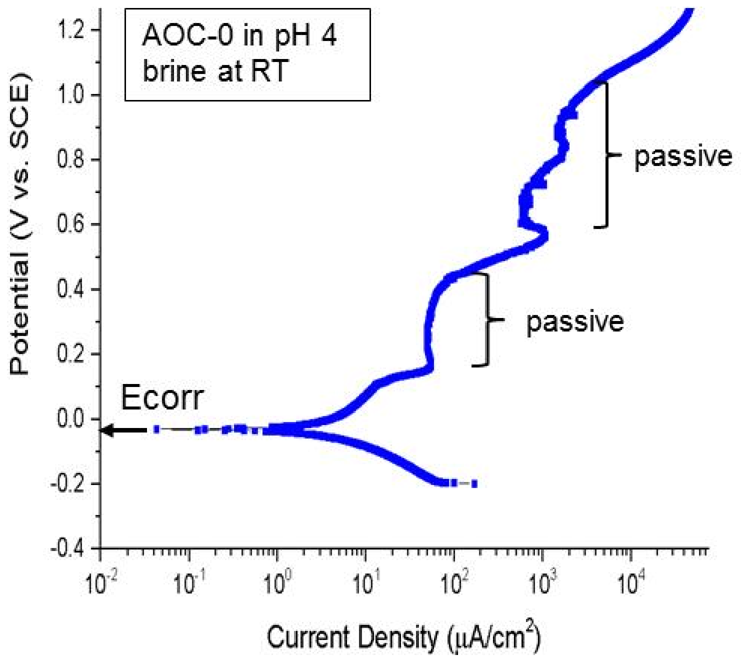


SEM examination
before and after

~15 mL electrolyte
in microcell

Experimental Protocol (PD)

- Conduct potentiodynamic (PD) scans to identify regions of active and passive corrosion behavior and measure corrosion potentials (Ecorr) in various test solutions.



AOC-0 is an alloy/oxide composite made at INL in 2012 to demonstrate oxides could be incorporated into metal waste form under normal production conditions. Made with 316L steel to represent **cladding** hulls, Zr and Mo to represent **metallic fuel waste**, and ZrO_2 to represent **oxide fuel waste**.

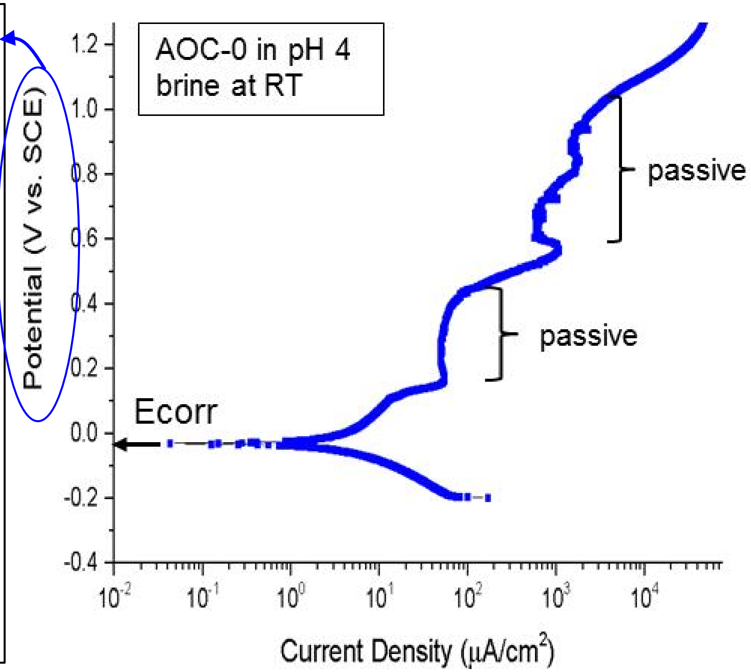
Experimental Protocol (PD)

- Conduct potentiodynamic (PD) scans to measure corrosion potentials (Ecorr) in various test solutions and identify regions of active and passive corrosion behavior.

Each imposed potential represents a possible redox (Eh) value of seepage water accumulated in breached waste package in disposal system.

Various solutions are used to represent relevant chemical environments (pH and Cl⁻).

Ecorr indicates potential at which cathodic and anodic currents (reaction rates) are equal. Value will change as surface and solution evolve.



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Experimental Protocol (PD)

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- Conduct potentiodynamic test to measure corrosion potential (Ecorr) in test solution and identify regions of active and passive behavior.

Each imposed potential represents a possible redox (Eh) value of seepage water accumulated in breached waste package in disposal system.

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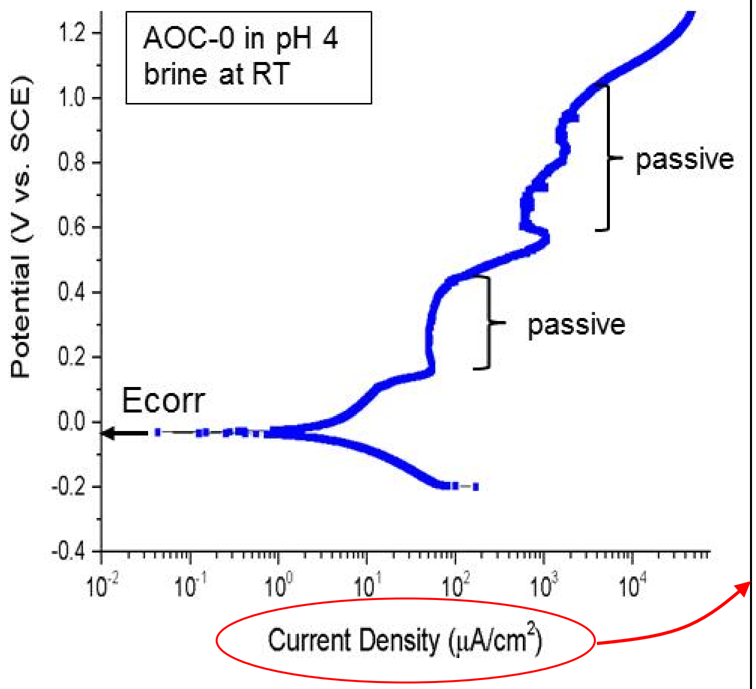


Measured current includes contributions from all phases, but corrosion of one phase usually dominates over a range of potentials.
(Current is normalized to electrode surface area)

Faraday's law relates corrosion current to mass dissolution rate:

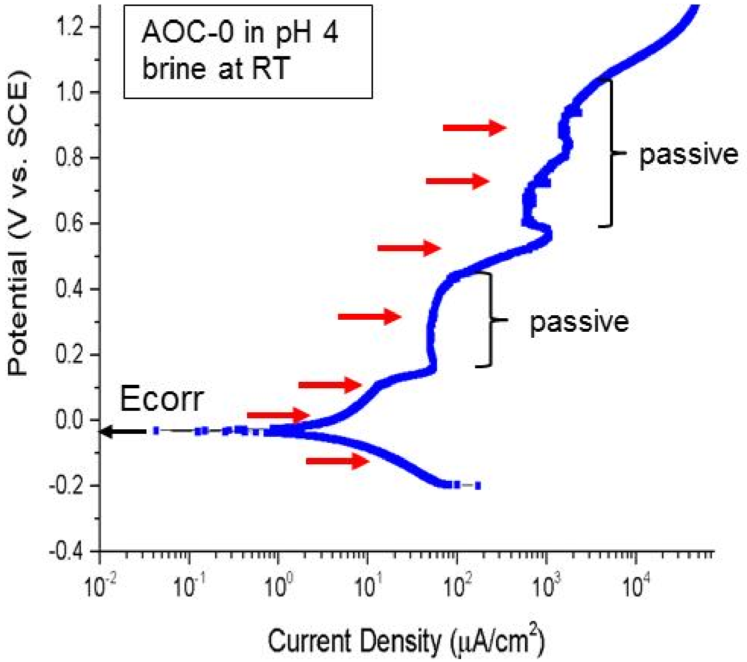
$$\frac{mass\ loss}{time} = \frac{i_{corr}\ AtWt / z}{F}$$

PD current density is used to represent bare surface corrosion rate for the B term.

AOC-0 is an alloy/oxide composite made with 316L steel to represent cladding hulls, Zr and Mo to represent metallic fuel waste, and ZrO_2 to represent oxide fuel waste. Made at INL in 2012 to demonstrate oxides could be incorporated into metal waste form under normal production conditions.

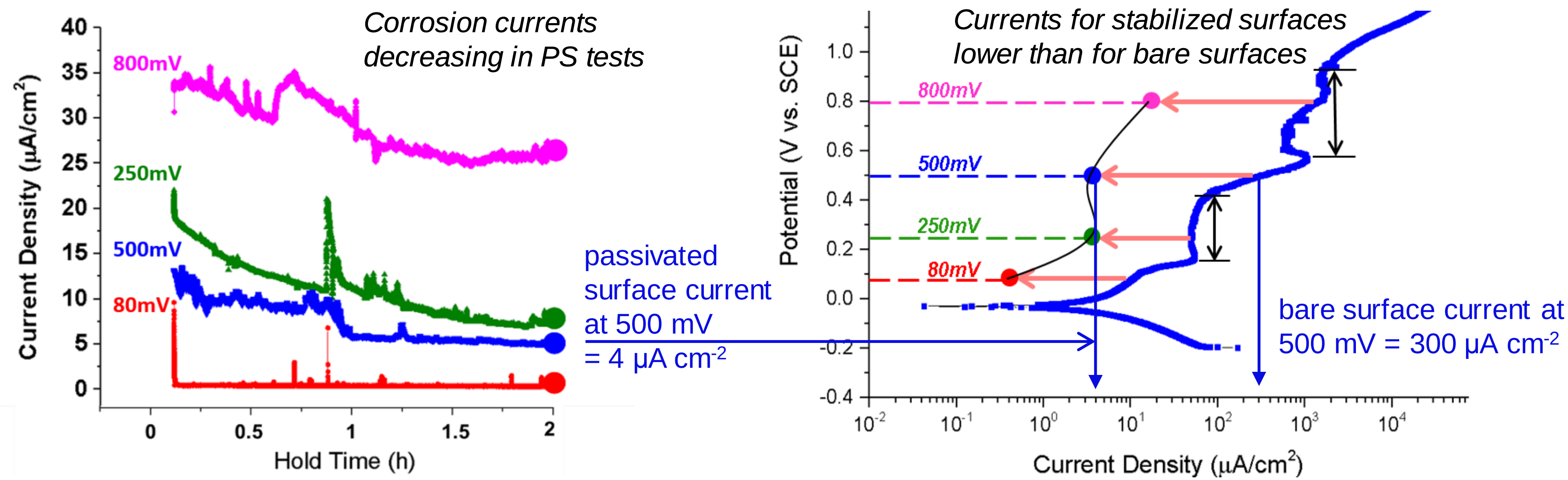
Experimental Protocol (PS)

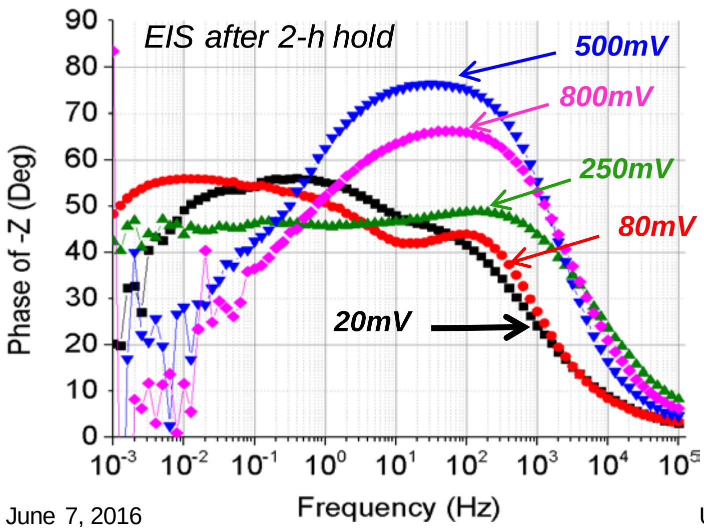
- Conduct potentiostatic (PS) tests to characterize time dependence of corrosion behavior (P terms) at voltages of interest
  - Track corrosion current for several days (or weeks) while the “steady-state” surface is being generated
  - Monitor evolution of surface electrical properties (e.g., as passivating layer forms or surface is pitted) by performing electrochemical impedance spectroscopy (EIS) while maintaining hold potential
  - Sample solution during test to measure element releases into solution (D terms)



- Examine corroded surface with SEM to identify phase(s) that were active during test.

Electrochemical Test Results for AOC-0 in pH 4 Brine (10 mM NaCl)





$$FR(RN) = fn(Eh)_{pH,Cl^-,T}$$

Stabilizing surface layers that form at 500 mV and 800 mV have electrical properties that differ from those of layers formed at 250 mV and lower potentials.

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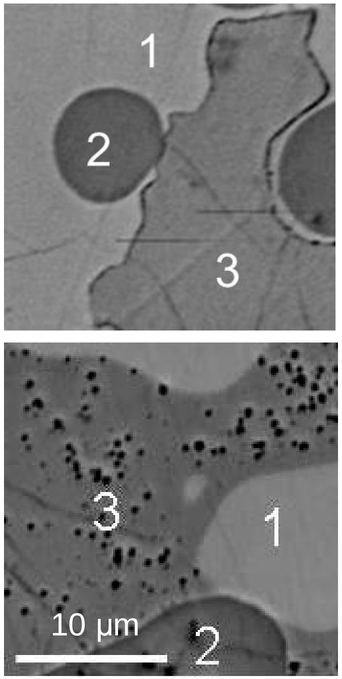
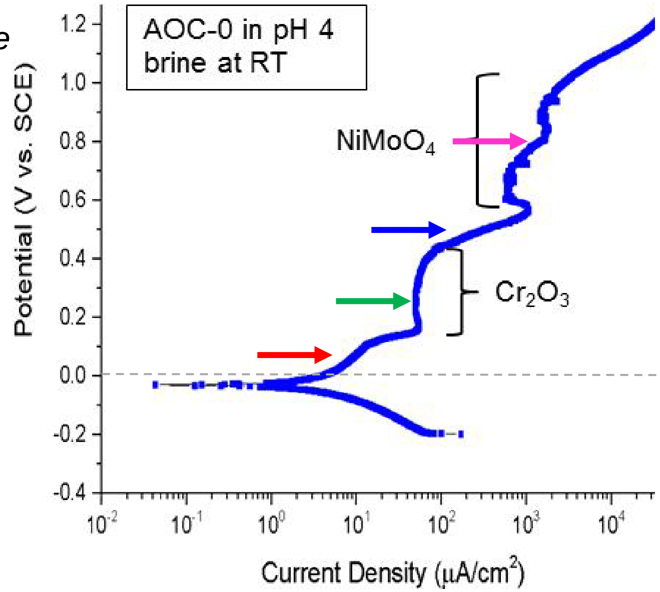
SEM and Solution Results

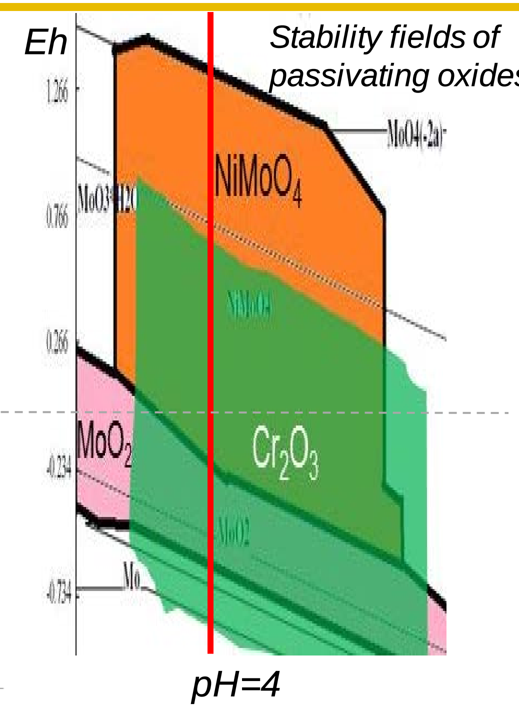
SEM analysis of corroded surface



Phase 3 corrodes uniformly at 800 mV

Phase 3 corrodes by pitting at 250 mV

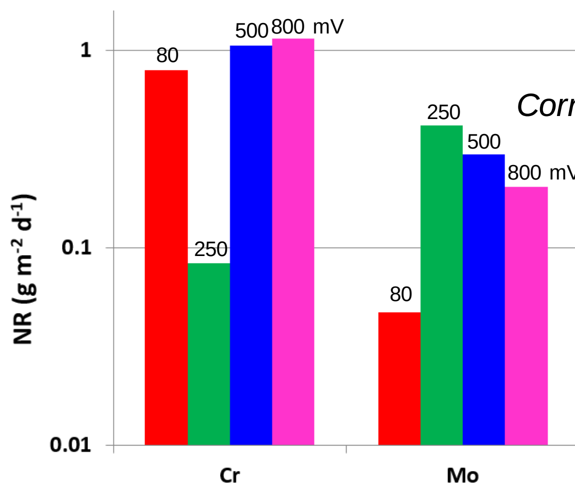




Phase Compositions, at %

	O	Cr	Mn	Fe	Ni	Zr	Mo
1	—	**10**	12	45	**10**	15	**11**
2	63	—	—	—	—	37	—
3	—	**25**	2	**47**	4	—	**18**

(Tc)

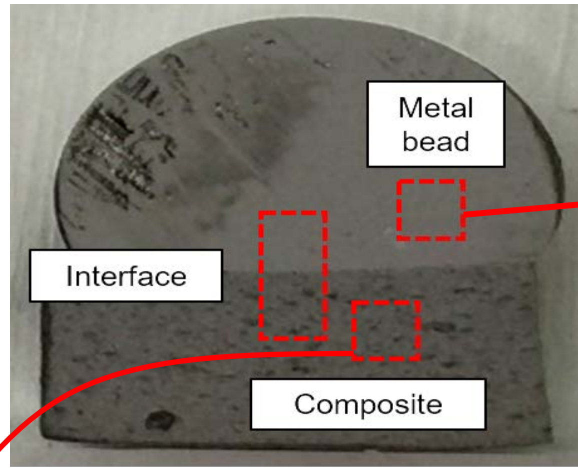


Corrosion rates from solution analyses

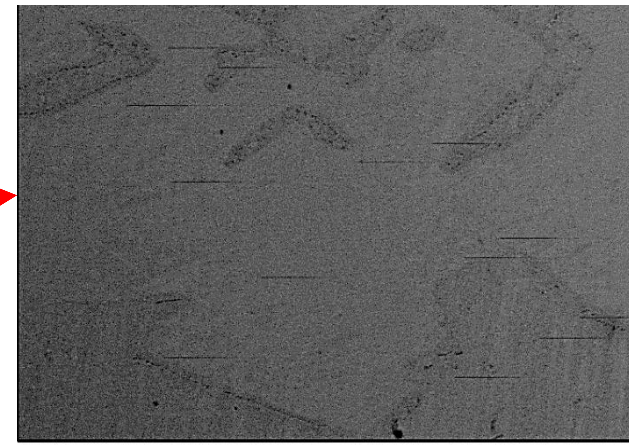
Cr release at 250 mV is mitigated by Cr_2O_3 formation

Mo release at 500 mV and 800 mV is mitigated by $NiMoO_4$ formation

HT9 SS/Zr,Mo/Ln-Oxides Composite

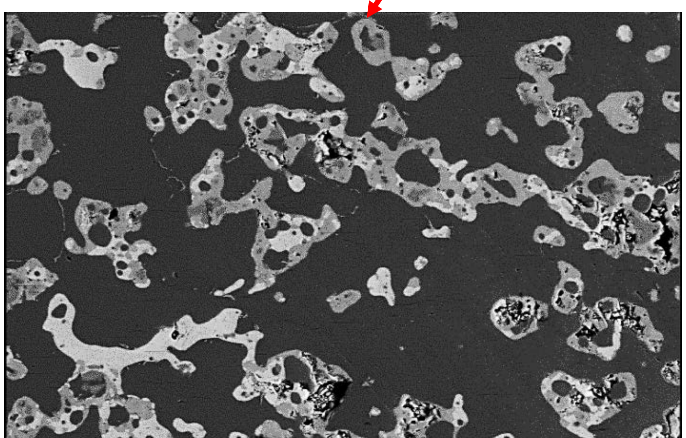


5 mm



HT9-like Martensite/Ferrite Alloy

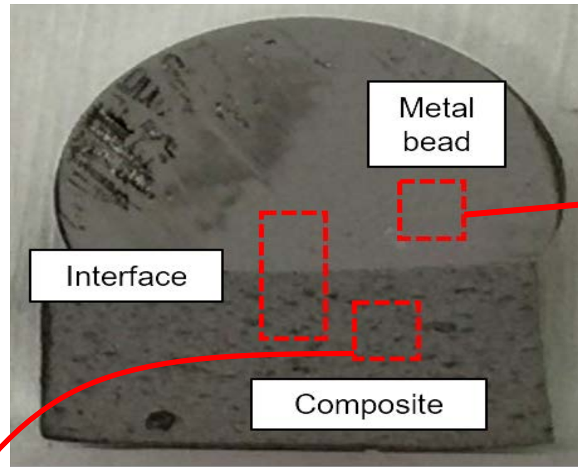
20 µm



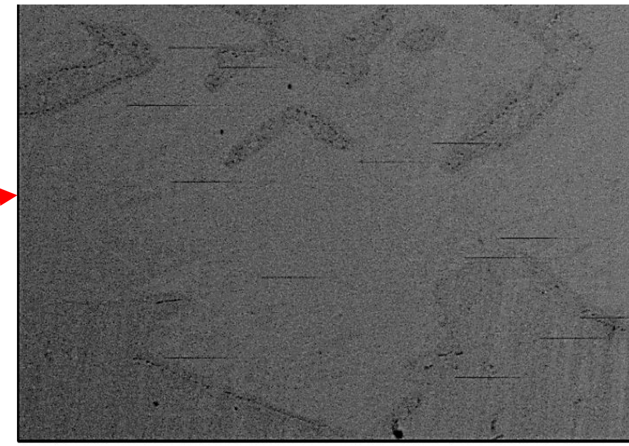
Alloy/Ceramic composite

50 µm

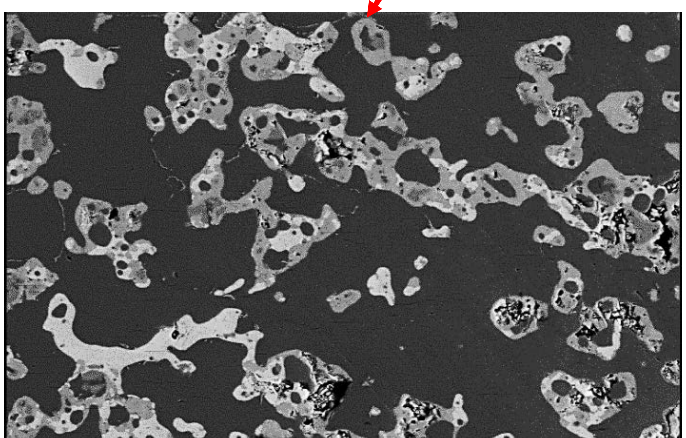
HT9 SS/Zr,Mo/Ln-Oxides Composite



5 mm

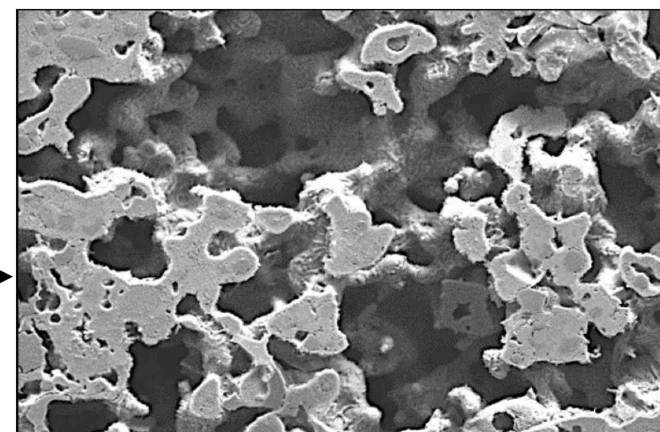


HT9-like Martensite/Ferrite Alloy 20 µm



Alloy/Ceramic composite 50 µm

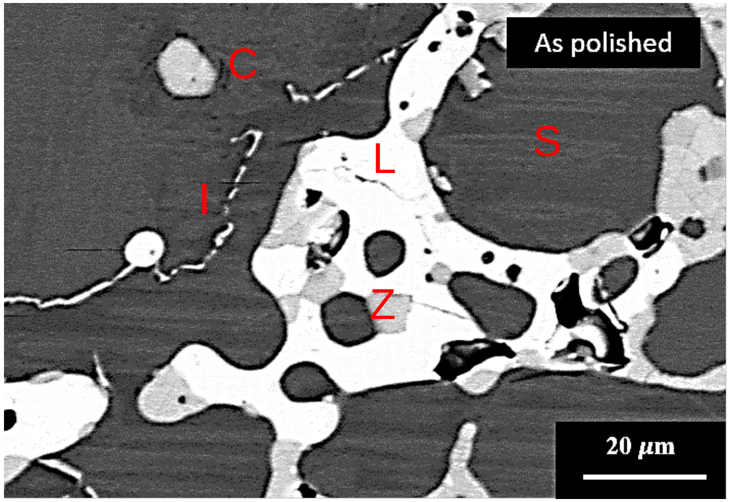
after extensive electrochemical corrosion

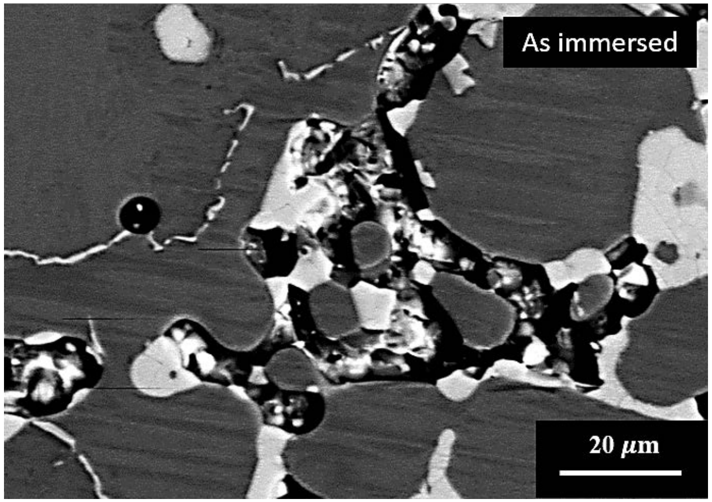


Ceramic skeleton 50 µm

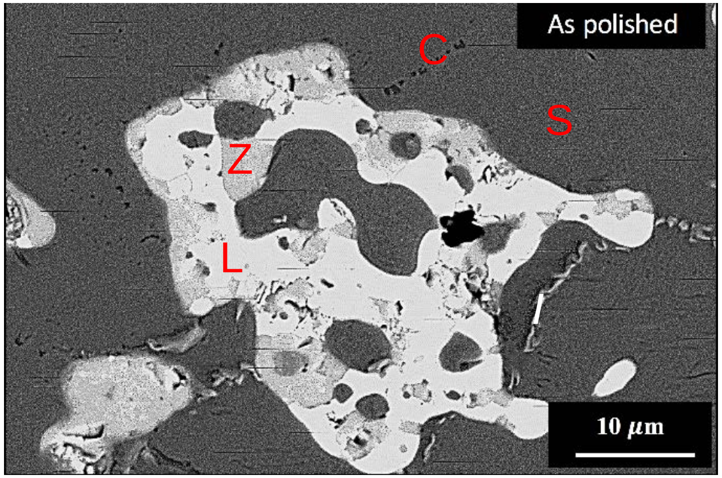
Chemical Corrosion of Ln-oxides (but not $Ln_2Zr_2O_7$) and Electrochemical Corrosion of Ferrite (but not Martensite)

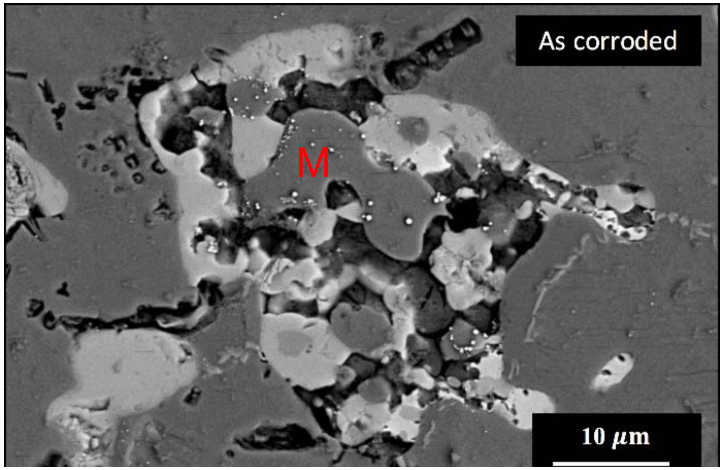
Chemical Corrosion in pH 4 brine





Electrochemical Corrosion in pH 4 brine





C = Cr-carbide
I = FeCrMo intermetallic
L = Ln-oxides*
S = steel
Z = $Ln_2Zr_2O_7$**
M = MoO_x

*La_2O_3, Nd_2O_3, CeO_2
**Ln=La, Nd, and Ce

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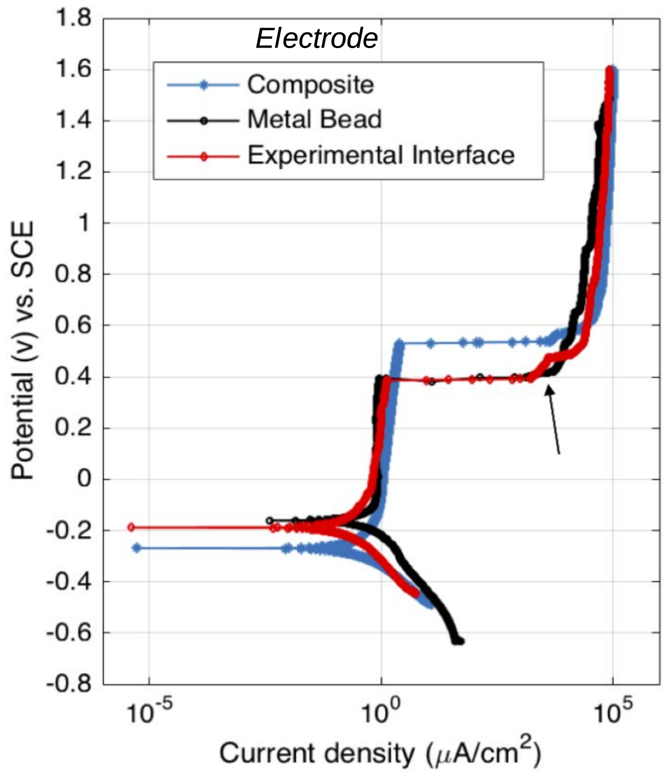
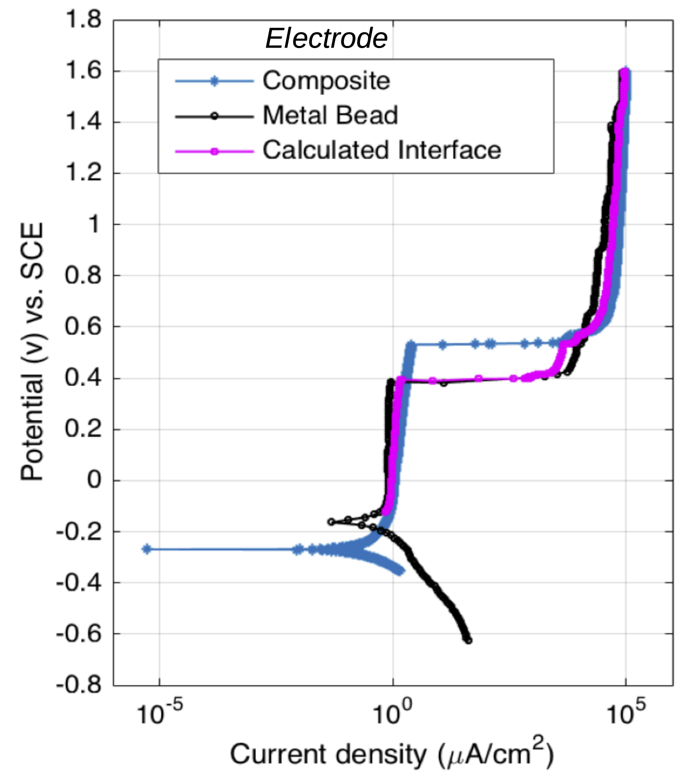
Potentiodynamic Scans



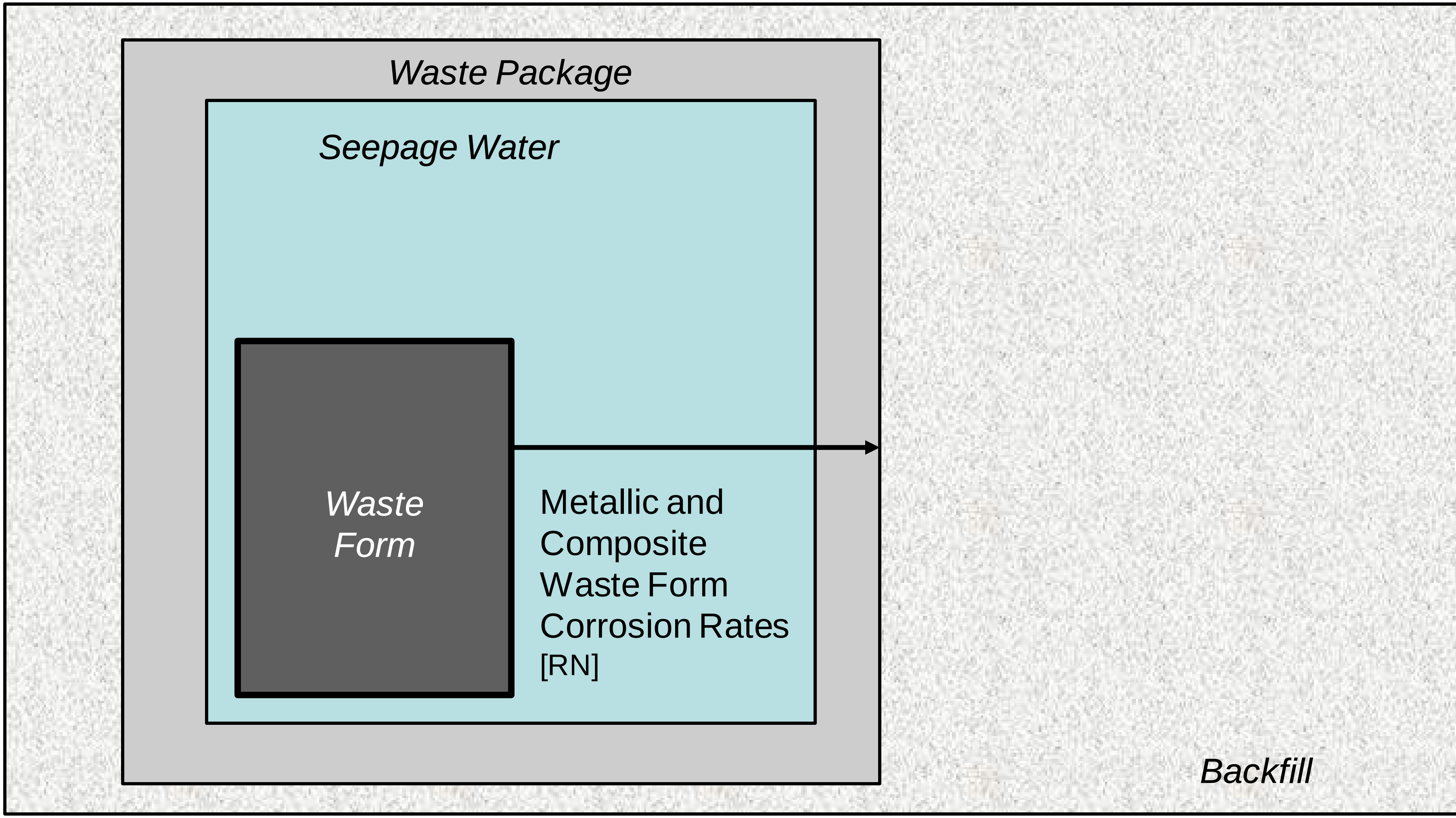


Area-based analysis of current density: $\mathrm{i}_{interface} = \mathrm{i}_{bead} \cdot A_{bead} + \mathrm{i}_{composite} \cdot A_{composite}$

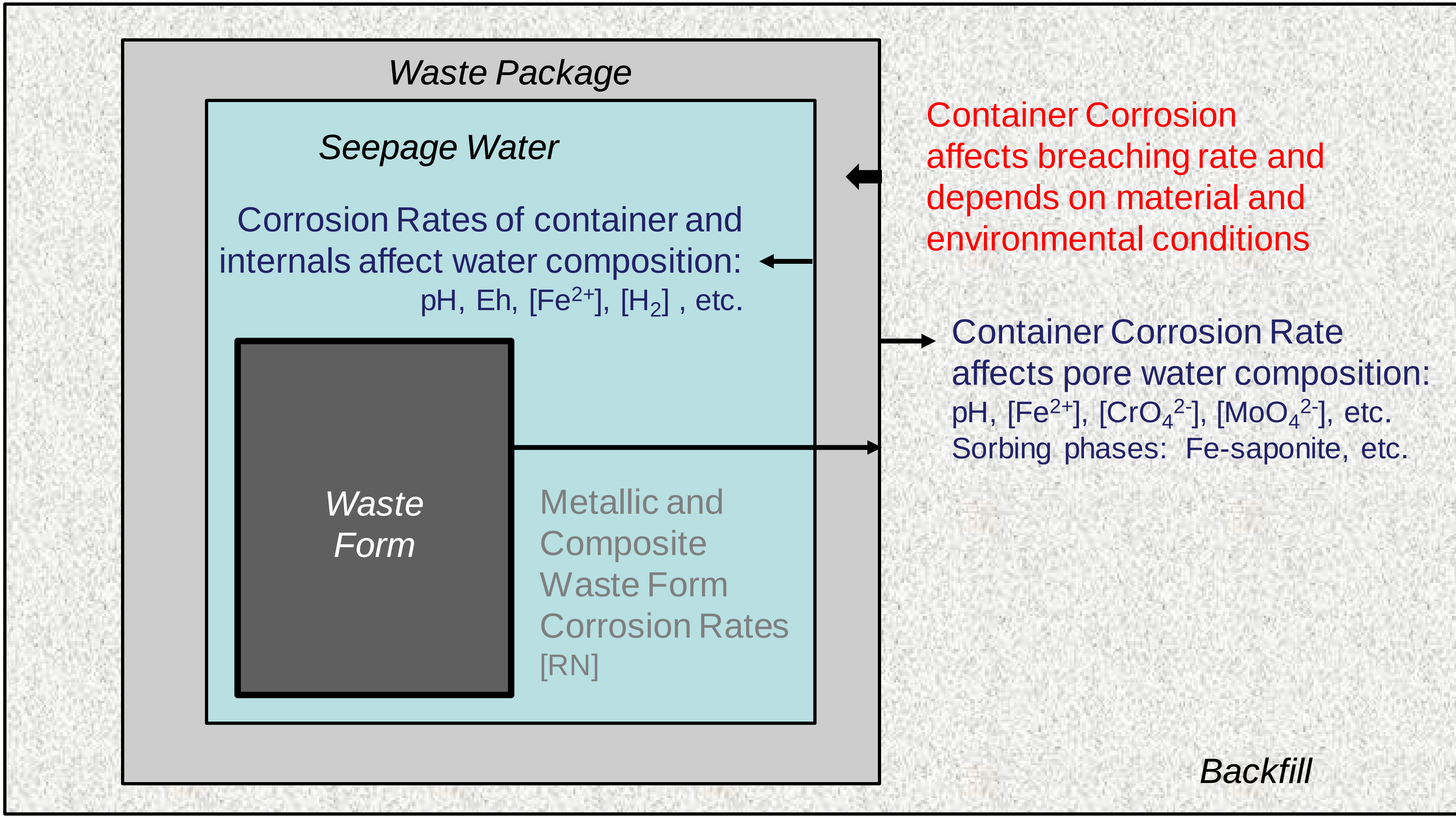
A = area of alloy in metal bead or composite

Differences in PDs attributable to areas of alloy in metal bead and interface electrodes.
Presence of ceramic phases does not affect corrosion of alloy phases.

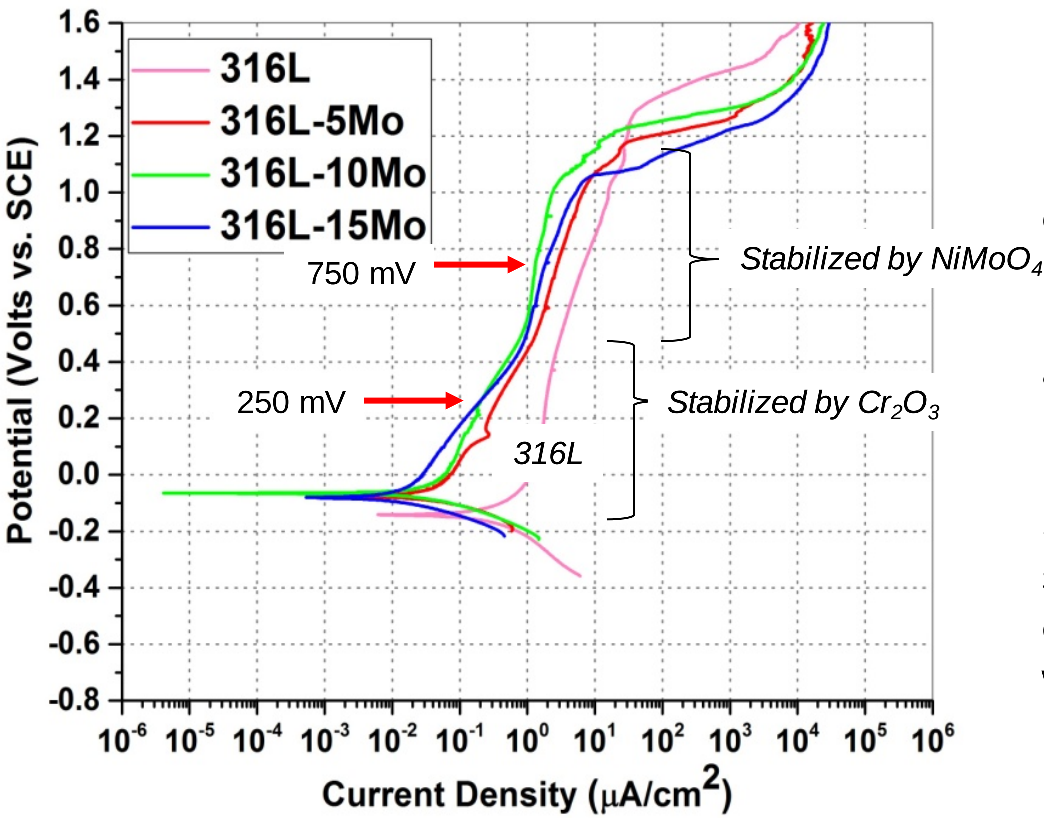
Applications of Metal Corrosion Model



Other Applications of Metal Corrosion Model



Potentiodynamic Corrosion of 316L-Mo Alloys (pH 4 brine)



Mo is a major constituent of metallic fuel waste that enhances corrosion resistance.

Fe-Mo intermetallics formed in alloy waste forms are primary hosts for Tc.

Several 316L-Mo alloys made to study effects of intermetallics on corrosion resistance to optimize waste form formulations.

Intermetallics Formed in 316L-5Mo and 316L-15Mo

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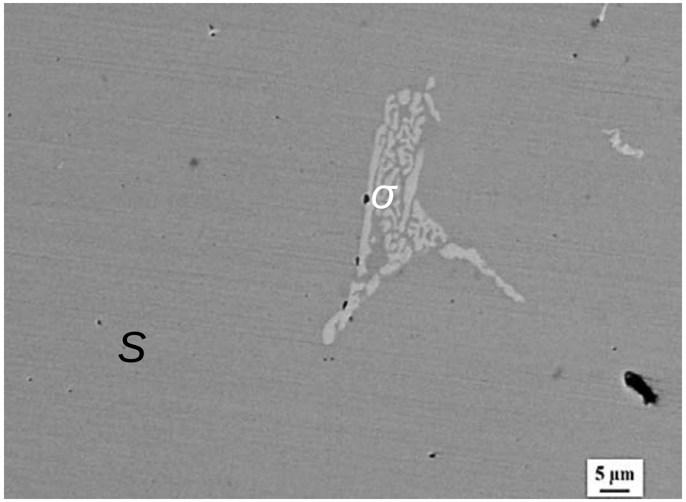
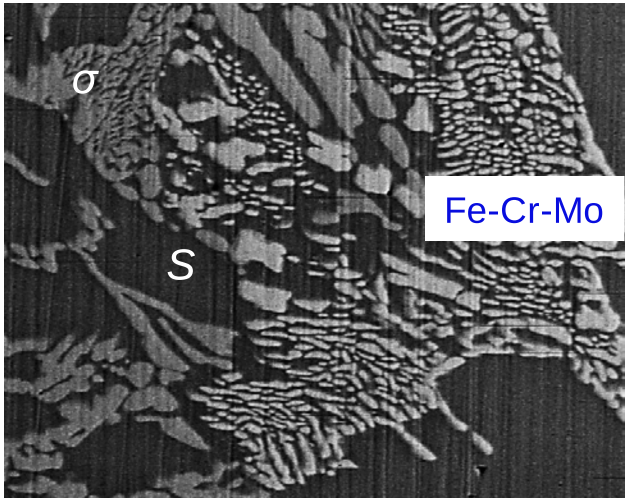
316L-5Mo

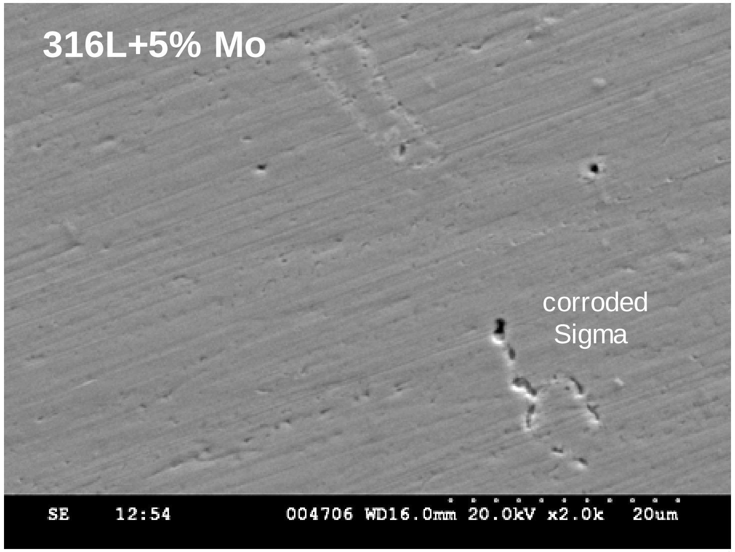


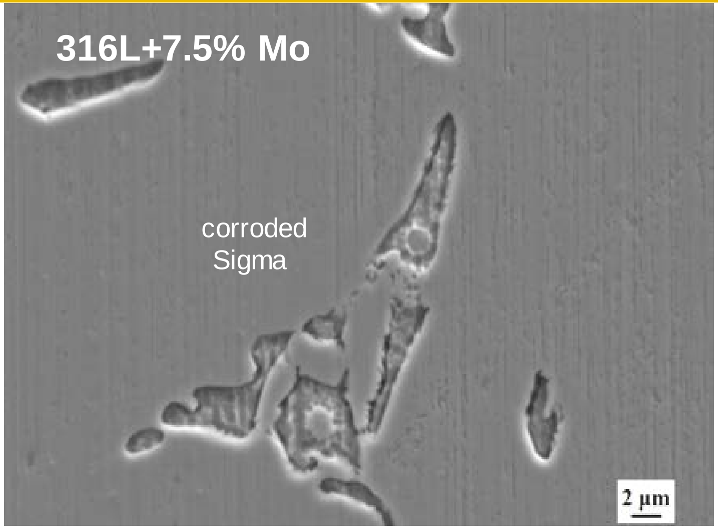
316L-15Mo

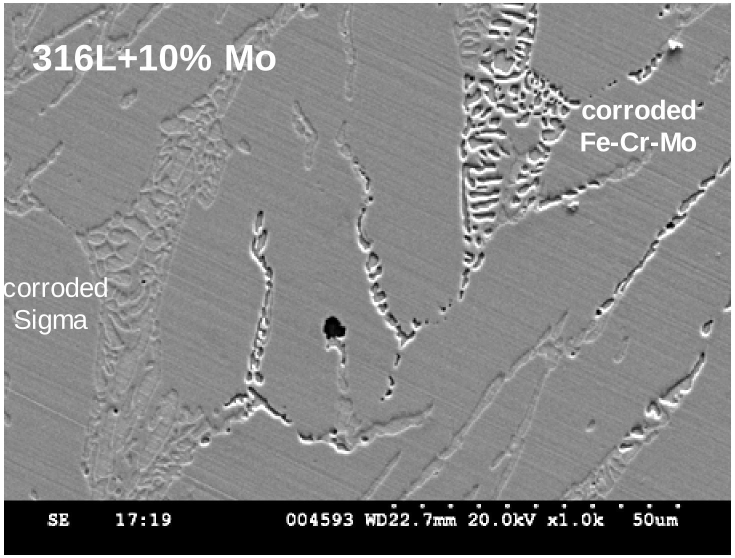


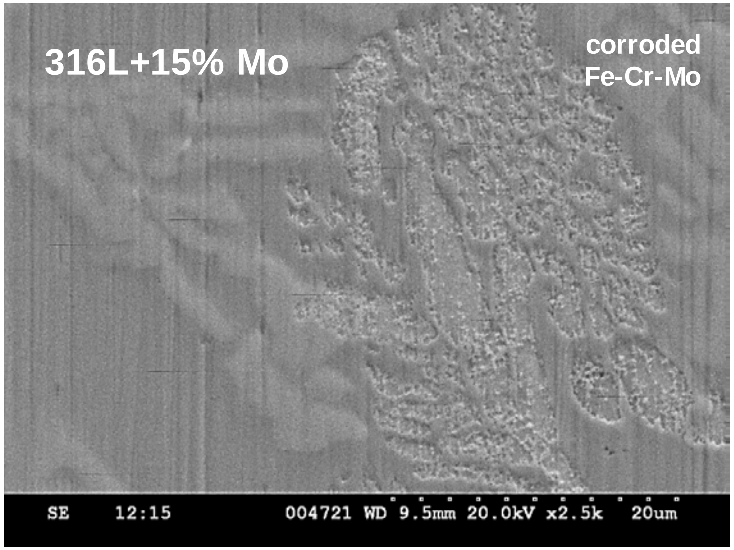
Alloy	Phase	Area%	Wt %				
			Si	Cr	Fe	Ni	Mo
316L	Steel	100	1.0	17	68	12	**2.5**
316L +5%Mo	Steel	98	0.8	18	63	12	**6.3**
	Sigma	2	1.3	20	**51**	5.4	22
316L +15%Mo	Steel	67	0.5	16	63	13	**8.3**
	Sigma	25	0.8	16	**50**	6.1	26
	Fe-Cr-Mo	8	1.2	14	42	4.8	**39**

Preferential Dissolution of Intermetallics during PDs

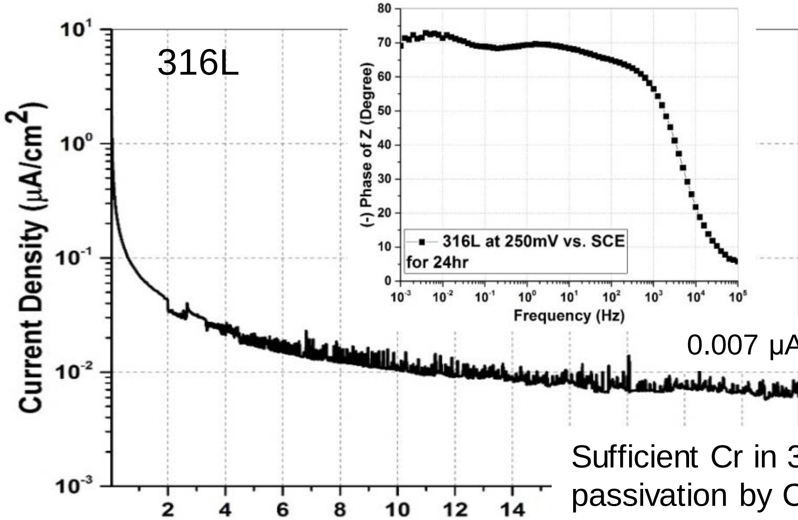




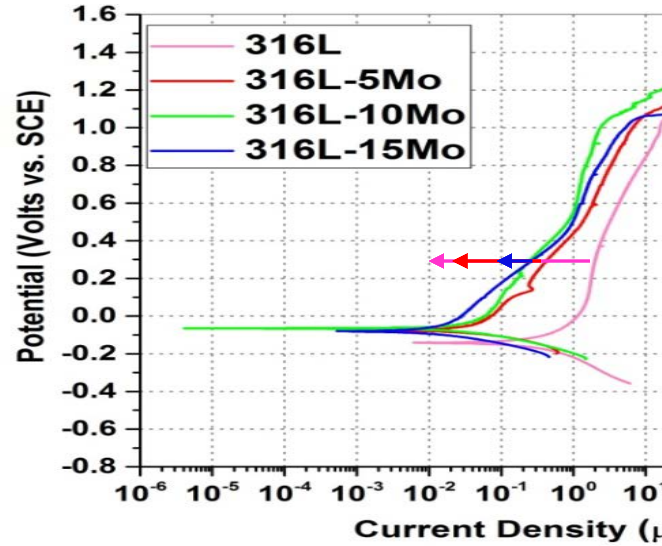


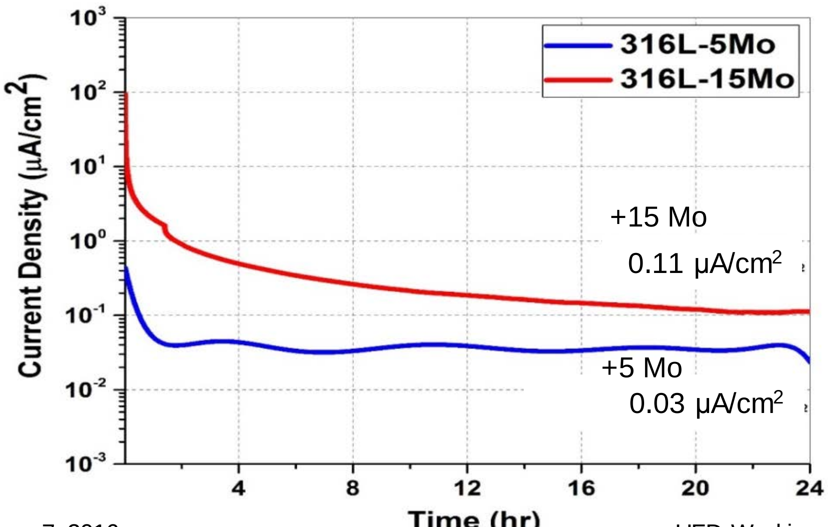


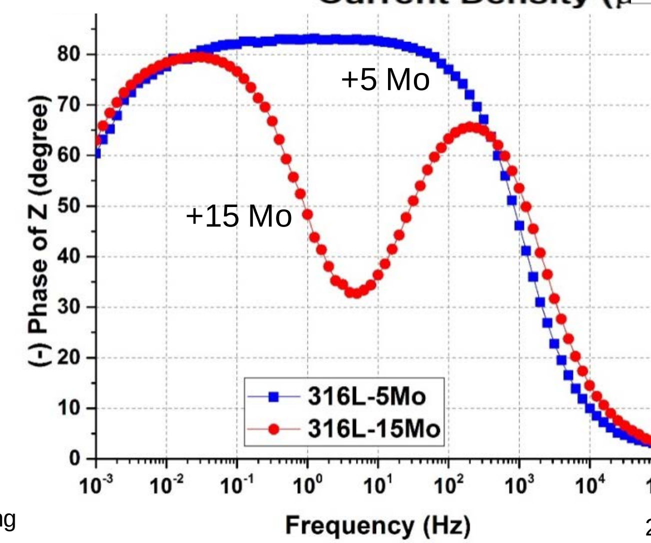
Potentiostatic Corrosion of 316L + Mo Alloys at 250 mV (pH 4 brine)



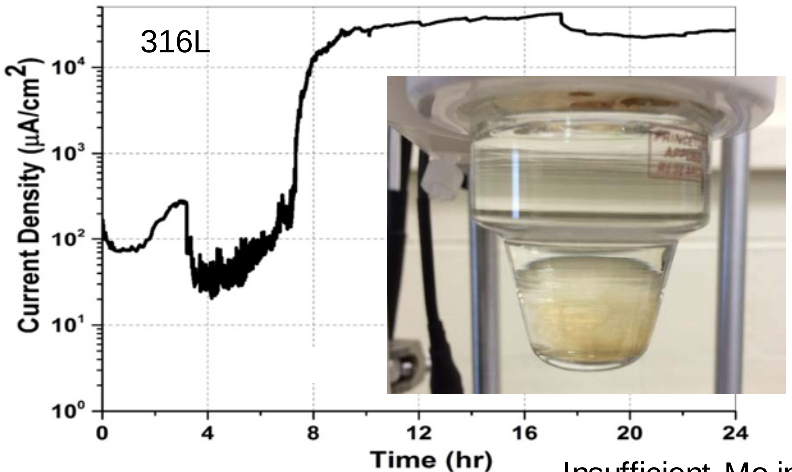
Sufficient Cr in 316L for passivation by Cr_2O_3

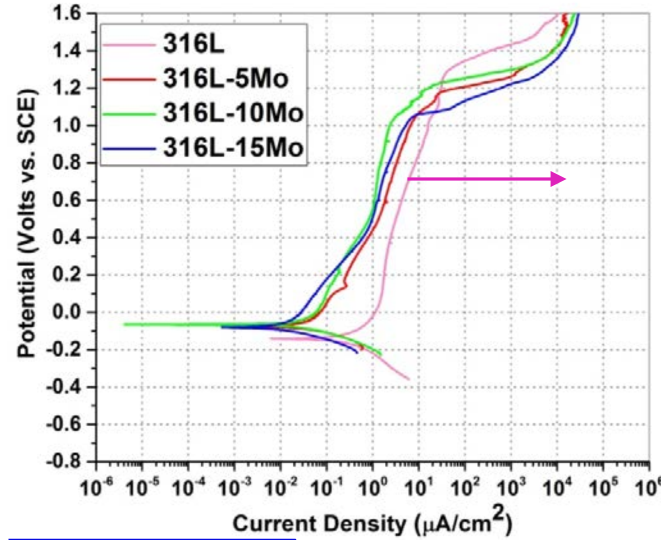




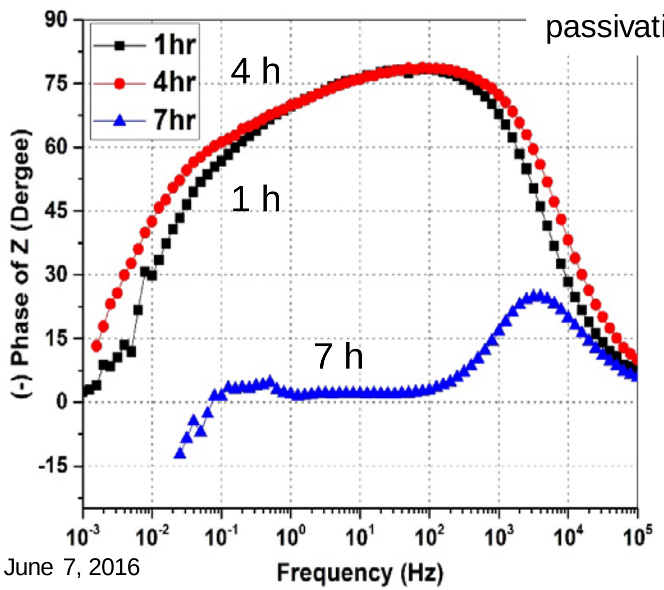


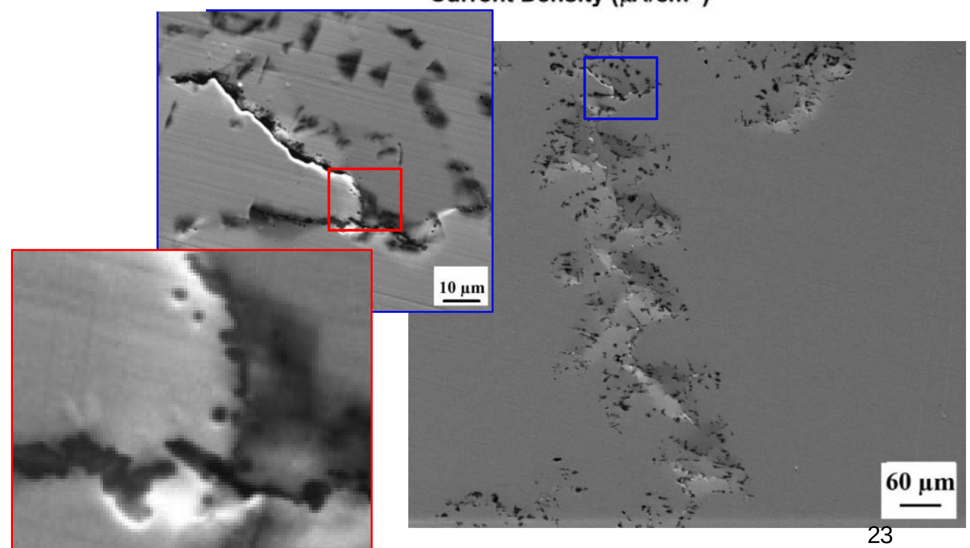
316L Corrosion at 750 mV (pH 4 brine)





Insufficient Mo in 316L for passivation by $NiMoO_4$





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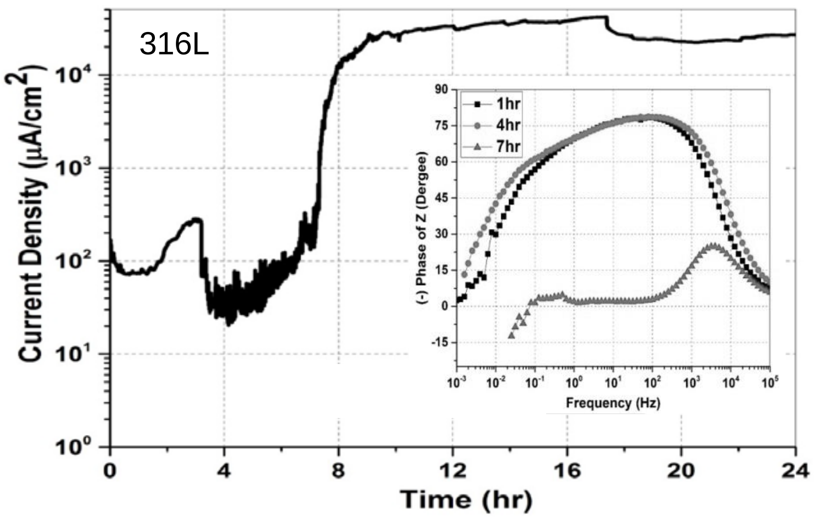
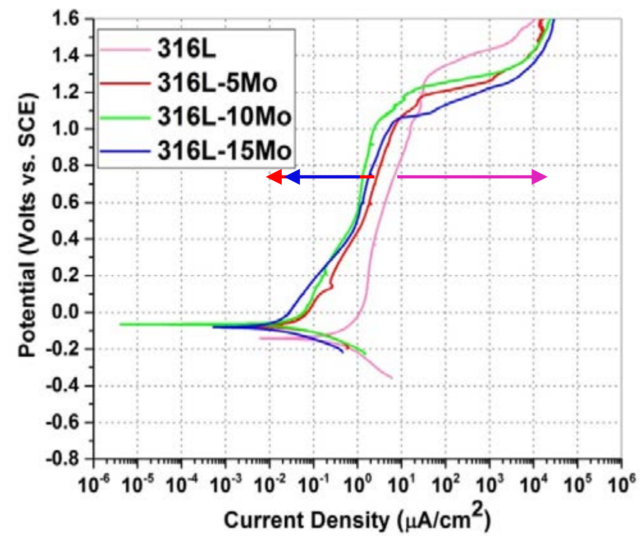
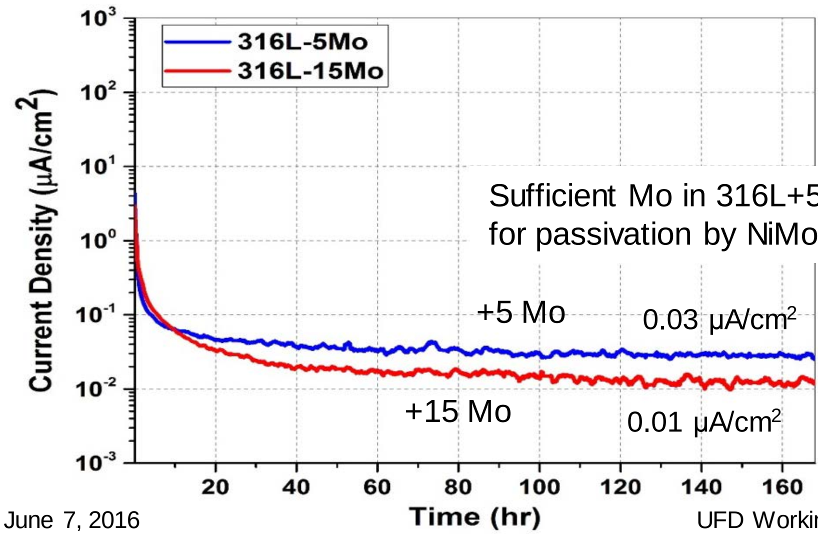
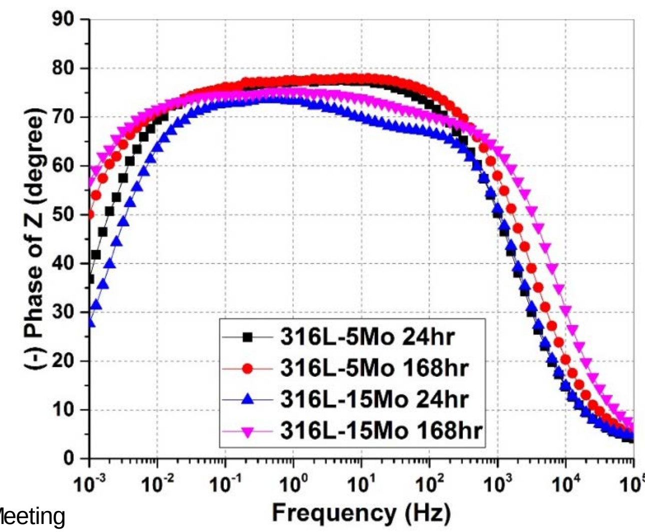
Potentiostatic Corrosion at 750 mV (pH 4 brine)









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Conclusions

- Experimental method and model developed to predict long-term corrosion of multi-phase alloyed waste forms based on short-term test results are relevant to alloy/oxide composites and single phase alloys.
  - Tracks corrosion kinetics and relates to surface stabilization/destabilization
  - Provides mechanistic basis for long-term predictions
- Key findings of NEUP
  - Zr reacts with Ln-oxides to form durable Ln-zirconates
  - Oxides form skeletal ceramic structures
  - Alloy and oxide corrosion can be modelled independently
- Experimental method and model can be applied to other performance models:
  - Breaching of waste packages as function of environmental conditions
  - Effects of metal corrosion on solutions in breached package and near field
  - Generation of metal corrosion products
  - Provides insights to formulating materials for enhanced long-term performance: e.g., small increase in Mo content of 316L greatly benefits long-term corrosion resistance.

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