NATIONAL ENERGY TECHNOLOGY LABORATORY

Computational Modeling of Microstructural Evolution in Alloys for Advanced Fossil Power Systems

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U.S. DEPARTMENT OF ENERGY

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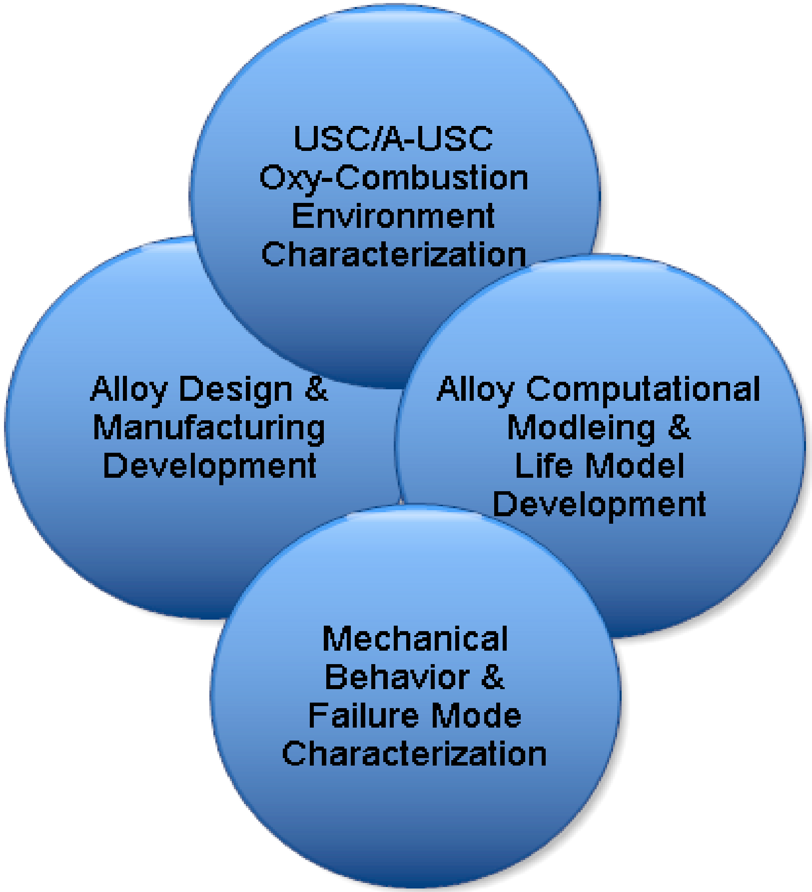
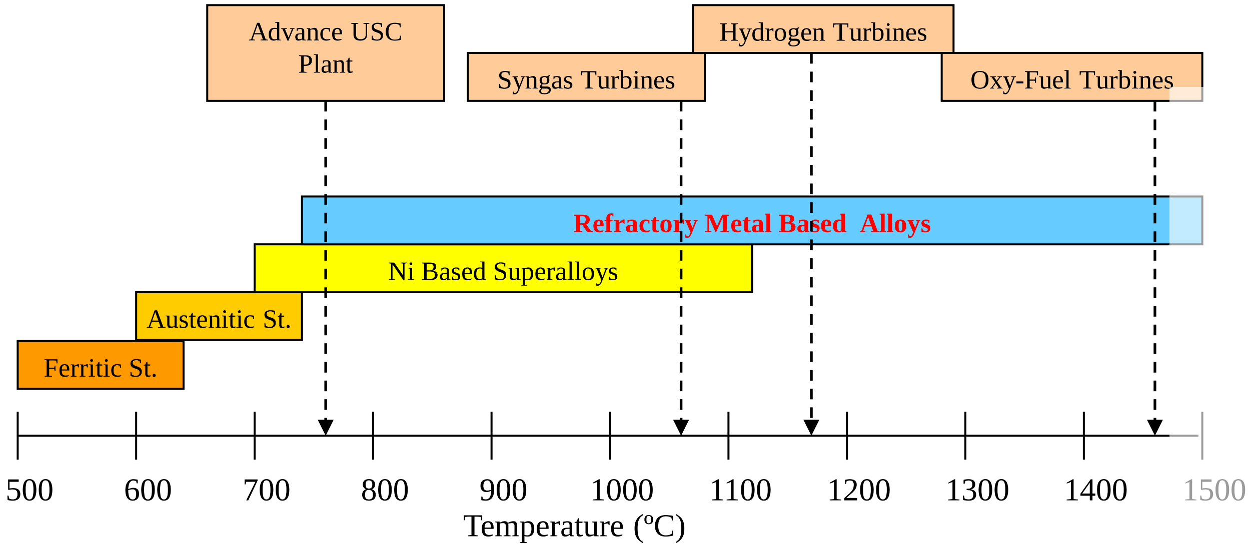
Advanced Combustion

- Integrated multi-scale computational approach, complimented with a focused experimental program, emphasizing the design & optimization of materials for advanced combustion systems.

  - *Computational material design & optimization.*
  - *Lab-scale synthesis of materials.*
  - *Mechanical & chemical assessment of materials performance in real environments*
  - *Simulation of component life in conventional & oxy-fuel combustion environments.*



New Energy Generating Technologies and High-Temperature Structural Materials for Boilers and Turbines



Advanced FE systems

- Extreme environment (corrosive,T,P)
- Components have to last 10,000's to 100,000's hours

- Lack of experience with alloy performance in these extreme conditions and times scales necessary for advanced FE systems
- Need for reliable and fast methods for predicting materials performance.
- **Integrated computational and focused experimental approach.**

Computational Materials Science

Objectives of Microstructural Evolution Modeling

- Identify the underlying thermodynamic driving force
- Identify the underlying kinetic mechanisms
- Understand the microstructure evolution path under a given condition
- Predict life of a component based on microstructure-property relationships

How to achieve optimum microstructure

Can we freeze it?

Can it survive?
If so, how long?

Kinetic processes at high T:
Phase transformation
Defect structure evolutions
Grain growth
Recrystallization
Precipitation

Environment effect: Oxidation

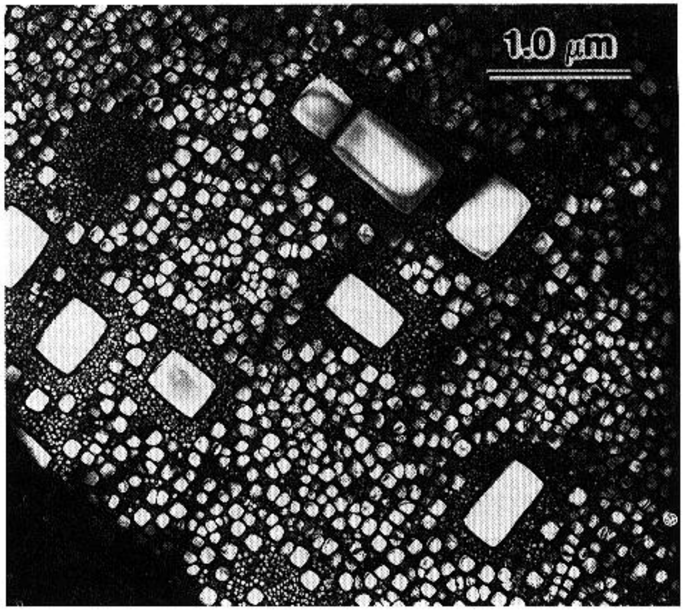
The Precipitation Modeling

Goal: Develop an engineering tool that can predict precipitation process under representative thermomechanical processing and service conditions

The Challenges

- **Volume fraction of precipitates can be as high as 70%**
- **Strong elastic interactions leads to non-spherical shape and strong spatial correlation**
- **Non-isothermal heat treating**
- **Multi-phase and multi-component**

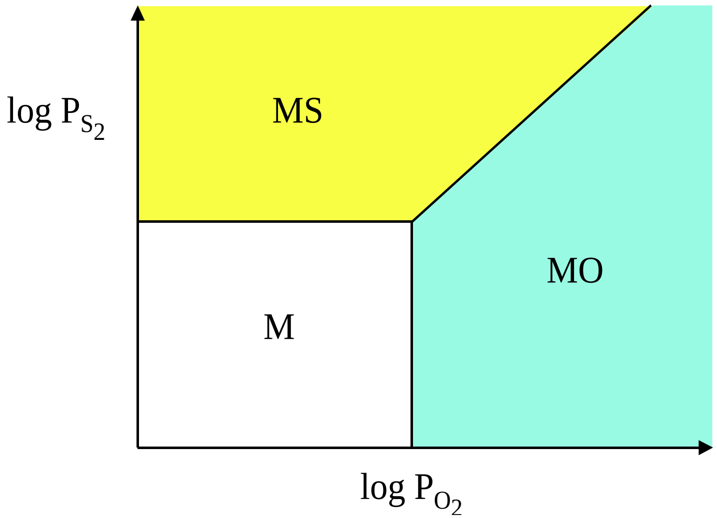
Phase-field method has the potential

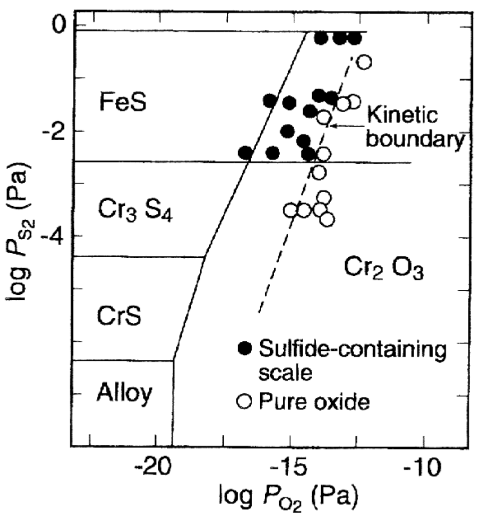


M.E. Gurtin and P.W. Voorhees.

The Oxidation Modeling

- High Temperature Materials in FE Power Systems are usually exposed to complex oxidizing environment.
- Computational approach available today is largely based on thermodynamic calculations. Kinetics is missing resulting large discrepancy.
- Phase-field approach takes into account both thermodynamic and kinetics.

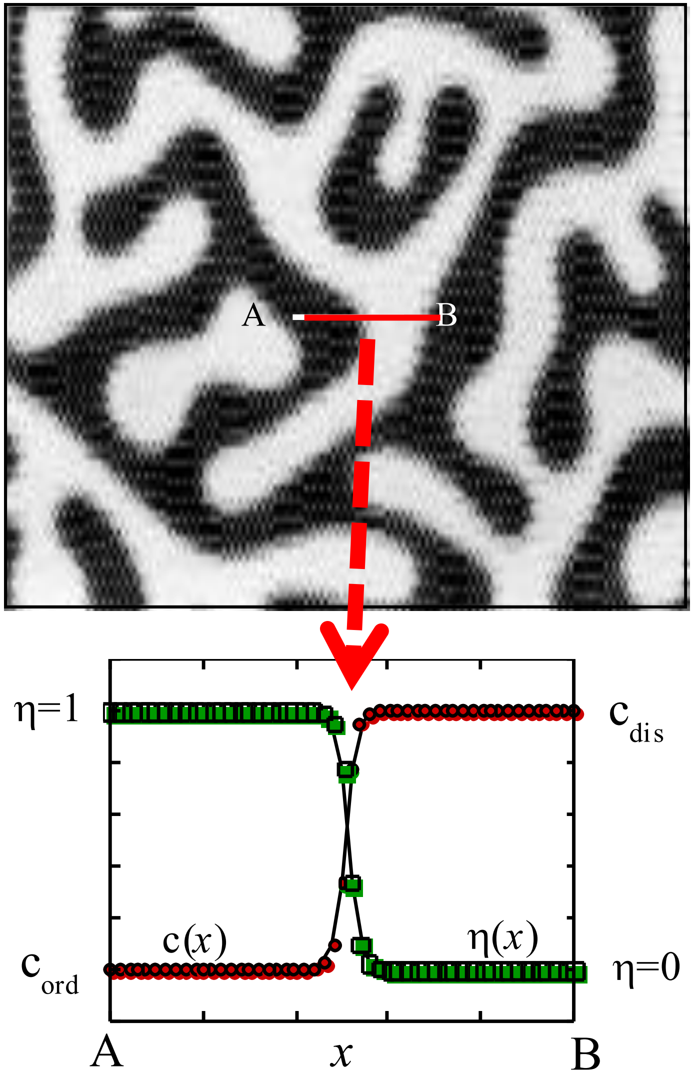




Corrosion of 310 type steel

Courtesy of Brian Gleeson

Phase-Field Method



- Complex microstructure represented by finite set of field variables
- Diffused interface (vs sharp interface in front tracking methods)

$$F = \int_V \left\{ f_{ch}(c,\eta,T) + \left[\frac{1}{2}\kappa_c(\nabla c)^2 + \frac{1}{2}\kappa_\eta(\nabla\eta)^2 \right] + F_{el} \right\} dV$$

$$\frac{\partial \eta}{\partial t} = -L\left(\frac{\delta F(c,T,\eta)}{\delta \eta}\right) + \varsigma_\eta$$

$$\frac{\partial c}{\partial t} = M\nabla^2\left(\frac{\delta F(c,T,\eta)}{\delta c}\right) + \varsigma_c$$

(Ginzburg-Landau, Cahn-Hilliard)

Phase-Field Method (cont.)

Choose field variables
Formulate the free energy
Find material parameters

↓

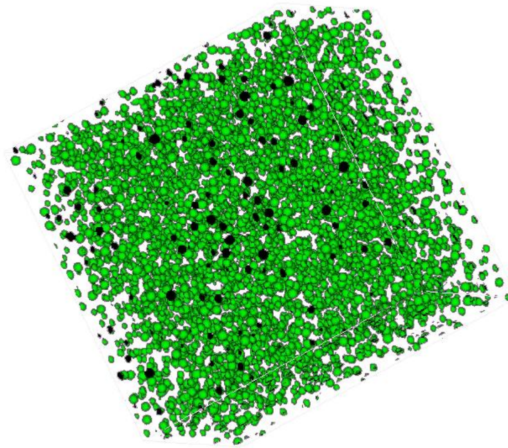
Define initial microstructure, e.g.
$c(\mathbf{r}, t=0)$, $\eta_i(\mathbf{r}, t=0)$

↓

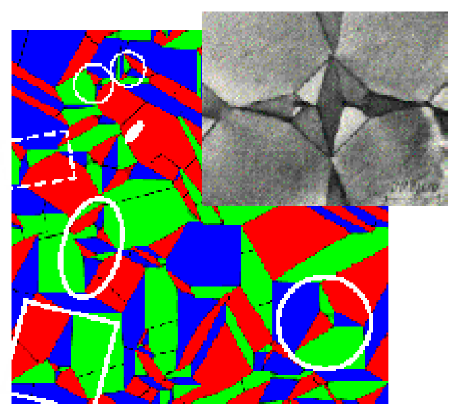
Calculate driving forces
$\delta F/\delta c$, $\delta F/\delta \eta_i$

↓

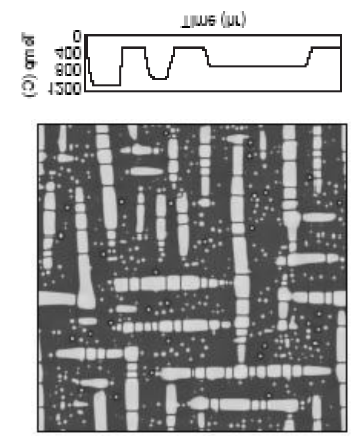
Integrate kinetic equations to update field variables
$c(\mathbf{r}, t+\Delta t)$, $\eta_i(\mathbf{r}, t+\Delta t)$



Wen'06: Effect of heterogeneous nucleation on microstructure in Al-Sc alloy



Wen et al: Hexagonal-to-orthorhombic transformation, Phil. Mag. A, 2000



Wen'08, Acta mater.

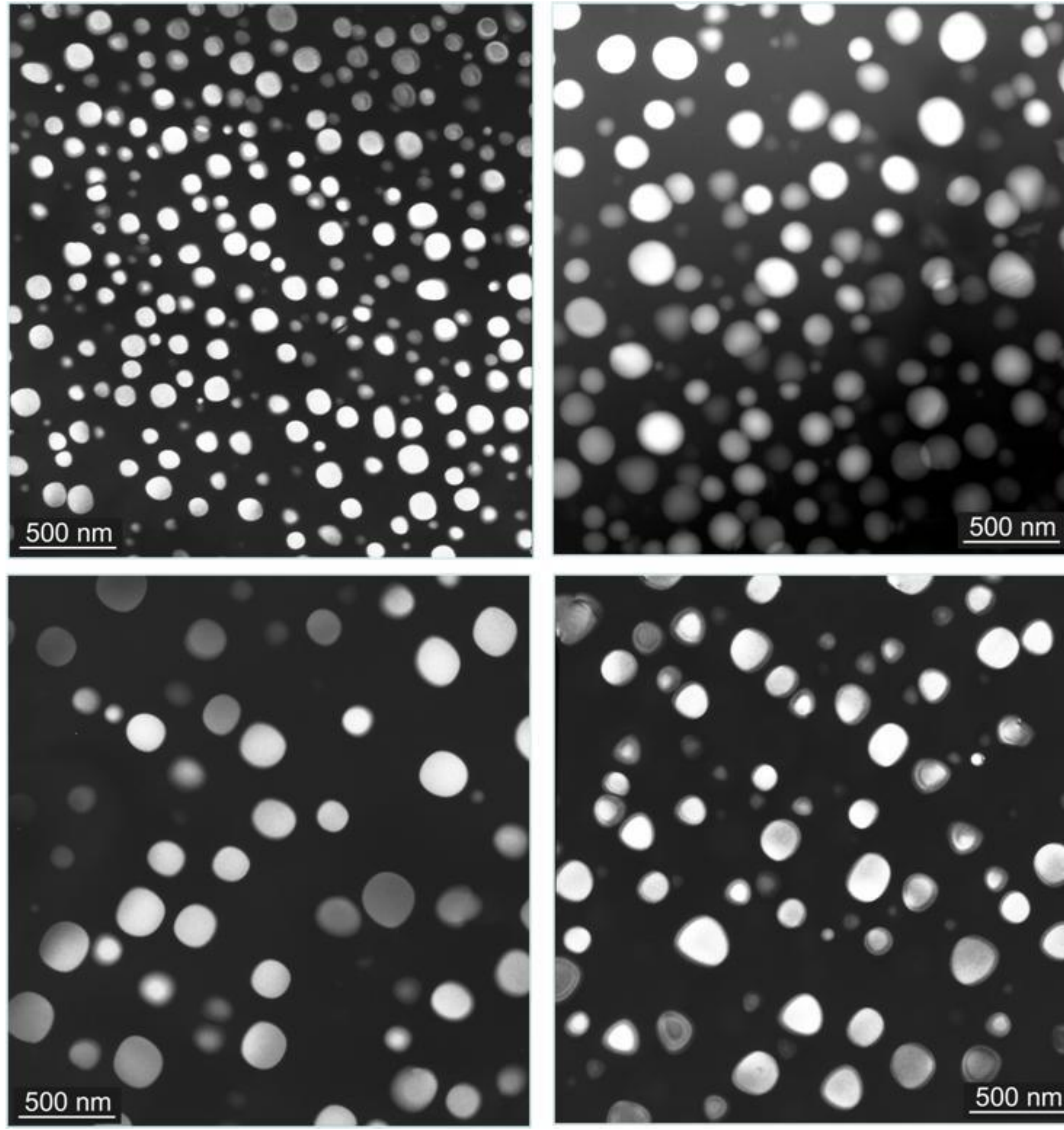
In-House Multi-Phase-Multi-Component Phase-Field Based Precipitation Model

- 1D, 2D, and 3D capability
- Multi-Component: 7 components in present work
- Multi-Phase? γ and γ' in Ni-base superalloys
- Direct link to CALPHAD Database: PanEngine from CompuTherm

Goal: Develop a tool for long-term microstructure stability testing in precipitation strengthened alloy systems

Haynes 282

- High temperature alloys typically use a combination of matrix strengthening precipitates, carbides and high dislocation density to impart strength.
- In Ni-base superalloys for use in steam power plants at temperatures up to 760°C, the main strengthening phase is gamma prime. Volume fraction and precipitate morphology are two important factors in alloy strength – both influence matrix strength and deformation behavior in the alloy.
- The character of grain boundaries and the phases found there are also important in generating high temperature creep strength and long-term microstructural stability.

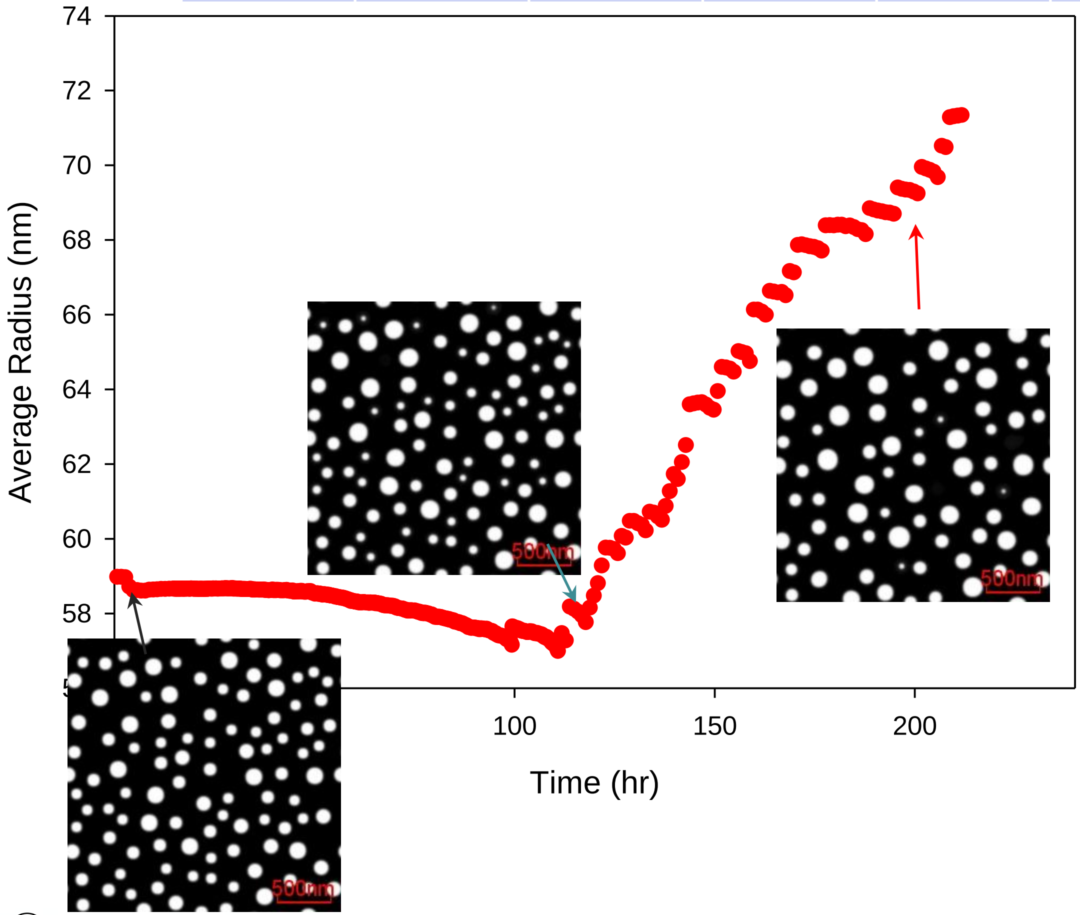


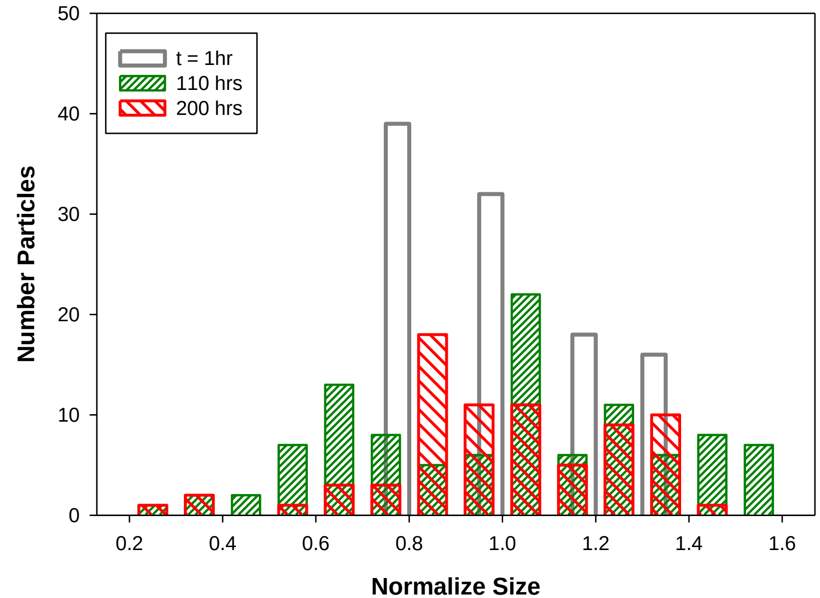
DF images showing γ' size and distribution in H282 with different test conditions

Coarsening

Haynes 282

	Al	Co	Cr	Fe	Mo	Ti	Ni	Vol.%
wt.%	1.5	10.0	20.0	1.5	8.5	2.1	bal	18.86

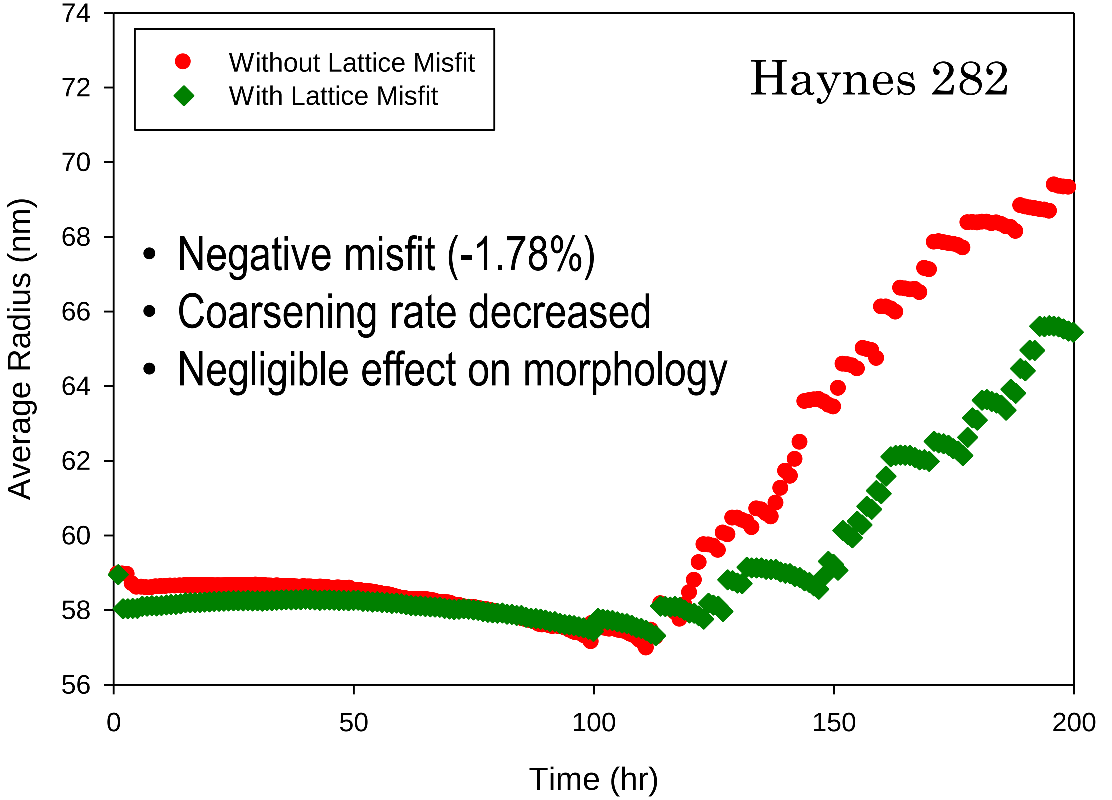




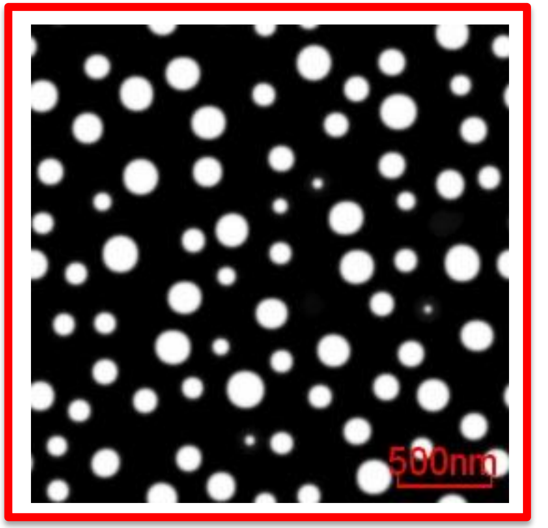
256x256 grid points, isothermal annealing at 760^{o}C, σ =90.0 mJ/m^2

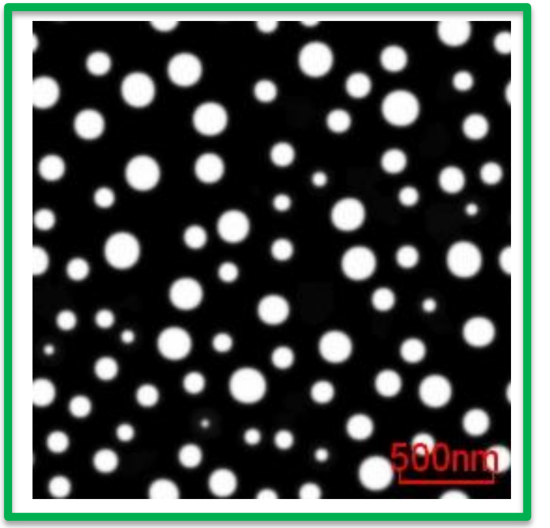
Effect of Lattice Misfit

t = 200hrs



- Negative misfit (-1.78%)
- Coarsening rate decreased
- Negligible effect on morphology

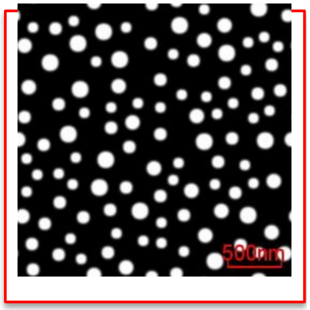


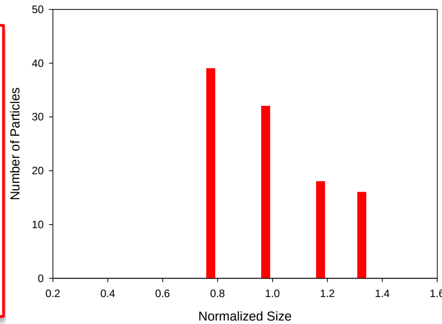


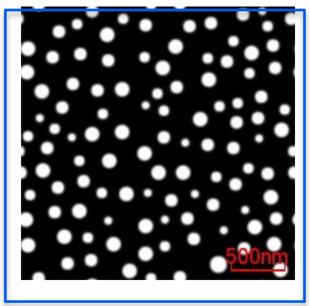
Lattice misfit good for microstructure stability

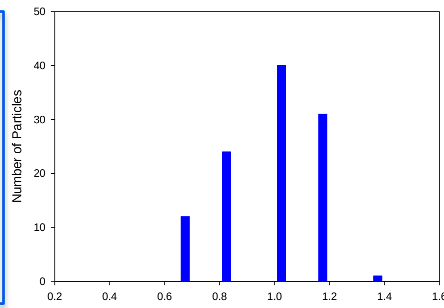
256x256 grid points, isothermal annealing at 760^{o}C, σ =90.0 mJ/m^2

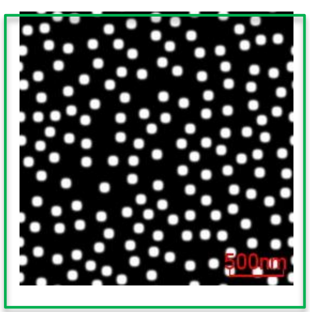
Effect of Initial Configuration

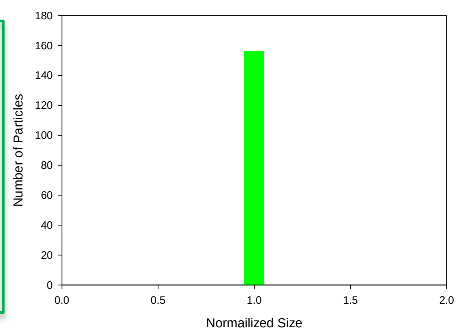


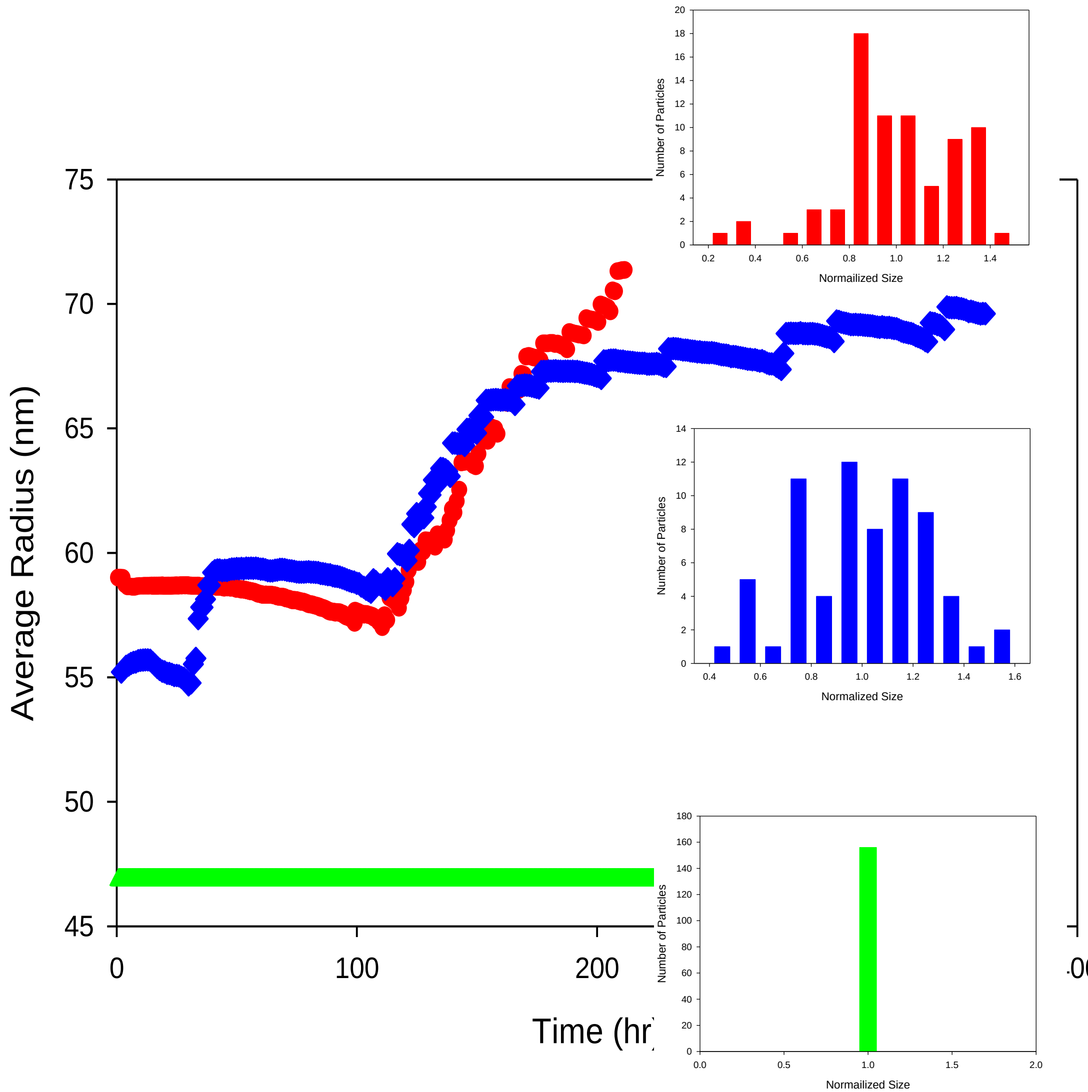










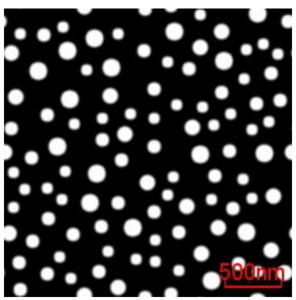


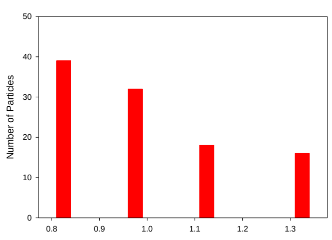
A virtual microstructural stability testing machine!

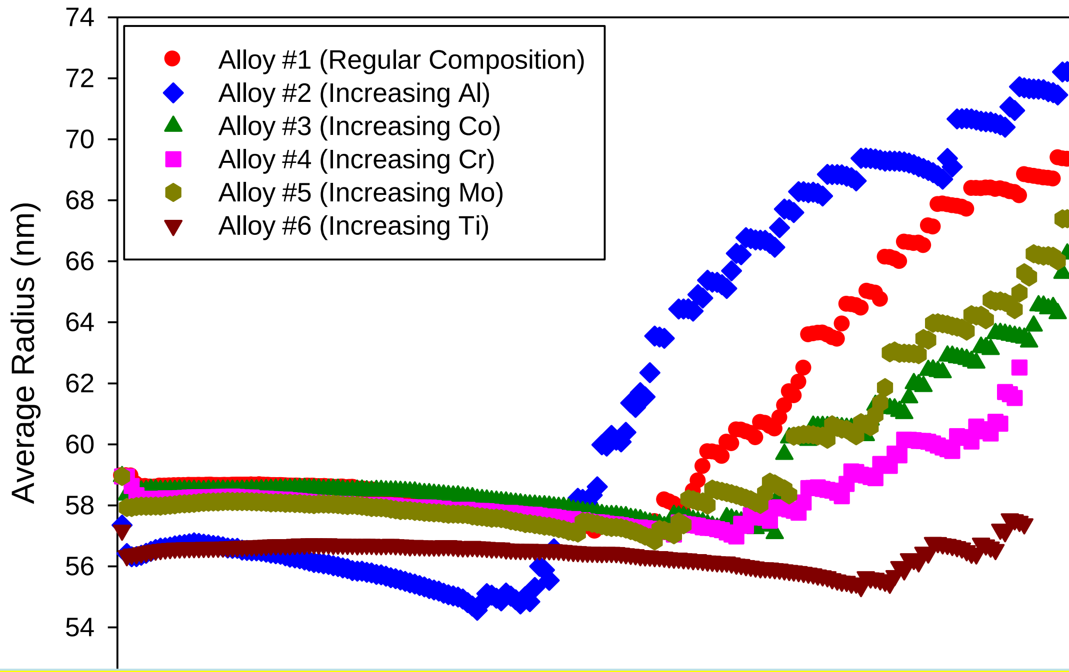
Simulated Alloying Chemistry Effect

	Al	Co	Cr	Fe	Mo	Ti	Ni	Vol.%
1	1.5	10.0	20.0	1.5	8.5	2.1	Bal	18.86
2	**1.8**	10.0	20.0	1.5	8.5	2.1	Bal	21.08
3	1.5	**11.0**	20.0	1.5	8.5	2.1	Bal	18.91
4	1.5	10.0	**21.0**	1.5	8.5	2.1	Bal	18.97
5	1.5	10.0	20.0	1.5	**9.5**	2.1	Bal	19.05
6	1.5	10.0	20.0	1.5	8.5	**2.5**	Bal	21.62

←Haynes 282

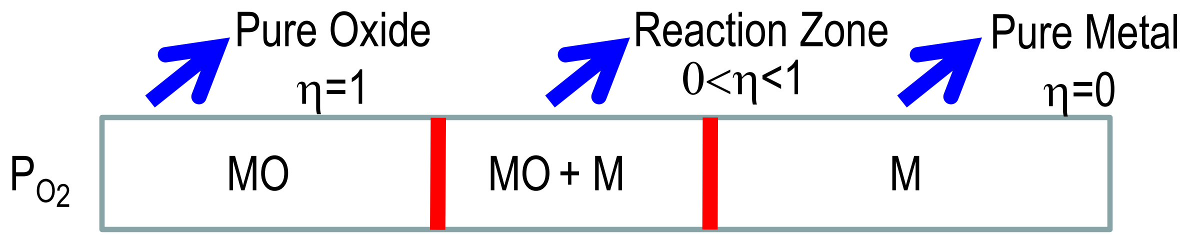


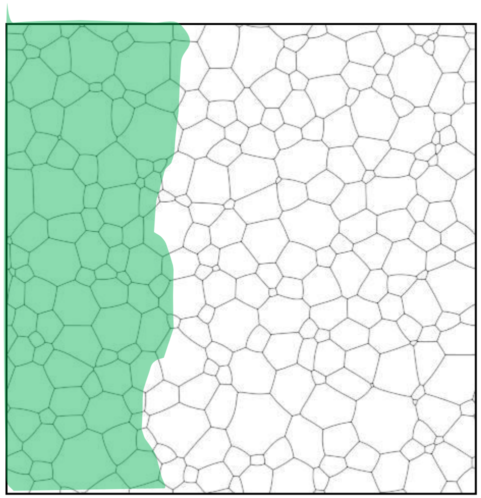




A virtual screening tool for composition selections!

Phase-Field Modeling of Oxidation





$$\eta(x,t) \rightarrow \textit{phase field to distinguish oxide and metal}$$

$$X(x,t) \rightarrow \textit{concentration of } O_2$$

$$f_{ch}(\eta, X) = h(\eta) f_o(X) + (1 - h(\eta)) f_m(X) + wg(\eta)$$

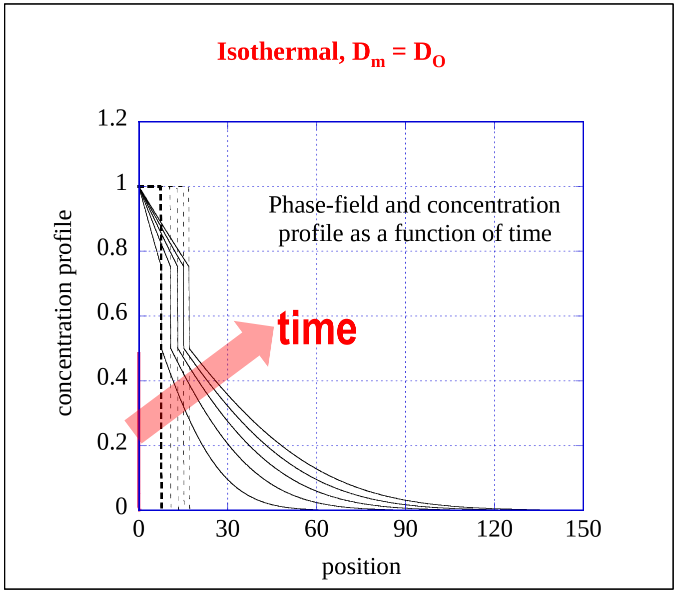
$$F = \int \left[f_{ch}(\eta, X) + \frac{\alpha}{2} (\nabla \eta)^2 \right] dV$$

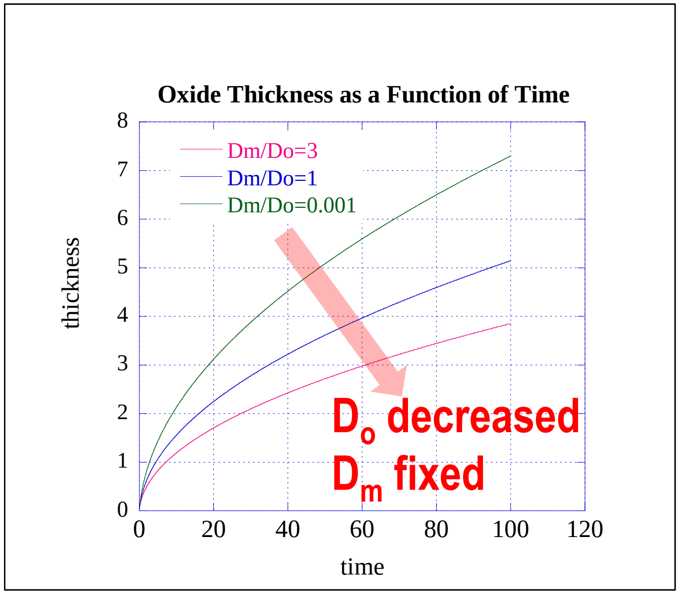
$$\frac{\partial \eta}{\partial t} = -L \frac{\delta F}{\delta \eta}; \qquad \frac{\partial X}{\partial t} = \nabla \left[M(\eta) \nabla \frac{\delta F}{\delta X} \right]$$

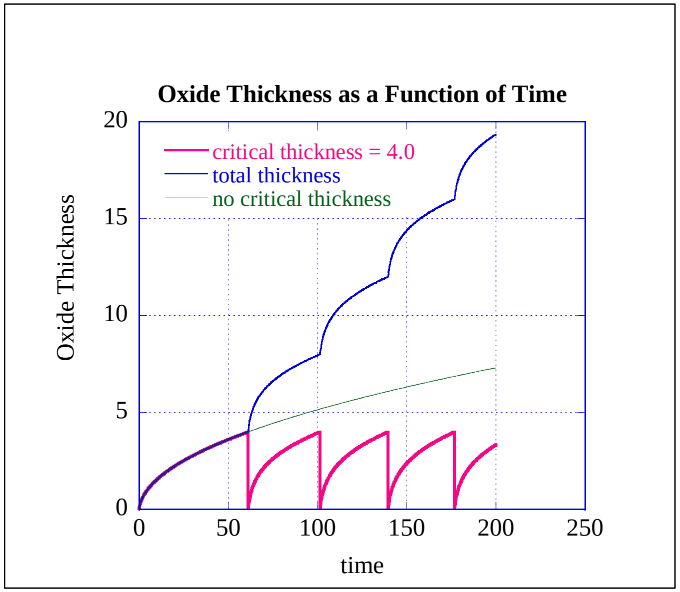
$$M + \frac{1}{2} O_2 \leftrightarrow MO$$

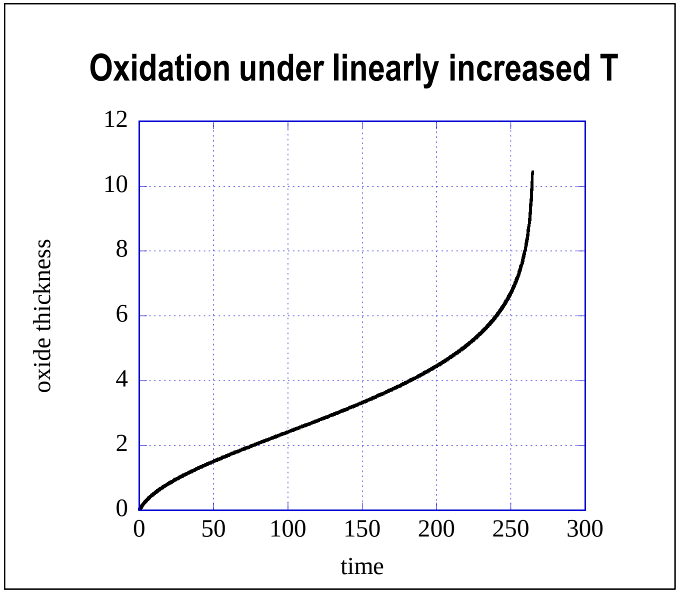
$$f_o(X) = \frac{1}{2}(X - X_o^{eq})^2; \qquad f_m(X) = \frac{1}{2}(X - X_m^{eq})^2$$

1-D Oxidation Modeling Results



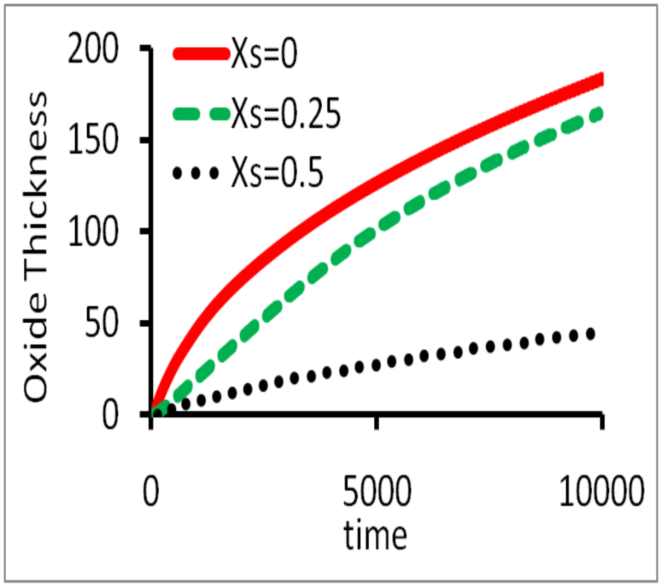




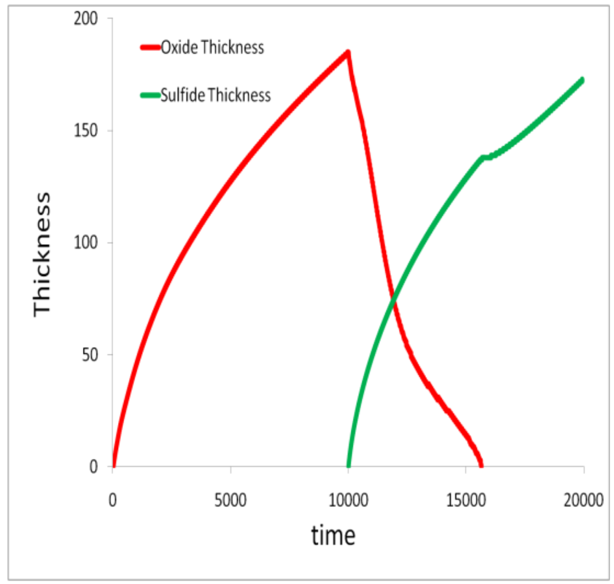


Dual-Oxidants Modeling

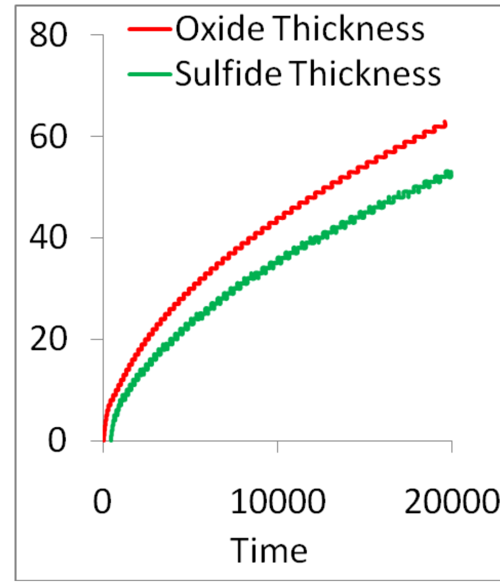
Y.H. Wen, L.Q. Chen, J.A. Hawk, Modeling Simul. Mater. Sci. Eng. 20(2012)



Effect of sulfur presence on oxidation kinetics (identical diffusivity)



Oxygen exposure followed by sulfur exposure



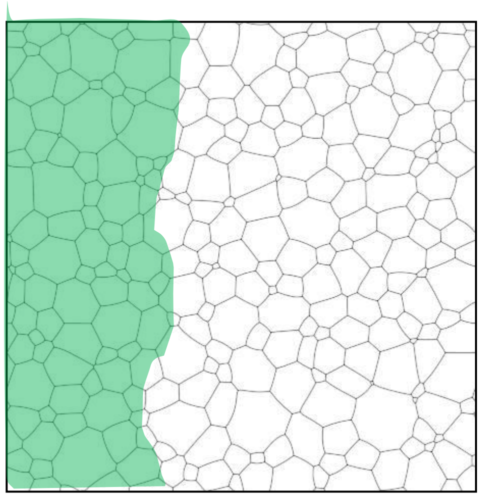
Simultaneous exposure to oxygen and sulfur

$$M_{O_2}^{m} = M_{O_2}^{mo} = M_{O_2}^{ms}$$

$$M_{S_2}^{m} = M_{S_2}^{mo} = M_{S_2}^{ms} = 10 M_{O_2}^{m}$$

The Path Forward

Oxidation Modeling



$$M+\frac{1}{2}O_2 \leftrightarrow MO$$

$$M+\frac{1}{2}S_2 \leftrightarrow MS$$

$$MO+\frac{1}{2}S_2 \leftrightarrow MS+\frac{1}{2}O_2$$

1. Microstructure effect beyond 1D modeling
2. Interaction among charged particles
3. Explore ways to link to ReaxFF potentials for surface reaction kinetics modeling
4. Explore ways to simulate corrosion under typical fossil power systems

The Path Forward

Precipitation Modeling

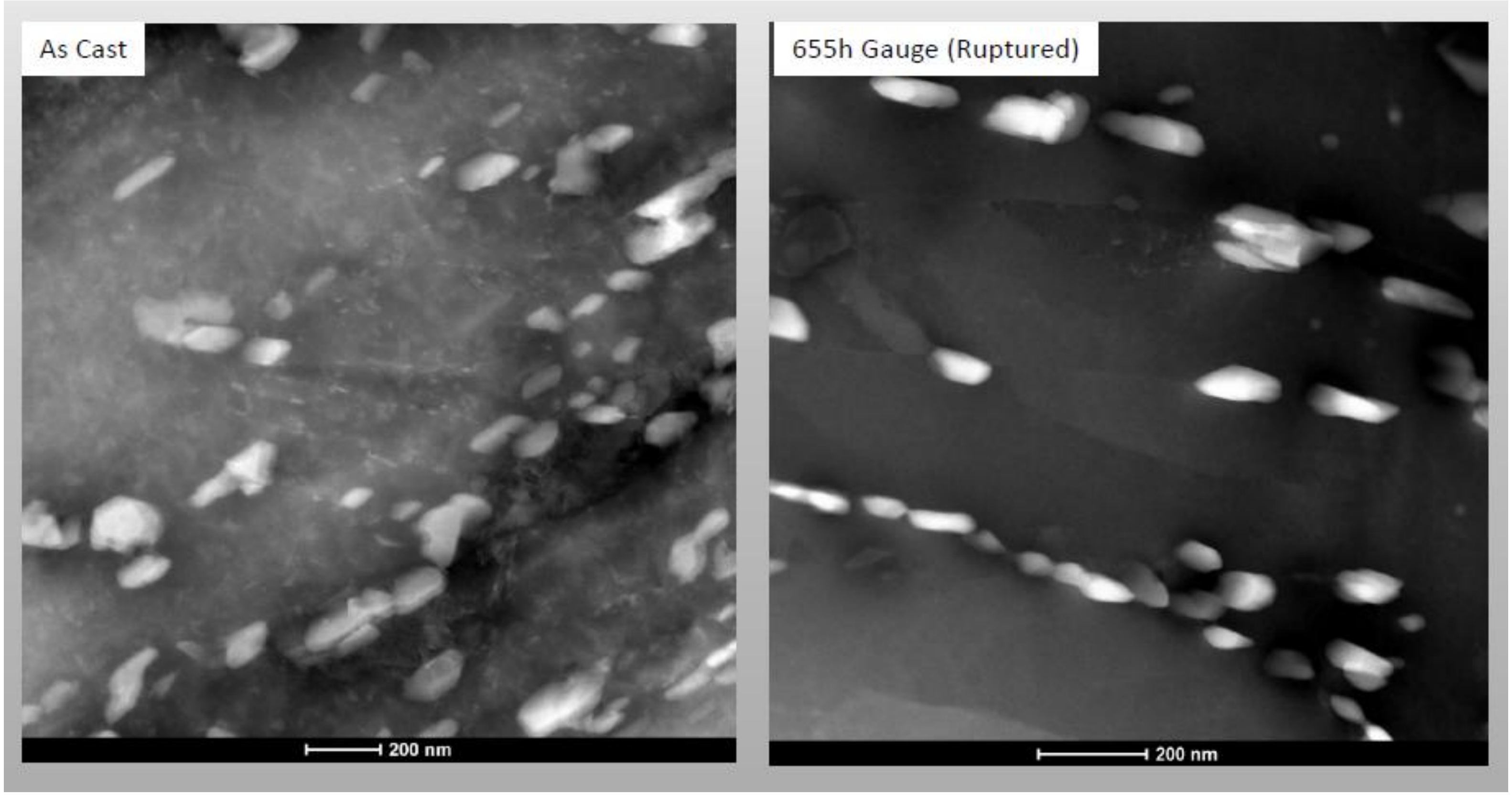
The major phases present in precipitate-strengthened Ni-base superalloys are:

- **Gamma (γ):** The continuous matrix – a face-centered cubic nickel-base austenitic phase, that usually contains a high percentage of solid-solution elements such as Co, Cr and Mo.
- **Gamma Prime (γ'):** The primary strengthening phase in nickel-base superalloys. γ' is a coherently precipitating phase, with the composition $Ni_3(Al,Ti)$, and being quite ductile, imparts strength to the matrix without lowering the fracture toughness of the alloy.
- **Carbides:** Carbon, added at levels of 0.05-0.2 wt%, combines with reactive and refractory elements to form carbides (such as TiC). These begin to decompose during heat treatment and service, forming lower carbides such as $M_{23}C_6$ and M_6C. The general opinion is that in superalloys with grain boundaries, carbides are beneficial by increasing rupture strength at high temperatures.
- **Topologically Close-Packed Phases:** These are generally undesirable, brittle phases that can form during heat treatment or service. They tie up γ and γ' strengthening elements in a non-useful form, reducing creep strength and acting as crack initiators.

Excerpted from TMS Superalloys: A Primer and History

The Path Forward

Precipitation Modeling



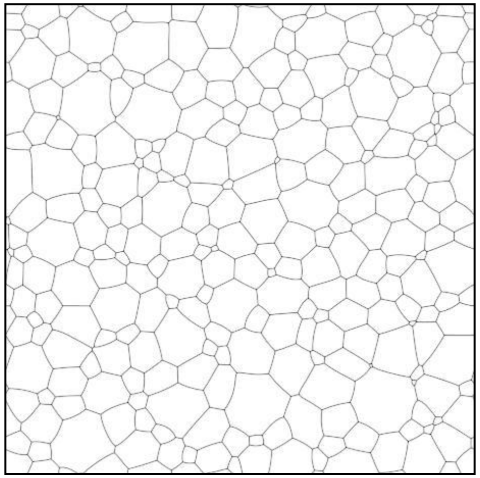
Phase-Field Modeling of Carbide Precipitations Kinetics in

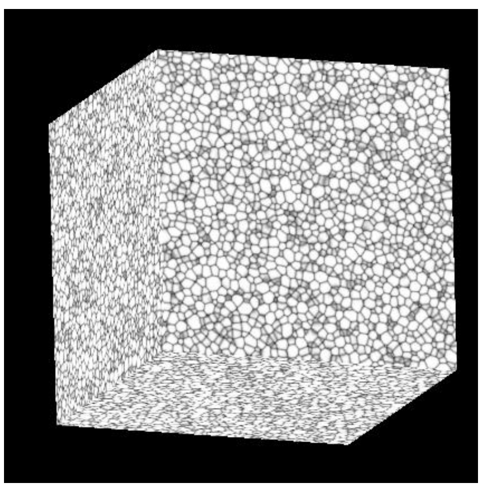
Ni-base superalloy and 9Cr Steel?

Courtesy of Mitsu Murayama at VirginiaTech

The Path Forward

Grain Growth Modeling





Develop a phase-field based engineering tool to predict location specific grain size distribution in a large component under thermo-mechanical processing.

Potential Modeling Subjects:

- Zener pinning effects due to 2nd-phase presence
- DRX, MDRX, and recovery modeling
- Abnormal grain growth due to: a) DRX & MDRX; b) large spread of misorientation dependent interfacial energies and grain boundary mobilities
- Plastic deformation, etc.

Summary

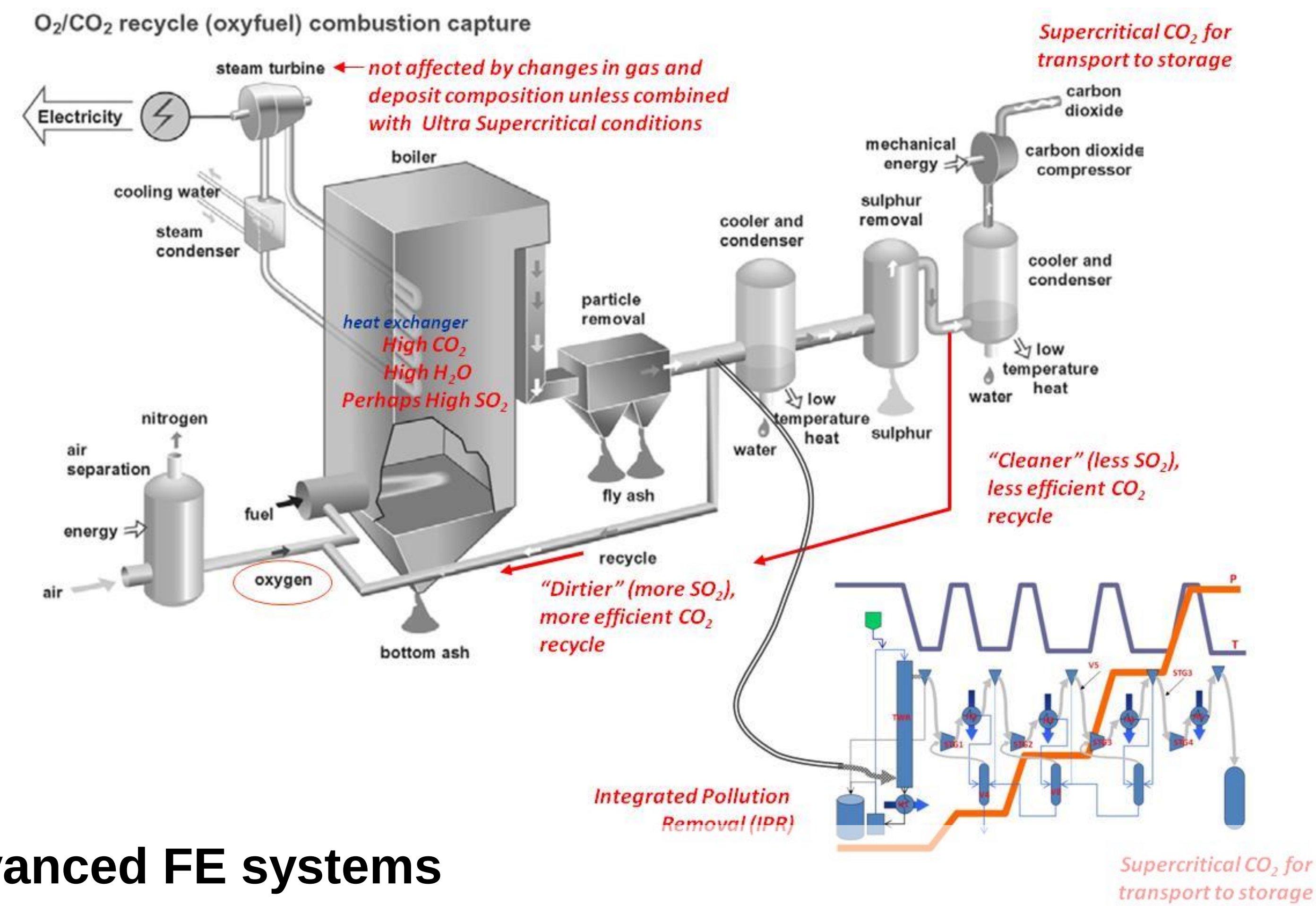
- **Described a Phase-Field model that can simulate precipitation kinetics in Ni-based commercial alloys. We demonstrated that this model can be used to help alloy design for a more stable precipitation microstructure.**
- **Presented some preliminary results for oxidation kinetics modeling in a simplified 1D case.**
- **Described the path forward for our modeling effort.**

Acknowledgements

- **Strategic Center for Coal, NETL for supporting this ORD activity through the IPT Program.**
  – Robert Romanosky (Technology Manager)
  – Patricia Rawls (Project Manager)
  – David Alman and Jeffrey Hawk (ORD Technical Coordinator)
- **Kevin Wu**

Backup Slides

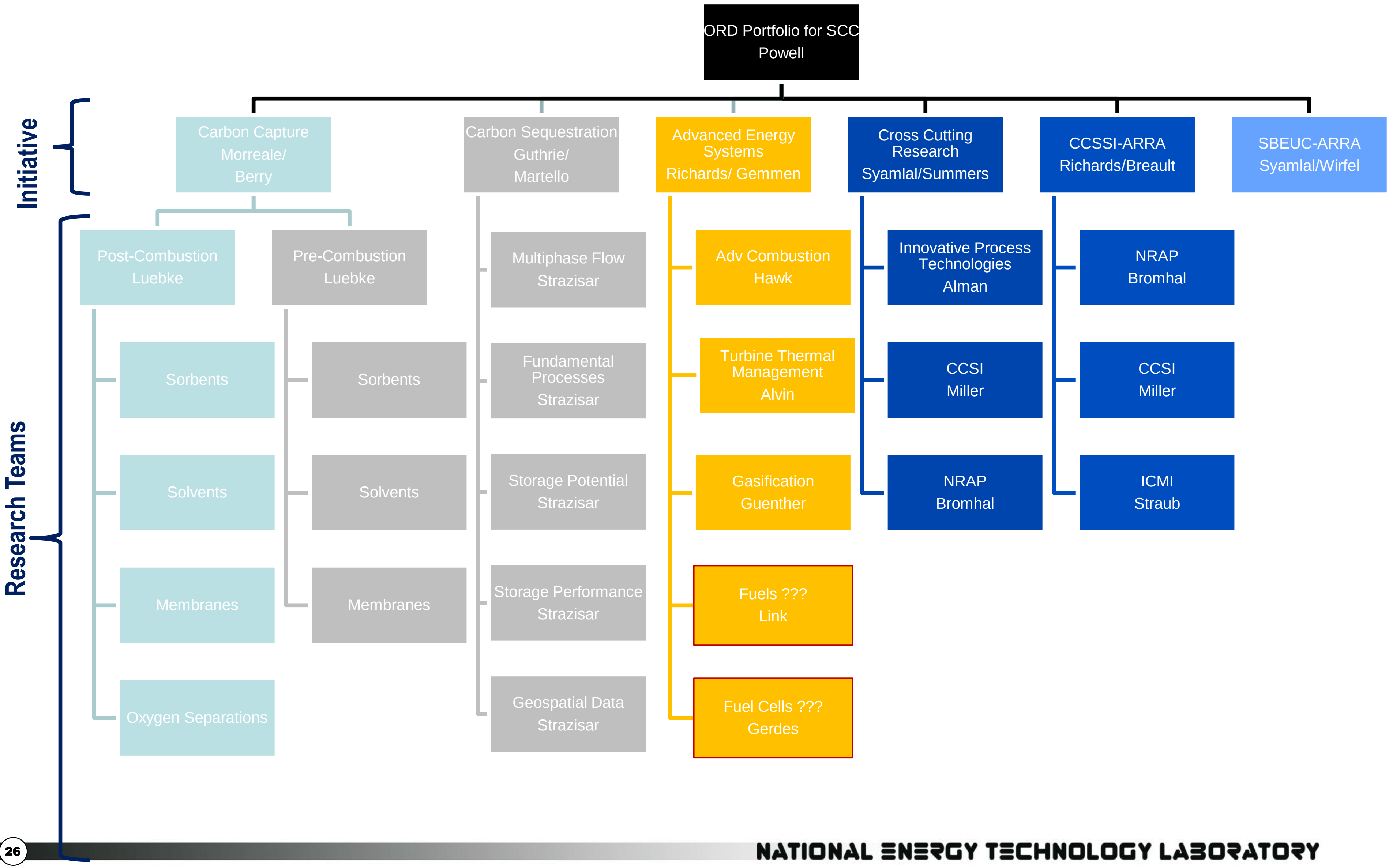
Materials for Advanced FE systems



Advanced FE systems

- Extreme environment (corrosive,T,P)
- Components have to last 10,000's to 100,000's hours
- ➢ ***Lack of experience with alloy performance in these conditions***

ORD FY 2012 R&D Portfolio--SCC

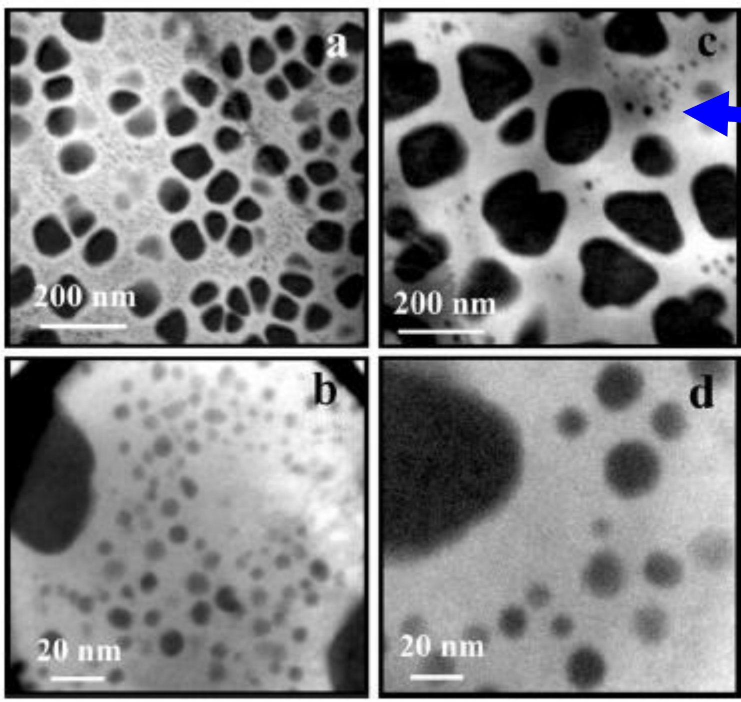


NETL-RUA Advanced Combustion Task

- **Task Description:**
  - Provide the mechanical and physical property information needed to allow rational design, development and/or choice of alloys, manufacturing approaches, and environmental exposure and component life models to enable oxy-fuel combustion boilers to operate at Ultra-Supercritical (650^{o}C & 22-30 MPa) and/or Advanced Ultra-Supercritical conditions (760^{o}C & 35 MPa).
- **How this task contributes to the program:**
  - Higher temperatures will allow higher efficiency oxy-fuel systems
  - Identifies how to address corrosion issues from wider coal choices/impurities
- **Unique or complimentary aspects:**
  - Applies existing DOE collaborations specifically to oxy-fuel issues:
    - DOE FE 1400F Boiler Consortium
    - US-UK FE Collaboration
  - Significant industrial collaborations already in place
  - Unique contribution to FE program for oxy-fuel systems
  - Results help both steam turbines* and oxy-fuel systems

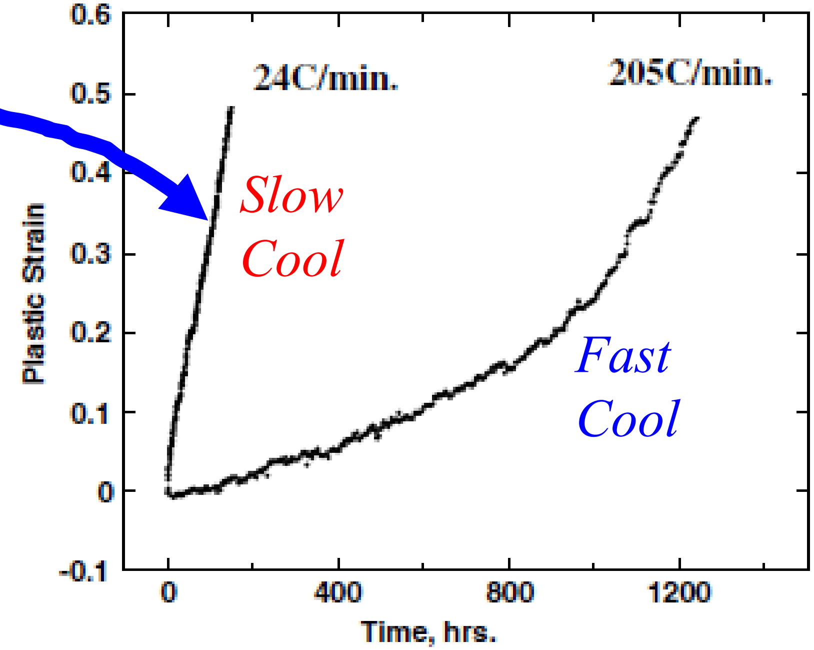
Why Care About Microstructure?

205 C/min 24 C/min



Rene 88DT Disk Alloy

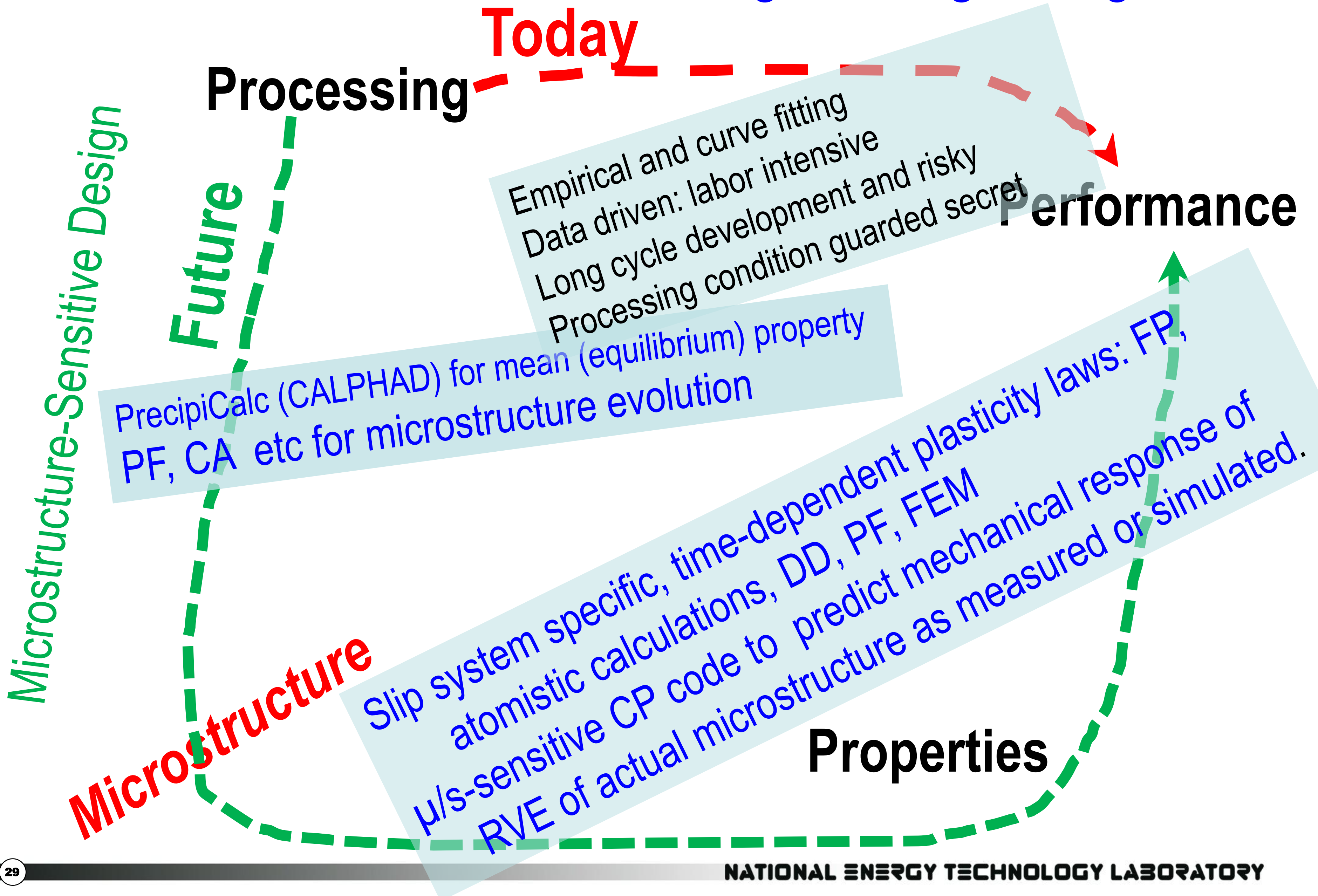
G.B.Viswanathan, et al Acta mater. 2005



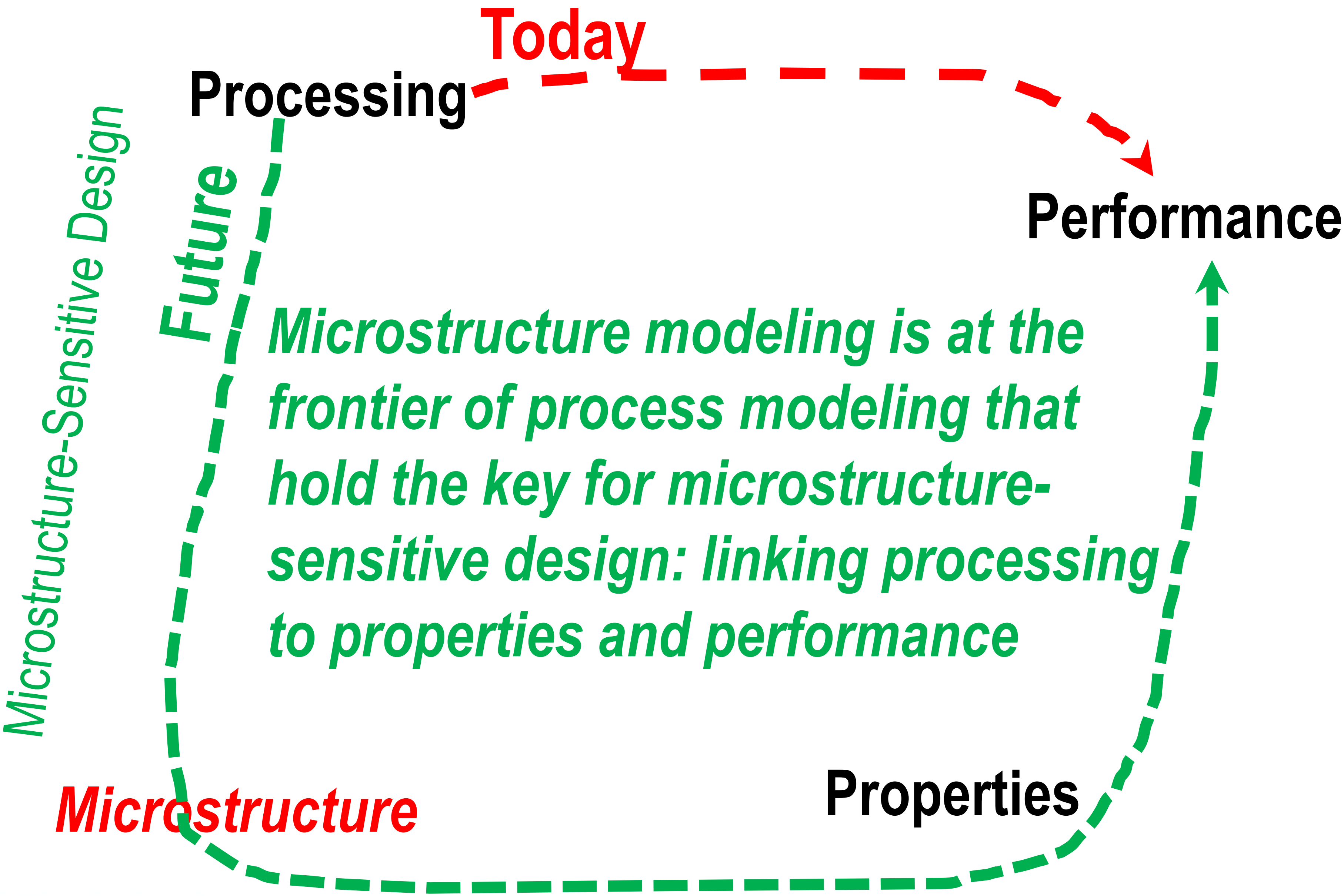
Creep Rate comparison
(650C, 838 MPa)

Why care about microstructure modeling?

Microstructure and Engineering Design

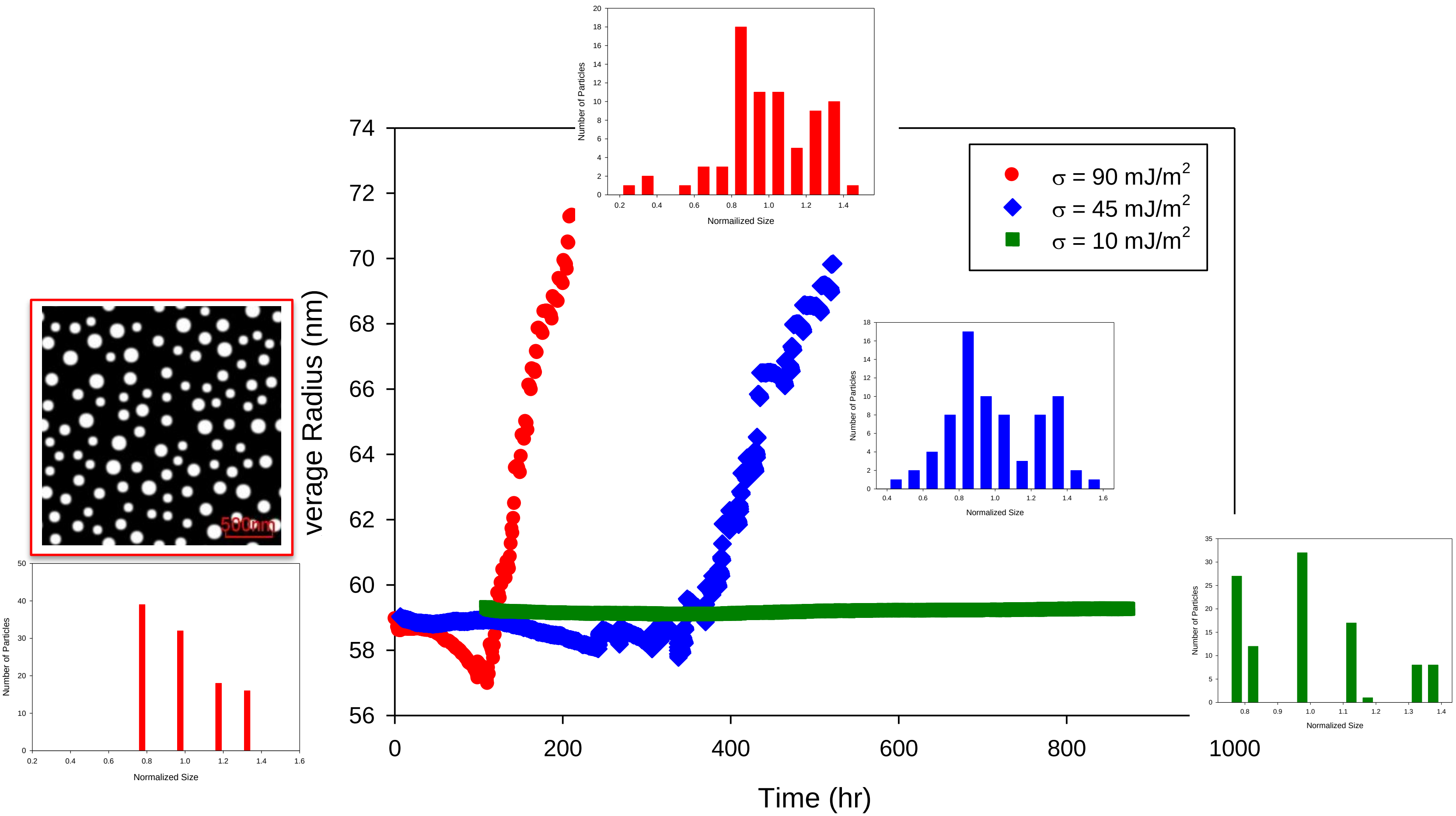


Why Care About Microstructure Modeling?



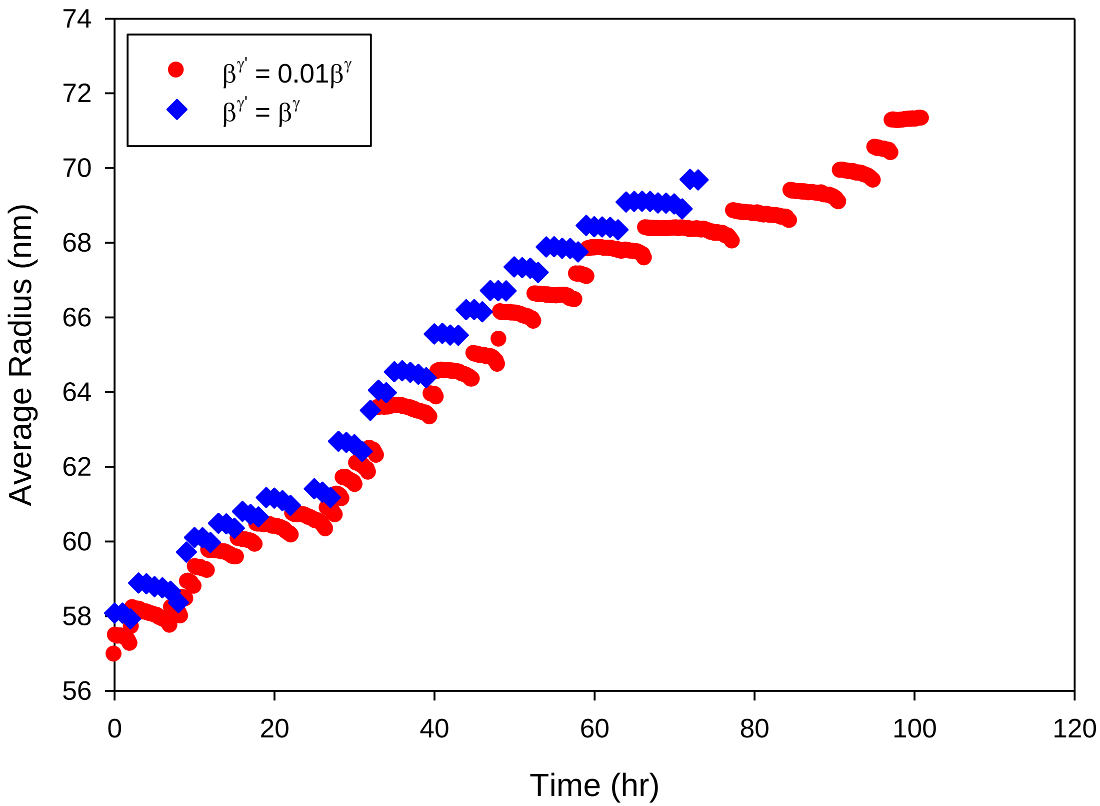
Microstructure modeling is at the frontier of process modeling that hold the key for microstructure-sensitive design: linking processing to properties and performance

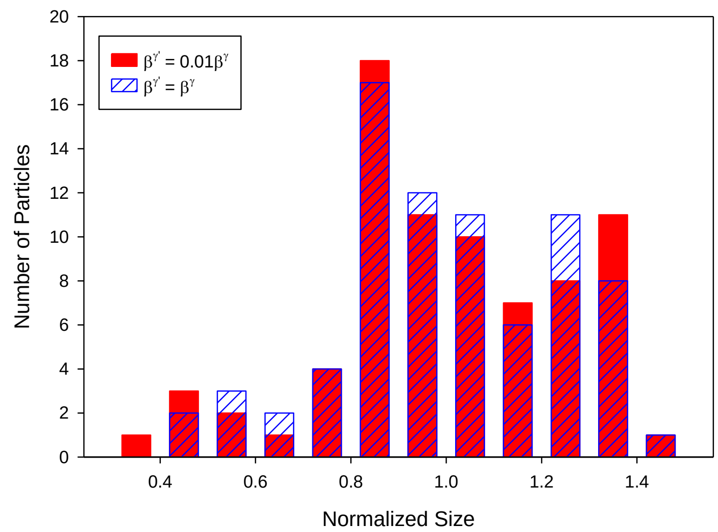
Effect of Interfacial Energy



256x256 grid points, isothermal annealing at 760°C

Effect of Mobility in γ' phase





– Larger diffusivity in γ' slightly increase the coarsening rate

256x256 grid points, isothermal annealing at 760°C, σ =90.0 mJ/m^2

Mean Field Strategy for Oxidation Modeling

Screening

Identify Protective Oxide
Cr_2O_3, Al_2O_3, …

⇩

Find Oxide Stability Range
Ni-(Al,Cr,..)-O Thermodynamic Database

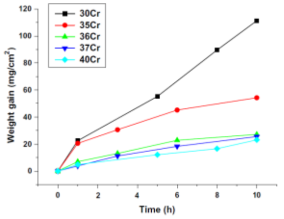
⇩

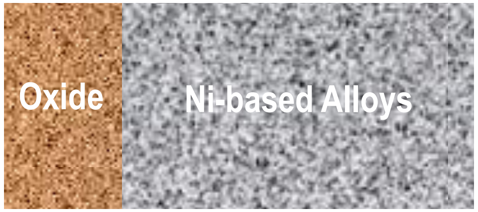
Find Alloy Composition Range
•Identify Key Reaction Element (Al, Cr…)
•Sufficient Supply of Reaction Element(Prevent Internal Oxidation)
•Ni-based Alloy Thermodynamic Database
•Ni-based Alloy Mobility Database

$$J_i = \left[C_i \beta_i \frac{\partial \mu_i}{\partial \bar{C}_d} \right] \frac{\partial \bar{C}_d}{\partial x} >> J_i^{ox}$$

⇨

Oxidation Lifetime Modeling





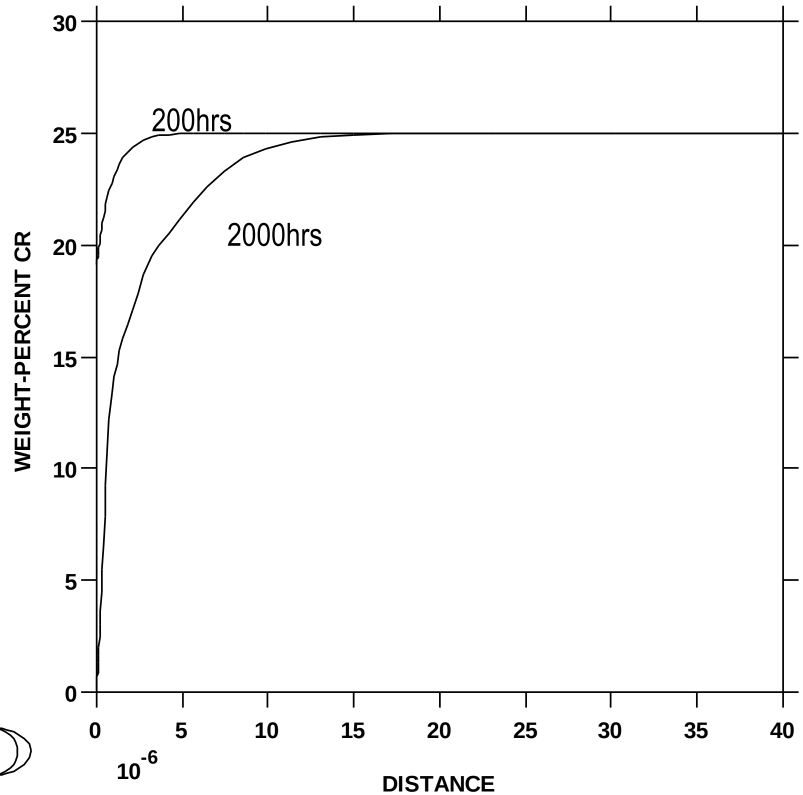
Diffusion Modeling
•Diffusion in Ni-based Alloys
•Oxidation Boundary Conditions
•Lifetime Prediction (Insufficient Supply of Reaction Element, Surface Condition Outside Stability Range…)

Cr Evaporation

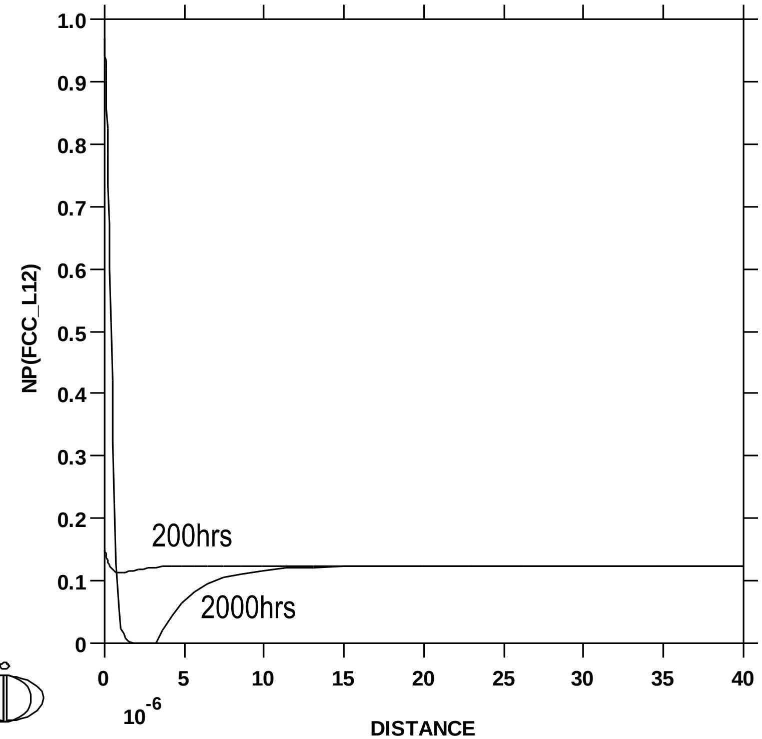
IN740

	Al	Co	Cr	Fe	Mo	Mn	Ti	Ni
wt.%	0.9	20.0	25.0	0.7	0.5	0.3	1.8	bal

Cr Concentration



γ′ volume fraction



Ke = 2.13×10^{-9} kg/(m_2s)

- Based on evaporation boundary condition proposed by G. R.Holcomb*

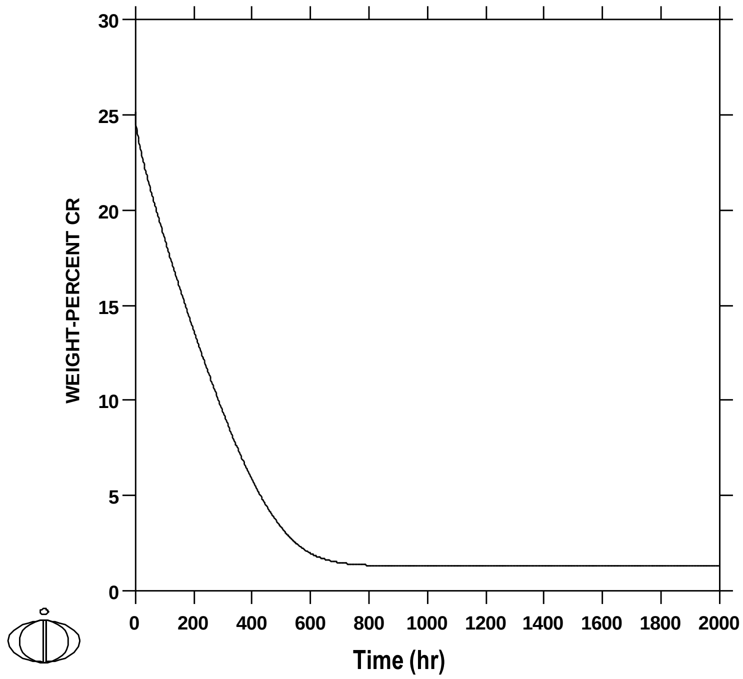
* G.R. Holcomb, J. Electochem. Soc., 156(9), C292(2009)

Cr Evaporation

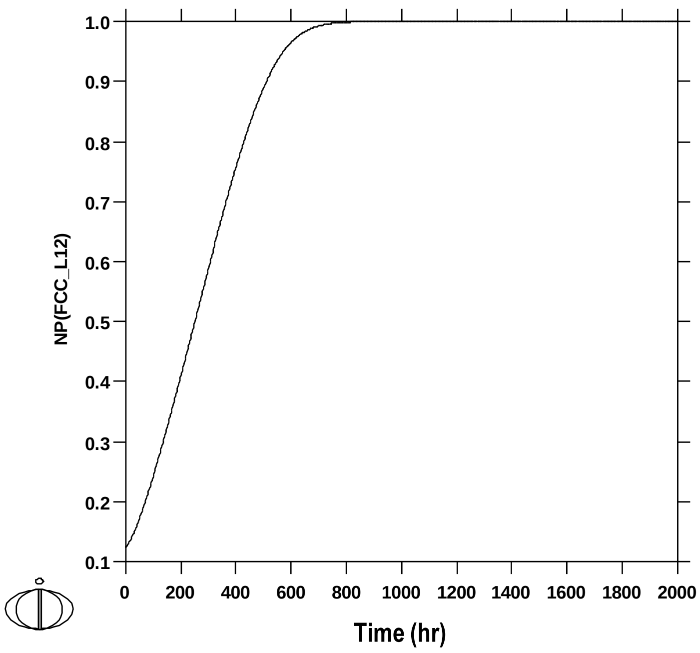
IN740

	Al	Co	Cr	Fe	Mo	Mn	Ti	Ni
wt.%	0.9	20.0	25.0	0.7	0.5	0.3	1.8	bal

Cr Concentration at the Surface



γ' volume fraction at the Surface

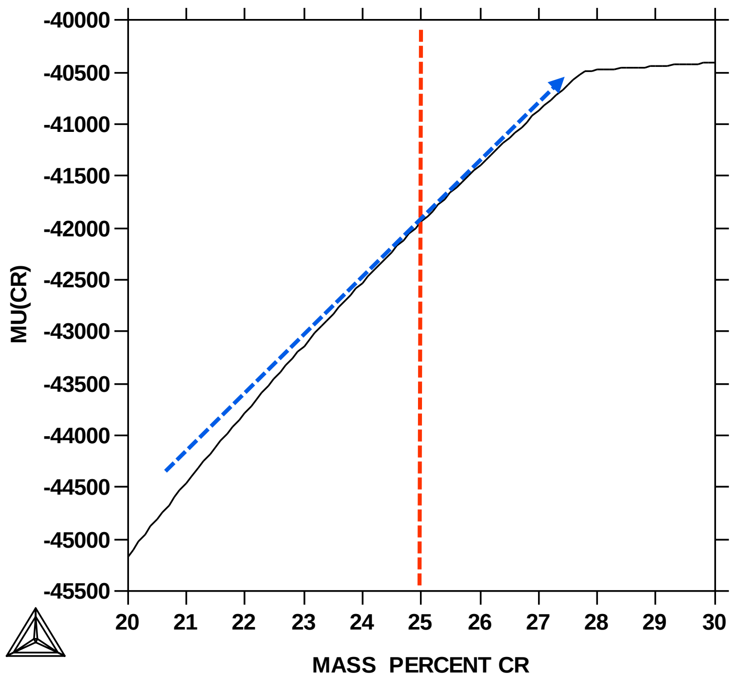


External Oxidation

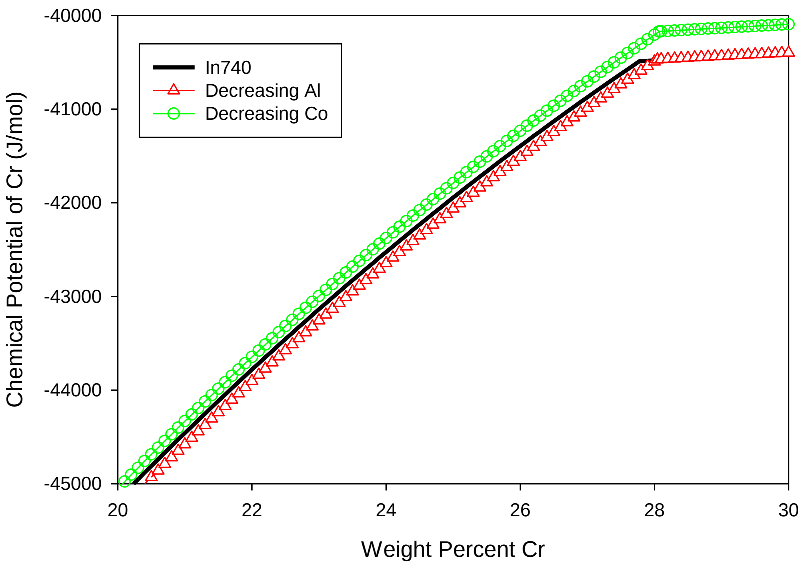
IN740

	Al	Co	Cr	Fe	Mo	Mn	Ti	Ni
wt.%	0.9	20.0	25.0	0.7	0.5	0.3	1.8	bal

Cr Chemical Potential μ_{Cr}



Effect of Alloying Elements on μ_{Cr}



- Region of Large & Positive Chemical Potential Gradient wrt Concentration of Cr

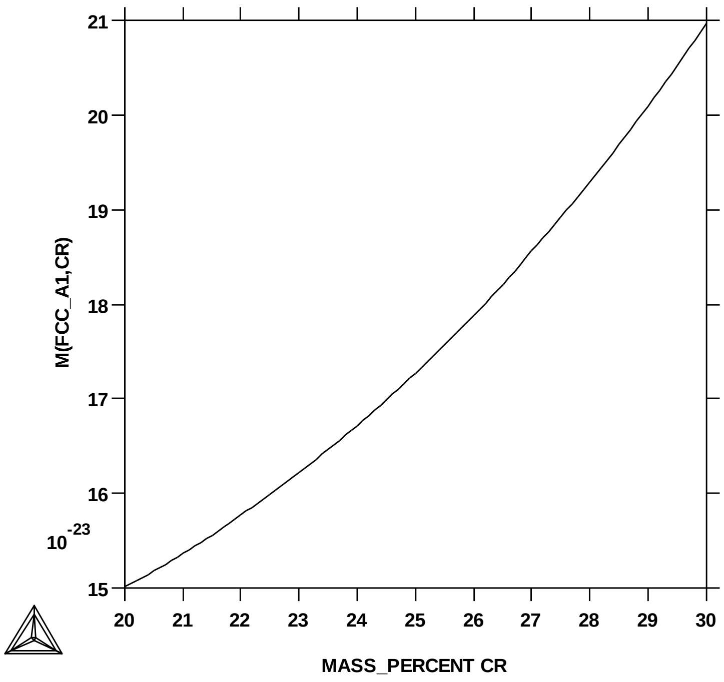
- Large Concentration Range

External Oxidation

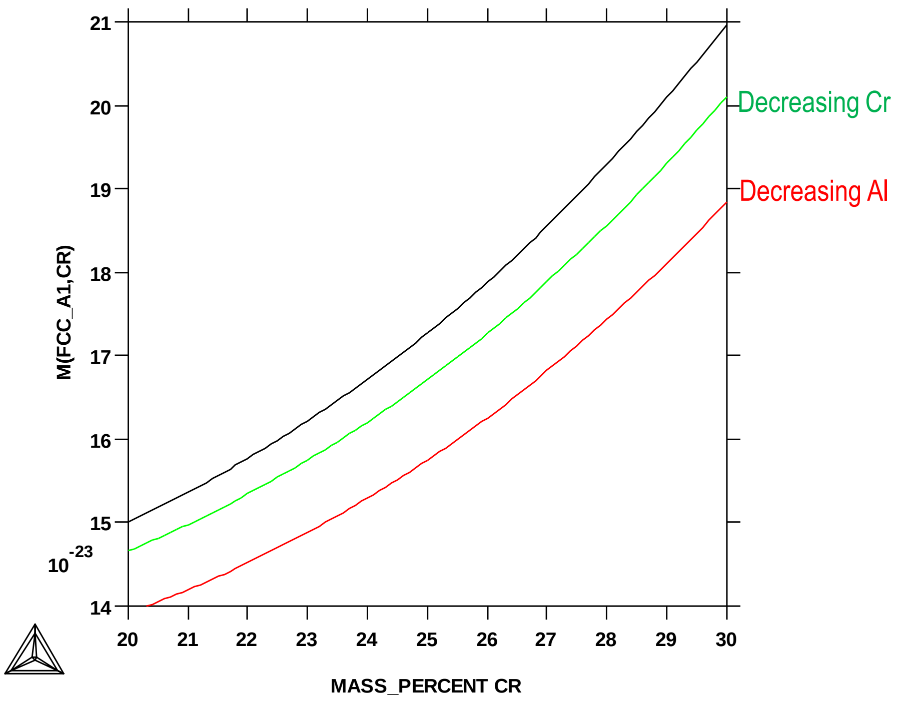
IN740

	Al	Co	Cr	Fe	Mo	Mn	Ti	Ni
wt.%	0.9	20.0	25.0	0.7	0.5	0.3	1.8	bal

Cr Atomic Mobility M_{Cr}



Effect of Alloying Elements on M_{Cr}



- Large Atomic Mobility (Diffusivity) of Cr

- **Search Region with Large** $\left(M_{Cr}\frac{\partial \mu_{Cr}}{\partial c_{Cr}}\right)$

Multi-Component Multi-Phase Phase-Field Model

Multi-Component, Multi-Phase

$$F(c,\eta) = \int_\Omega \left[f(c,\eta) + f^{grad} + \ldots\right] d\Omega$$

Kim-Kim-Suzuki(KKS) Model*

- ✓ flexible interfacial energy
- ✓ practical length scale

$$f(c,\eta) = \sum_{i=1}^{m} \eta_i g^i(c)$$ Link to CALPHAD Database

$$c_k = \sum_{i=1}^{m} \eta_i c_k^i$$ Mass Conservation

$$\frac{\partial g^i}{\partial c_k} = \frac{\partial g^j}{\partial c_k}$$ Equal Chemical Potential

Multiphase Model**

- ✓ multiphase
- ✓ multi-variant
- ✓ poly-crystal

$$f(\eta) + \sum_{i=1}^{m} \sum_{j>i}^{m} \omega_{ij} \eta_i^2 \eta_j^2$$ Local Free Energy Barrier

$$f^{grad} = \sum_{i=1}^{m} \sum_{j>i}^{m} \frac{\epsilon_{ij}}{2} (\eta_j \nabla \eta_i - \eta_i \nabla \eta_j)^2$$ Gradient Energy

* Kim et al., Phys. Review E, 60(6), 7186(1999) ** Steinbach et al., Physica D, 94, 135(1996)

Phase-Field Model: (cont.)

Elastic Effect t due to Lattice Misfit

$$\varepsilon_{ij}^{00}(m) = \delta_{ij}\varepsilon_m^{00} = \delta_{ij}\left[\partial a(X) \big/ a_o \partial X_m\right]$$

Vegard's law

$$\varepsilon_{ij}^{00}(\vec{r}) = \sum_{m=1}^{n} \varepsilon_{ij}^{00}(m) X_m(\vec{r})$$

Composition-dependent eigenstrain

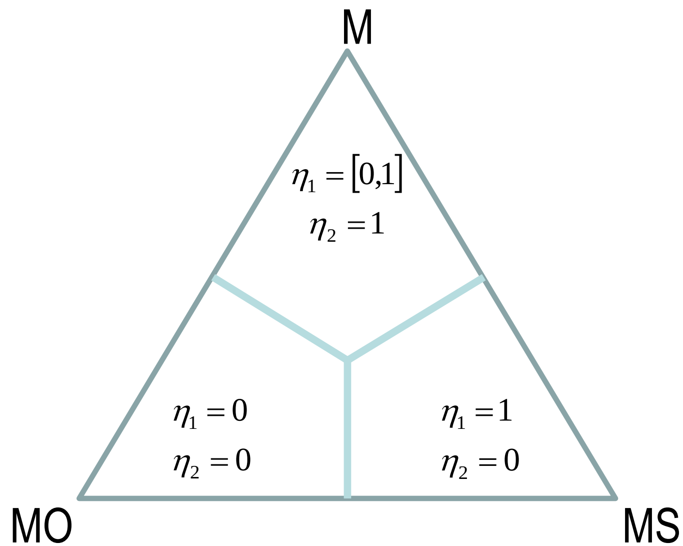
$$F_{el} = \frac{1}{2}\int \frac{d^3\mathbf{g}}{(2\pi)^3}\left[C_{ijkl}\left\{\varepsilon_{ij}^{0}(\mathbf{r})\right\}_{\mathbf{g}}\left\{\varepsilon_{kl}^{0}(\mathbf{r})\right\}_{\mathbf{g}}^{*} - n_i\left\{\sigma_{ij}^{0}(\mathbf{r})\right\}_{\mathbf{g}}\Omega_{jk}(\mathbf{n})\left\{\sigma_{kl}^{0}(\mathbf{r})\right\}_{\mathbf{g}}^{*} n_l\right]$$

Phase-Field Model for Dual-Oxidants Corrosion

$$M + \frac{1}{2} O_2 \leftrightarrow MO$$

$$M + \frac{1}{2} S_2 \leftrightarrow MS$$

$$MO + \frac{1}{2} S_2 \leftrightarrow MS + \frac{1}{2} O_2$$



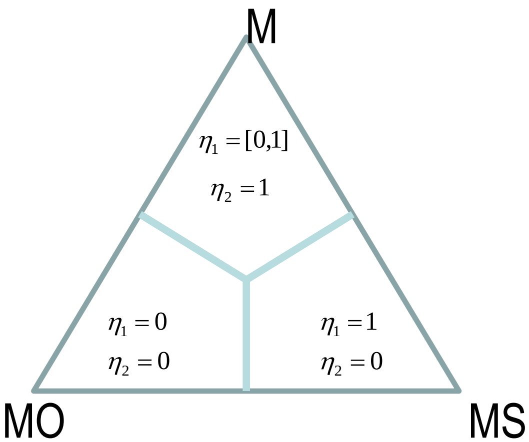
$\eta_1(x,t) \rightarrow$ *phase field to distinguish oxide and sulfide*

$\eta_2(x,t) \rightarrow$ *phase field to distinguish metal and oxide/sulfide*

$X_o(x,t) \rightarrow$ *concentration of* O_2

$X_s(x,t) \rightarrow$ *concentration of* S_2

Phase-Field Model for Dual-Oxidants Corrosion



$$f_{ch}^{mo/ms}(\eta_1, X_o, X_s) = h(\eta_1) f_{ms}(X_o, X_s) + \left(1 - h(\eta_1)\right) f_{mo}(X_o, X_s) + w_1 g(\eta_1)$$

$$f_{ch}(\eta_1, \eta_2, X_o, X_s) = h(\eta_2) f_m(X_o, X_s) + \left(1 - h(\eta_2)\right) f_{ch}^{mo/ms}(\eta_1, X_o, X_s) + w_2(\eta_1) g(\eta_2)$$

$$F = \int \left[f_{ch}(\eta_1, \eta_2, X_o, X_s) + \sum_{i=1,2} \frac{\alpha_i}{2} (\nabla \eta_i)^2 + \sum_{i=o,m} \frac{\gamma_i}{2} (\nabla X_i)^2 \right] dV$$

$$\frac{\partial \eta_i}{\partial t} = -L_i \frac{\delta F}{\delta \eta_i}; \qquad \frac{\partial X_j}{\partial t} = \nabla \left[M_j(\eta_1, \eta_2) \nabla \frac{\delta F}{\delta X_j} \right]$$

Thermodynamics

$$f_i(X_o, X_s) = \frac{1}{2} (X_o - X_i^o)^2 (X_s - X_i^s)^2 \quad (i = m, mo, ms)$$

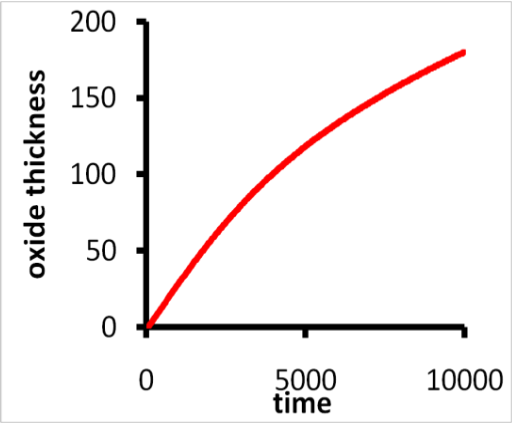
$w_i, \quad \alpha_i, \quad \gamma_i$

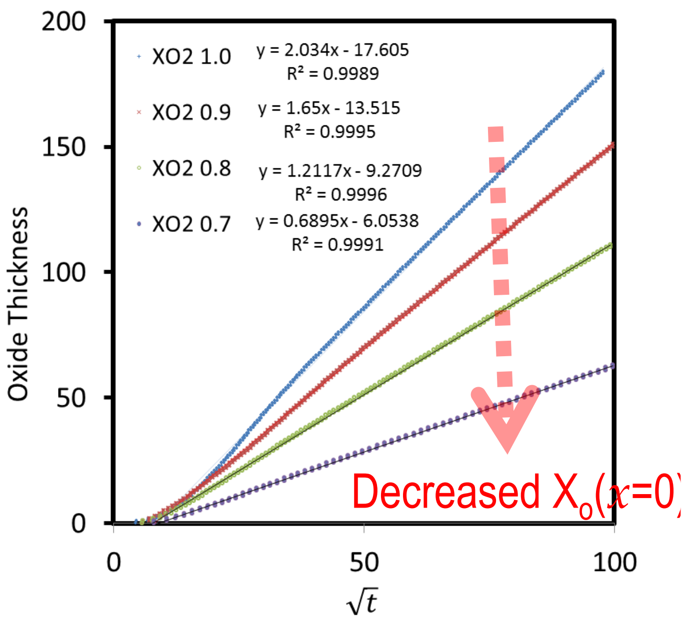
Kinetics

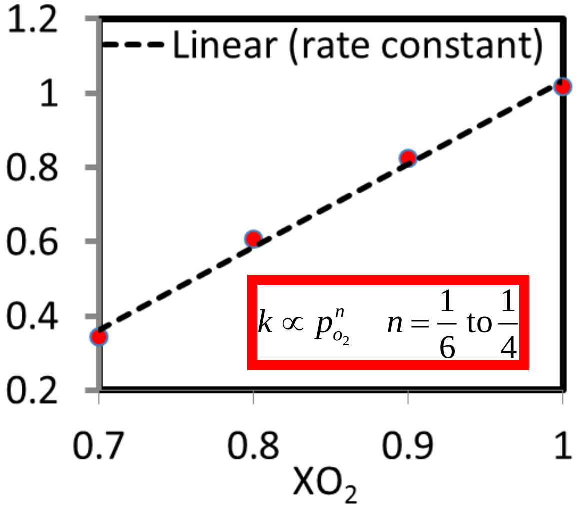
$$M_i = \eta_2 M_i^m + \eta_1 (1 - \eta_2) M_i^{ms} + (1 - \eta_1)(1 - \eta_2) M_i^{mo} \quad (i = O_2, S_2)$$

$L_i \quad (i = 1,2)$

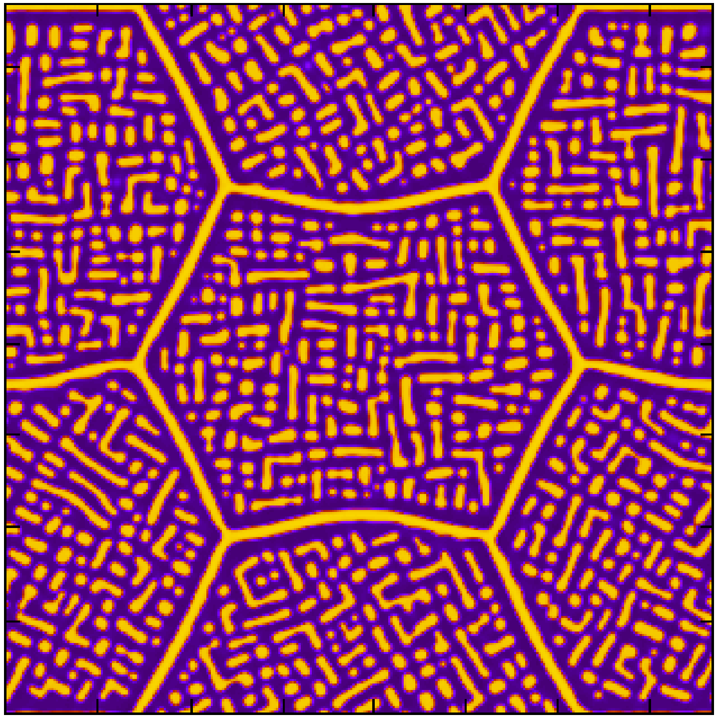
Oxidation Modeling: Exposure to O_2 only







The Path Forward
Precipitation Modeling



Effect of anisotropic elasticity on precipitations with presence of grain boundaries

Courtesy of Longqing Chen at PSU