Computational Modeling of Metal Oxidation

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US Department of Energy - NETL

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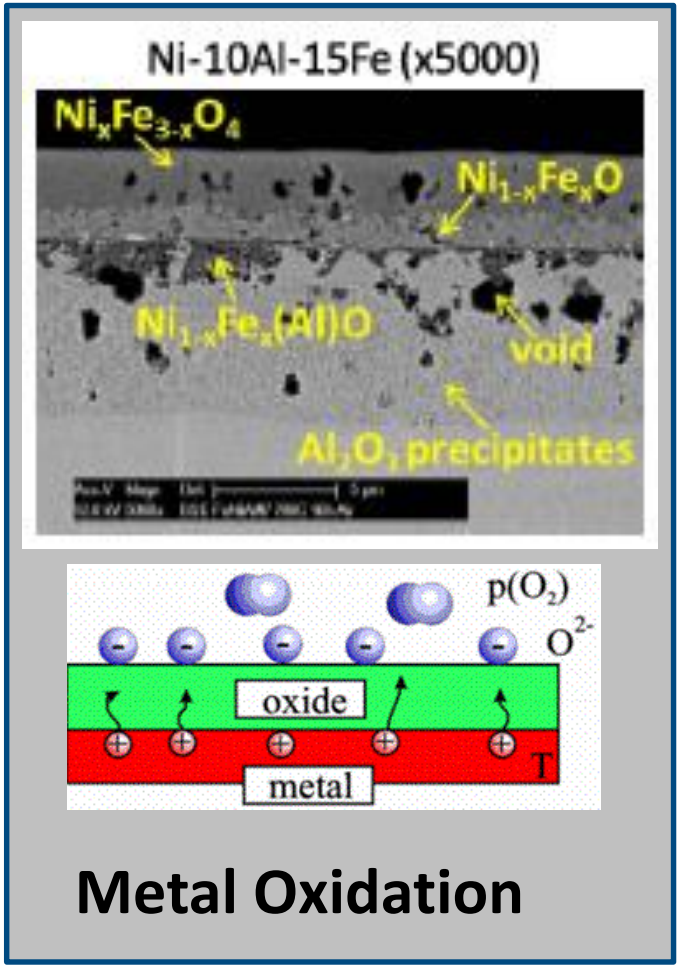
Metal Oxidation Modeling Challenge



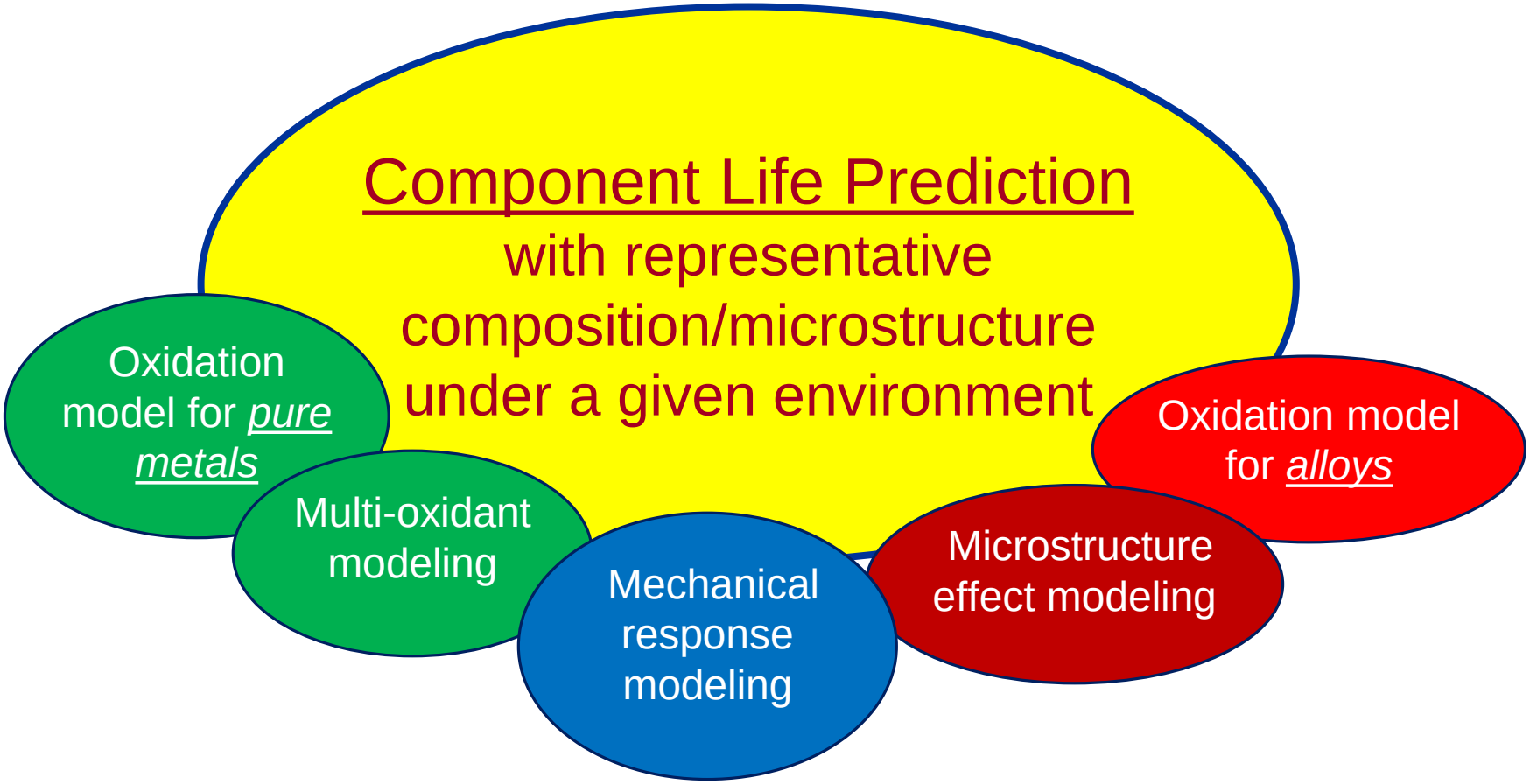
(Source: Internet)

Material's operating conditions

Modeling toolbox

Material Performance

Modeling Toolbox

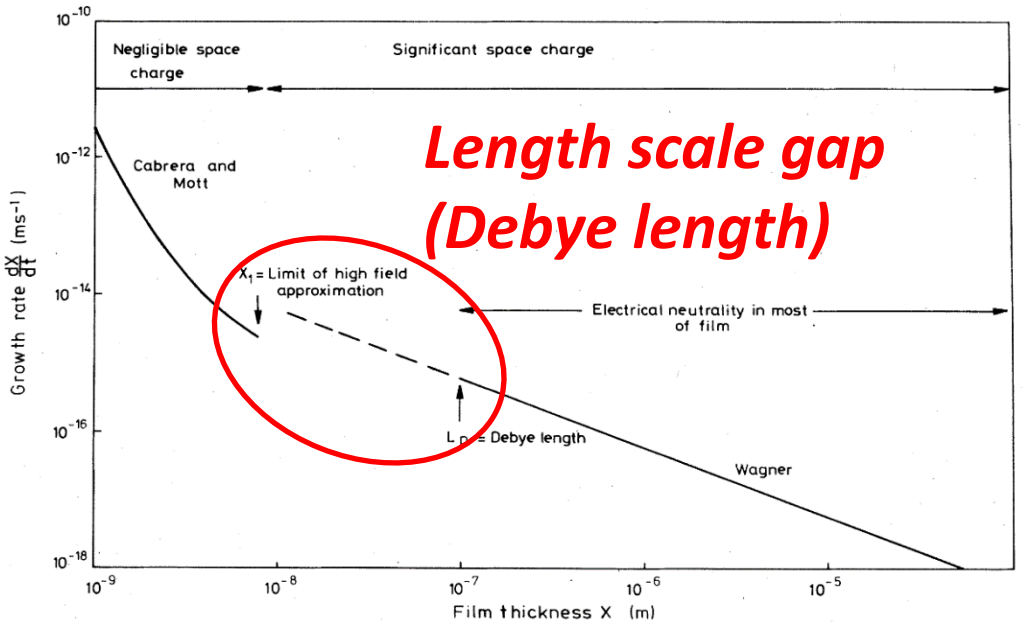


State-of-the-art of Computational Modeling

Cabrera -Mott Theory

Moderate film thickness

Wagner Theory



(Atkinson, *Review of Modern Physics*, 1985)

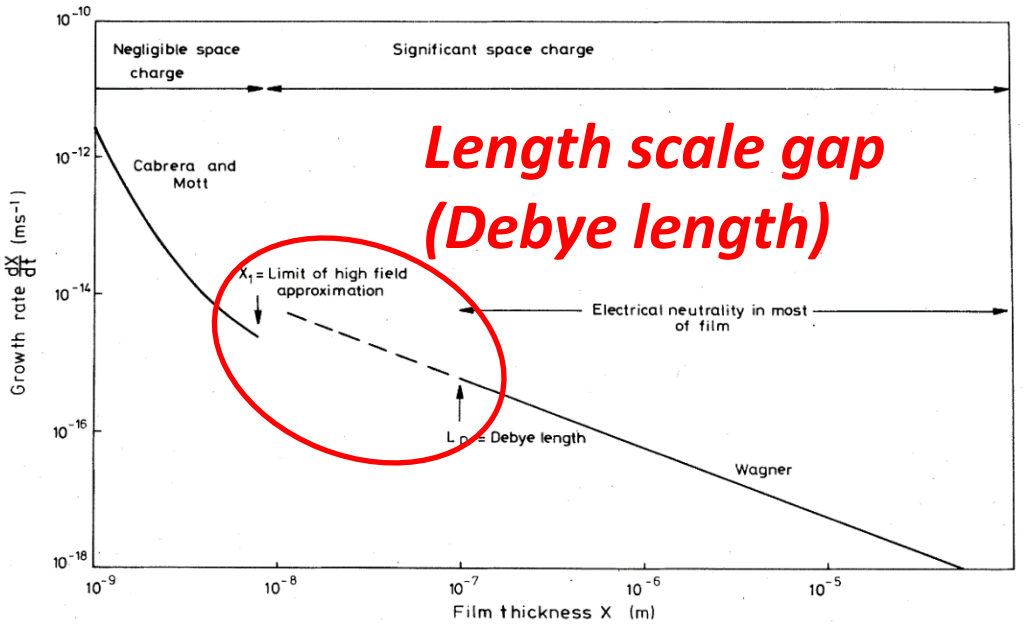
In this intermediate length regime, some common simplifications are not applicable such as local charge neutrality or constant electric field.

Length Scale Gaps in Oxidation Theories

Cabrera -Mott Theory

Moderate film thickness

Wagner Theory

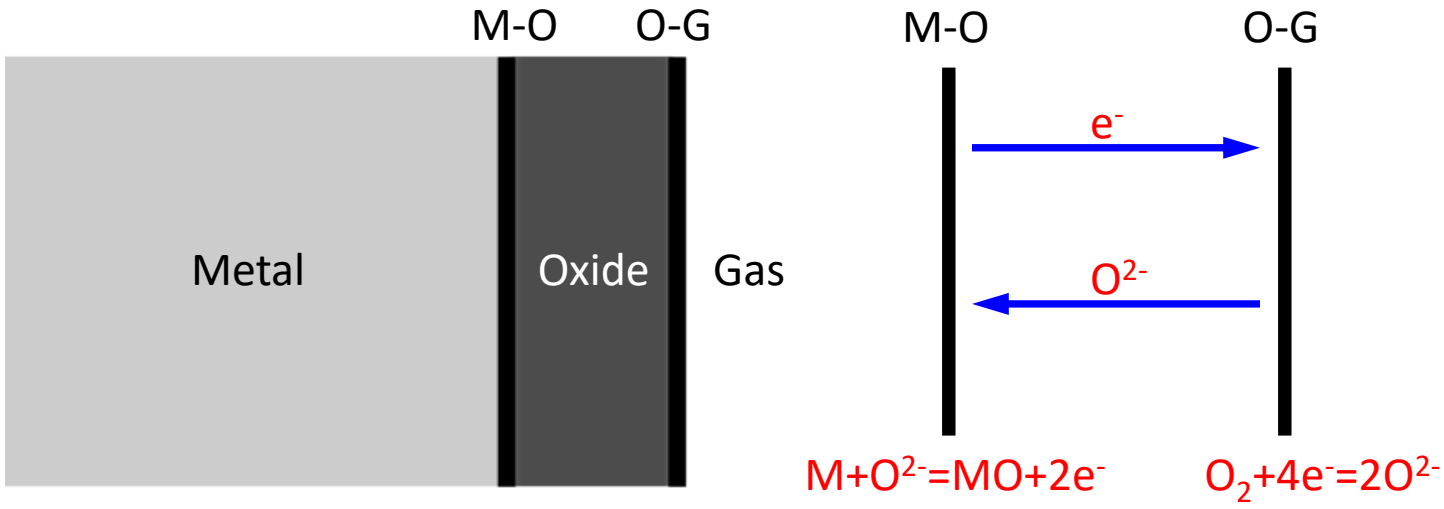


(Atkinson, *Review of Modern Physics*, 1985)

***Moderate film thickness regime*:**

The coupling of charge interaction, ionic diffusion, and chemical reaction have to be addressed.

Oxidation Modeling in Pure Metals



Coupling physics with no viable simplification

- **Chemical reaction**
- **Mass transport**
- **Charge interaction**
- **Evolving structure**
- **Evolving electric field**

Phase-field Method

Governing Equations for Metal Oxidation

Reaction | Diffusion + Electromigration

$$[X^-]: \quad \frac{\partial c_1}{\partial t} = K_I \Lambda_\zeta (Q\tilde{c}_2 - \tilde{c}_1) - K_{II}\Lambda_\eta \tilde{c}_1 + \nabla\cdot(\tilde{D}_1 \nabla \tilde{c}_1) - \frac{e}{k_B T}\nabla\cdot(D_1 c_1 z_1 \mathbf{E})$$

$$[e^-]: \quad \frac{\partial c_2}{\partial t} = K_I \Lambda_\zeta (Q\tilde{c}_2 - \tilde{c}_1) + K_{II}\Lambda_\eta \tilde{c}_1 + \nabla\cdot(\tilde{D}_2 \nabla \tilde{c}_2) - \frac{e}{k_B T}\nabla\cdot(D_2 c_2 z_2 \mathbf{E})$$

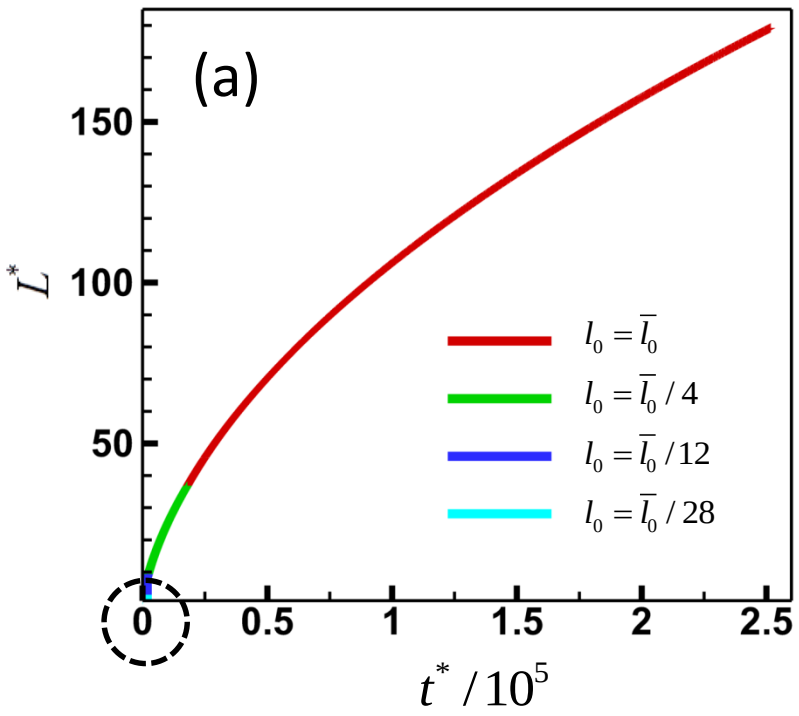
$$[c^+]: \quad \frac{\partial c_3}{\partial t} = \nabla\cdot(D_3 \nabla c_3) - \frac{e}{k_B T}\nabla\cdot(D_3 c_3 z_3 \mathbf{E})$$

$$[M]: \quad \frac{\partial \eta}{\partial t} = -K_V K_{II}\Lambda_\eta \tilde{c}_1 + M_\eta \nabla^2 \left(\partial f / \partial \eta - \beta \nabla^2 \eta\right)$$

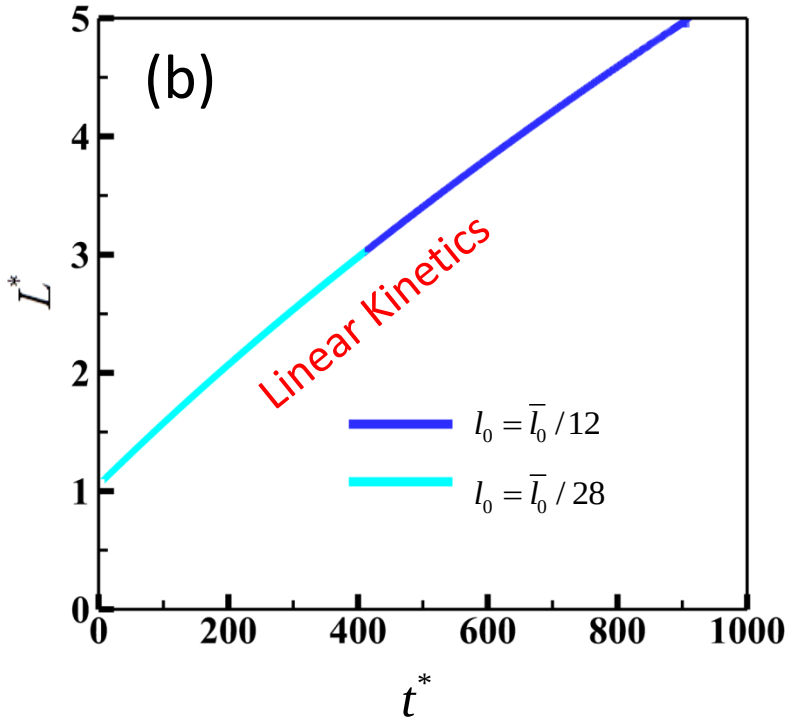
The electric field, satisfying Poisson's equation, is solved by **an efficient numerical scheme** for arbitrary **dielectric heterogeneity**

$$\nabla\cdot[\varepsilon(\mathbf{r})\nabla\varphi(\mathbf{r})] + \rho_f(\mathbf{r}) = 0$$

Simulated Results on Oxidation Kinetics Modeling
Linear → Parabolic kinetics Transition



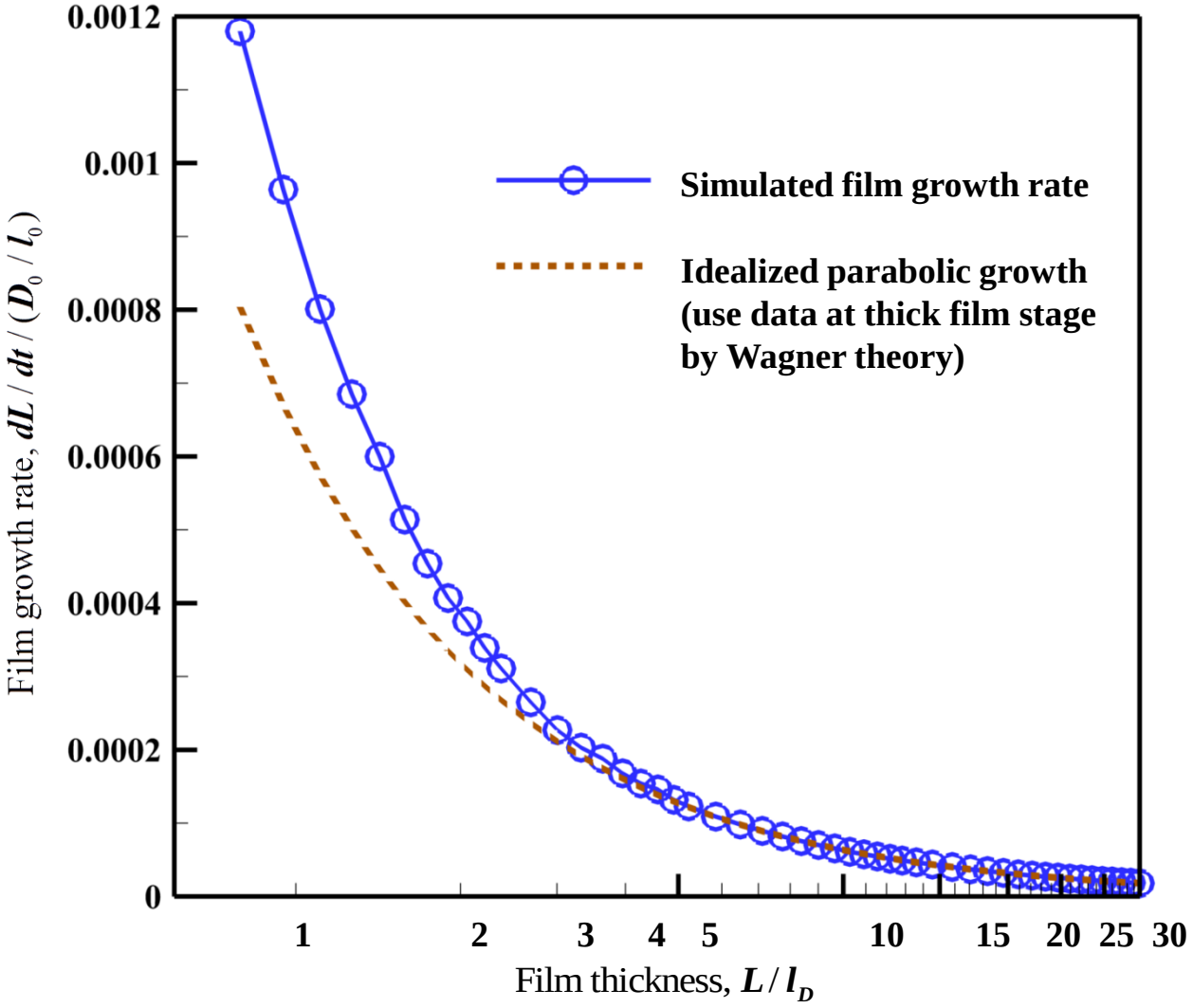
Overall growth kinetics



Initial stage growth kinetics

T Cheng, Y Wen and J Hawk, J. Phys. Chem. C 118(2014), 1269-1284

Oxide Growth Rate vs. Film Thickness

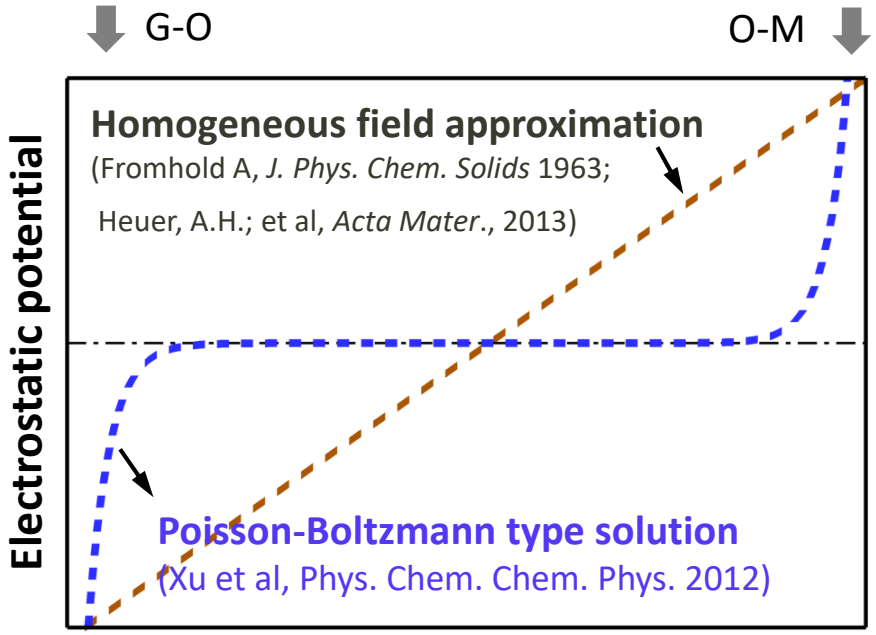


Space charge effect can not be ignored

Results on Electric Field in a Growing Oxide Film

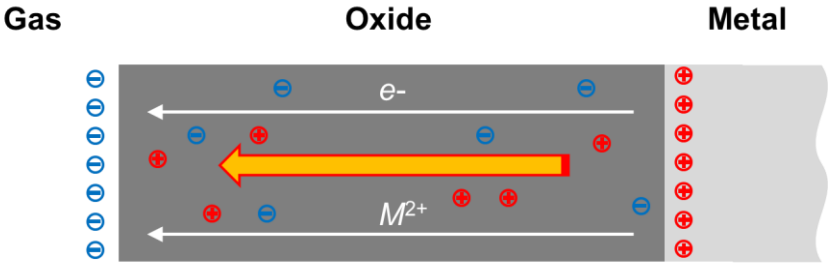
Two dominant representations:

- Homogeneous electric field across the film
- Electric field decays to zero exponentially away from the surface or interface

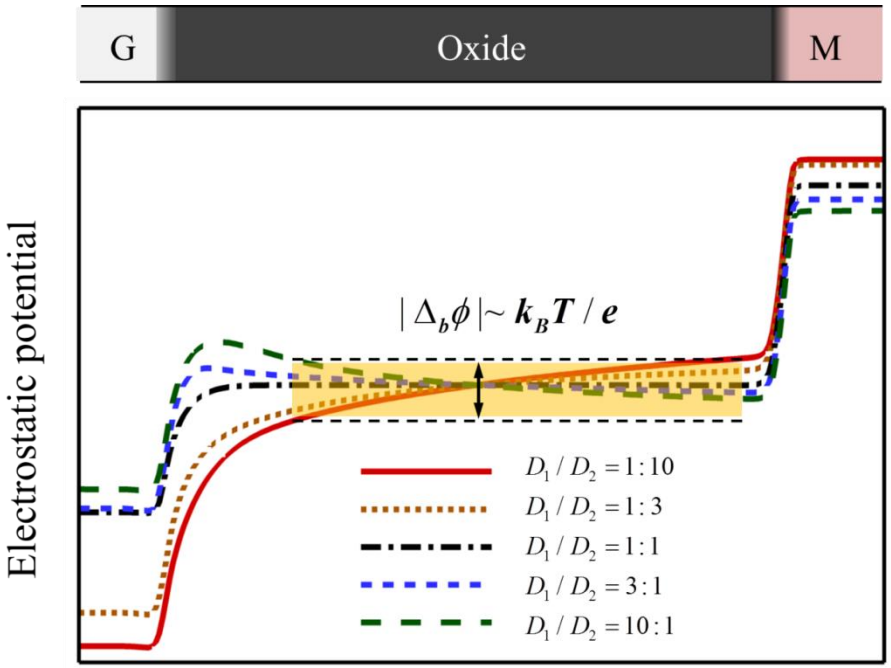


Kinetics is missing!

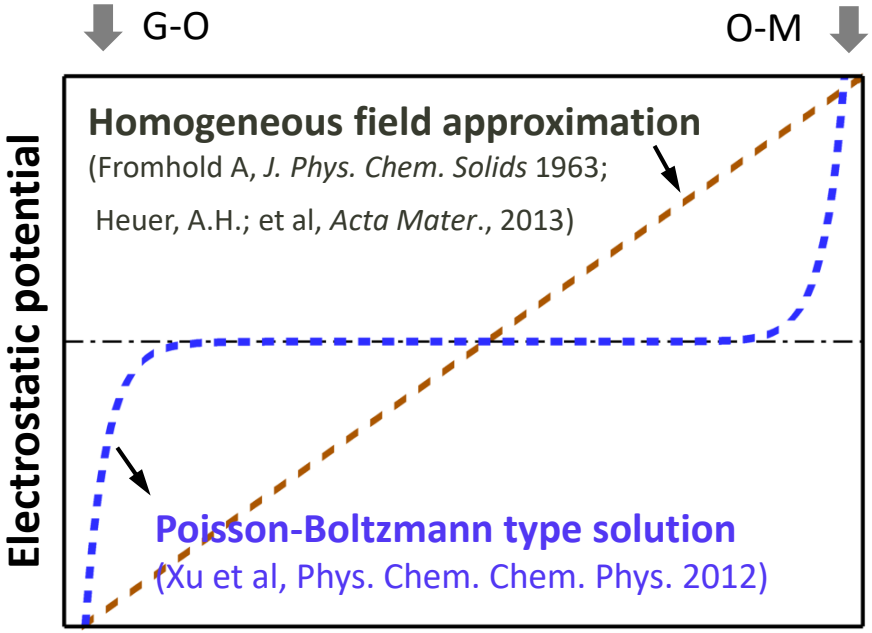
Electric Field in a Growing Oxide Film



Outward diffusion of metal ions and electrons with different valences



Simulated electrostatic potential profiles with different defect mobility ratios.



T Cheng, Y Wen, J. Phys. Chem. Lett. 5 (2014), 2289-2294

On-going Effort: Internal → External Oxidation

Significance and Overview

Fe-, Ni-, or Co-base structural alloys applied at high temperatures invariably rely on formation of an externally oxidized, slowly growing layer (mainly Al_2O_3 or Cr_2O_3), for oxidation protection. Consequently, the transition from internal to external oxidation is a basis for design of those alloys.

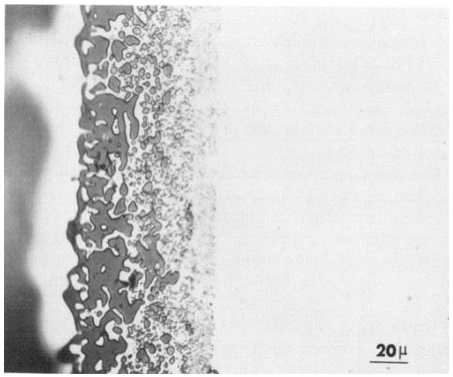


Fig. 1 Transition from internal to external oxidation in Co-8.99%Ti at 900˚C for 528h, (G.H. Meier et al, 1976)

Outstanding challenges to model this with Phase-Field:

a) Modeling plasticity due to volume expansion with oxidation

1. Guo, X. H.; Shi, S. Q.; Ma, X. Q, Appl. Phys. Lett. 2005, 87;
2. Yamanaka, A.; Takaki, T.; Tomita, Y., Mater. Sci. Eng. A-Struct. Mater. Prop. Microstruct. Process. 2008, 491, 378.

- **Elastic-perfect plasticity – No hardening behavior**
- **Deviatoric stress-free strain only – No dilatational deformation**

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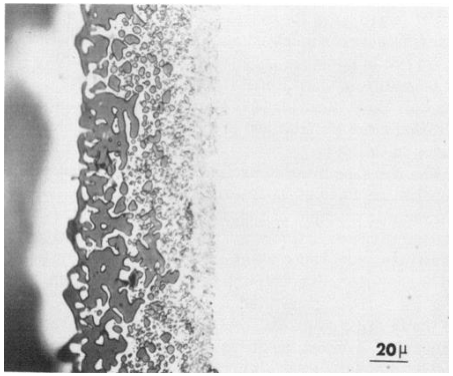

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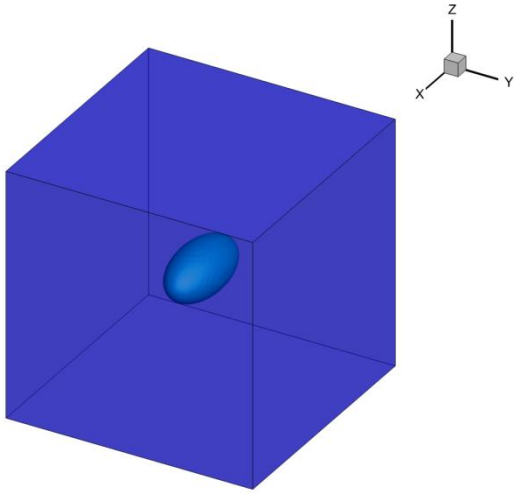
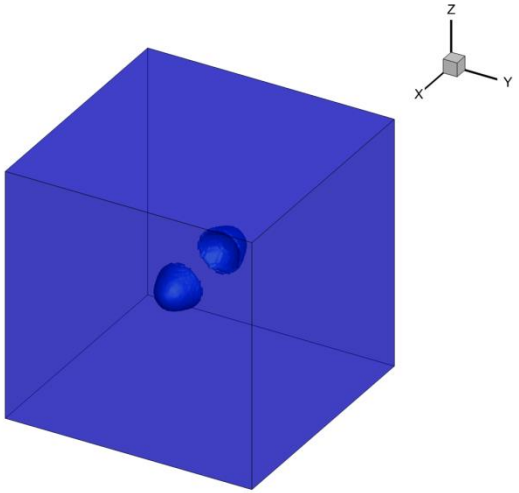
b) Modeling coherency loss involving transition between coherent, semicoherent, and incoherent interfaces

3D Phase-field Elasto-Plasticity Simulation Demo

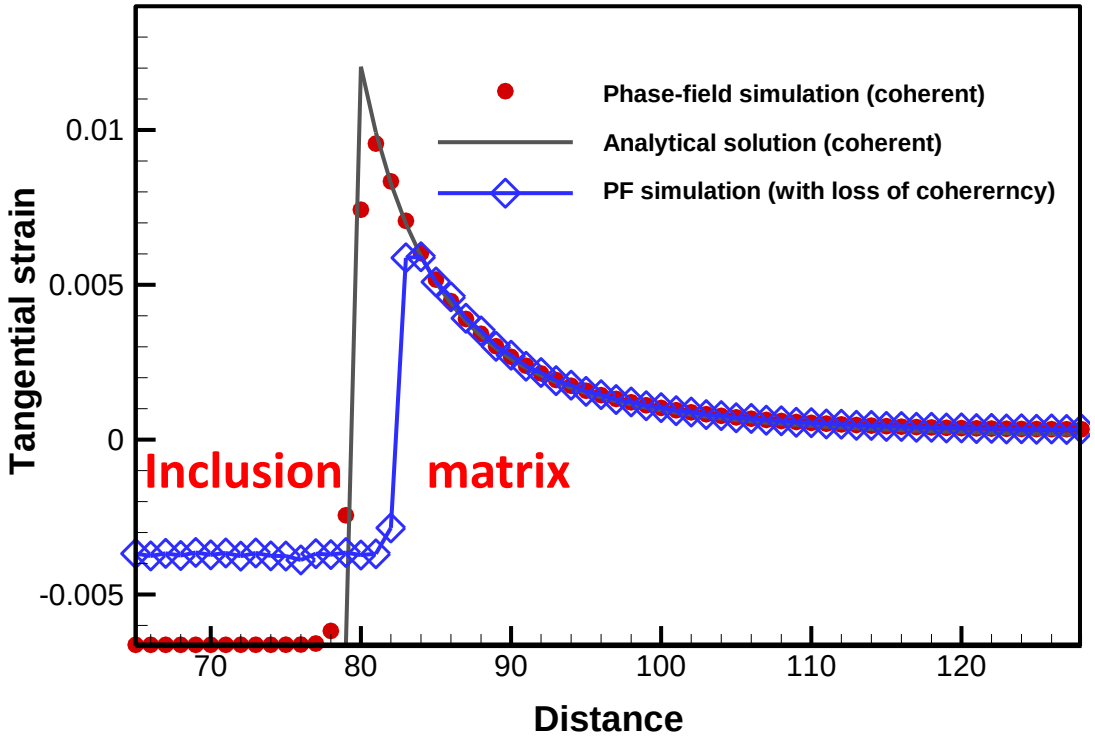


Ellipsoidal inclusion undergoes
5% elongation along x-axis



Plastic deformation zone in the matrix

Interface Coherency Effect on Elastic Energy
A 3-D Simulation Demo



Tangential strain for a spherical inclusion with isotropic eigenstrain of 2% volume change

Even for a dilatational inclusion, coherency loss can appreciably reduce elastic energy.

Summary

- **Developed a *simulation capability* based on Phase-Field Method to simulate oxidation in simple systems – Oxidation kinetics and electric field**

- ***Further development* of the model is on-going to advance this model into a useful tool that can be used to eventually predict the life of an alloy**

Electric Field in a Growing Oxide Film

Two dominant representations:

- Homogeneous electric field across the film
- Electric field decays to zero exponentially away from the surface/interface assuming thermodynamic equilibrium

$$J_i = -D_i \nabla c_i + \varpi_i \mathbf{E} c_i \quad \text{Flux equations}$$

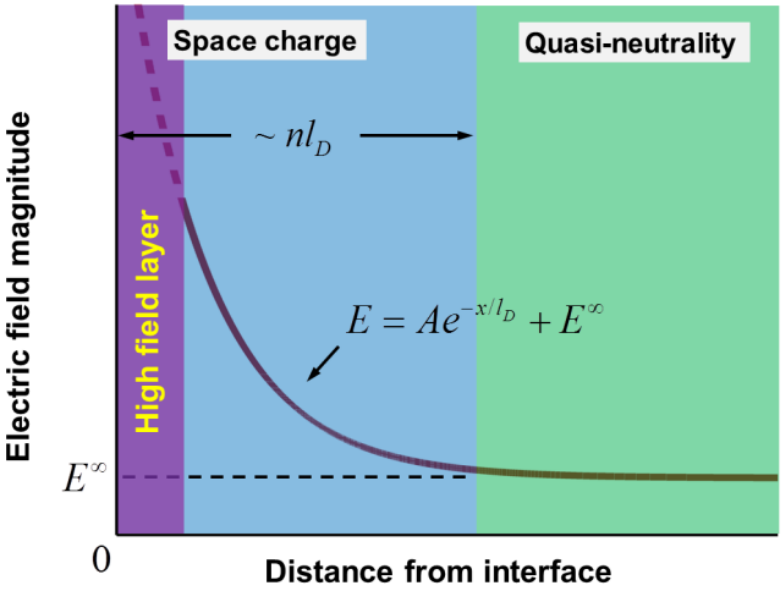
$$\varepsilon \nabla \bullet \mathbf{E} = \sum_i z_i e N_A c_i \quad \text{Linearized Poisson Boltzmann}$$

- Two negatively charged transporting species with identical valences: i.e. z1=z2=-1 for electrons and interstitial anions
- Assume coupled-current condition

$$E = Ae^{-x/l_D} + E^o$$

$$E^o = \frac{k_B T}{e\bar{c}} \frac{D_1 - D_2}{D_1 D_2} J^o$$

$$l_D = \sqrt{\varepsilon k_B T / N_A e^2 \bar{c}}$$



Schematic of the electric field near an interface with a decaying screening term plus a permanent remnant term .