Progress in High Temperature Oxidation Modeling: Internal and External Oxidation

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IPT Task 3.4: Computational Aspects in Alloy Design & Life Prediction

Metal Oxidation Modeling

(Source: Internet)
State-of-the-art of Computational Modeling

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

Moderate film thickness regime:

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

Length scale gap (Debye length)

(Atkinson, Review of Modern Physics, 1985)
Oxidation Modeling in Pure Metals

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

Coupling physics with no viable simplification
Phase-field Method

Governing Equations for Metal Oxidation

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 \rightarrow 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

Simulated film growth rate

Idealized parabolic growth (use data at thick film stage by Wagner theory)

Space charge effect cannot be ignored
Summary

Physics-based Modeling Capability on External Oxidation so far ...
Why we care?

- Oxidation usually starts with internal selective oxidation of certain solute elements.
- Transition from internal to external oxidation is the basis for alloy design regarding oxidation resistance.

**Modeling Internal Oxidation**

**Oxidation Map:** Compositional effects on the oxidation of Ni-Al alloys  
(N. Birks, G. Meier, F. Pettit, 2006)

Transition from internal to external oxidation in Co-8.99%Ti: 900°C for 528h  
(J. Megusar; G. Meier, 1976)
Modeling Internal Oxidation

State-of-the-art about theoretical understanding

- Analyzed by C. Wagner in 1959 for a binary system with 1D assumption – Oversimplification!
- Remains an open problem especially in consideration of the complex microstructure in 3D situations

**Oxidation Map:** Compositional effects on the oxidation of Ni-Al alloys (N. Birks, G. Meier, F. Pettit, 2006)

Transition from internal to external oxidation in Co-8.99%Ti at 900°C for 528h, (J. Megusar; G. Meier, 1976)
Wagner’s theory on the transition from internal to external oxidation

(a) internal oxidation, (b) external oxidation with higher $C_B$

(after N. Birks, G. Meier, F. Pettit, 2006)

Transition criterion (C. Wagner 1959):

$$N_B^{(O)} > \left[ \frac{\pi f^* V_m}{2v} \frac{D_O N_O^{(S)}}{V_{ox} D_B} \right]^{1/2}$$

Schematic: Concentration profiles for internal oxidation of A-B (Birks, Meier, Pettit, 2006)
Wagner’s theory on the transition from internal to external oxidation

Transition criterion (C. Wagner 1959):

\[ N_B^{(O)} > \left( \frac{\pi f^* V_m}{2\nu V_{ox}} \frac{D_O N_O^{(S)}}{D_B} \right)^{1/2} \]

\[ f^* = 0.3 \quad \text{(for Ag-In system)} \quad \text{(R. A. Rapp, 1961)} \]

\[ f^* \sim 0.5 \quad \text{(for Fe-Si system)} \quad \text{(W. Zhao, Y. Kang, J. Orozco, B. Gleeson, 2015)} \]

There is no universal/general \( f^* \) even just for binary systems!

No Predication Capability!
Microstructure evolution in internal oxidation can be very different depending on specific material systems and it is no surprise that the critical volume fraction for the transition from internal to external oxidation is not a constant.
Technical Challenges #1

Plastic deformation with oxide growth quite common
- relieves elastic strain energy (oxide morphology evolution)
- may be time dependent (viscoplasticity)

(Hancock and Hurst, 1974)

Need to Develop a Plastic and Viscoplastic Deformation Modeling Capability!
Oxide-matrix interface:
- typically coherent for small precipitates
- Loses coherency upon growth

\[ \Delta G = 4 \mu \delta^2 \cdot \frac{4\pi r^3}{3} + 4\pi r^2 \cdot \gamma \]

(after D. Porter and K. Easterling, 1996)
Technical Challenges #II

Oxide-matrix interface:
- typically coherent for small precipitates
- Loses coherency

Coherency Transition/Loss is Natural & Unavoidable with Oxide Growth!

(after D. Porter and K. Easterling, 1996)
Technical Challenges #II

An incoherent interface typically:
- Higher interfacial energy but lower elastic energy
- No accommodation of shear stress
- Short-circuit diffusion path

Coherency state should have a dominant effect on oxide morphology and growth kinetics!

Coupling between stress and diffusion: affect oxide precipitate morphology & its evolution

Need to develop a comprehensive coherency transition modeling capability!
Outstanding Challenges for Phase-Field Modeling of Internal Oxidation

I. Modeling plasticity due to volume expansion with oxidation

II. Modeling coherency loss involving transition between coherent, semicoherent, and incoherent interfaces
State of the Art

Phase-field models for plasticity:
• Proposed by X. Guo, S. Shi and X. Ma (2005)
  1) Assumed elastic-perfect plasticity – no hardening behavior
  2) Solves plastic strain by calculating the variation of deviatoric strain energy
State of the Art

Phase-field models for plasticity:
- Proposed by X. Guo, S. Shi and X. Ma (2005)
  1) Assumed elastic-perfect plasticity – no hardening behavior
  2) Solves plastic strain by calculating the variation of deviatoric strain energy

Can the deviatoric strain energy be expressed as $E_{\text{dis}}^{\text{dis}} = E_{\text{dis}}^{\text{dis}}(e_{ij}^{0}, \varepsilon_{ij}^{p})$?

$(e_{ij}^{0} = \varepsilon_{ij}^{0} - \varepsilon_{kk}^{0} \delta_{ij} / 3$ is the deviatoric part of eigenstrain)

Considering the solution of classical elastic inclusion problem by Eshelby, for a spherical inclusion with dilatational eigenstrain

$$\varepsilon_{r} = \varepsilon_{t} = \frac{1}{3} \frac{1 + \nu}{1 - \nu} \varepsilon^{00} \ (\text{inside})$$

$$\varepsilon_{r} = -\frac{2}{3} \frac{1 + \nu}{1 - \nu} \frac{a^3}{r^3} \varepsilon^{00}, \ \varepsilon_{t} = \frac{1}{3} \frac{1 + \nu}{1 - \nu} \frac{a^3}{r^3} \varepsilon^{00} \ (\text{outside})$$

Deviatoric stress is large near the interface outside the inclusion!
Phase-field models for plasticity:
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Can the deviatoric strain energy be expressed as \( E^{\text{dis}}_{ij} = E^{\text{dis}}_0 (e_{ij}^0, e_{ij}^P) \) ?

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\[
\varepsilon_r = \varepsilon_t = \frac{1}{3} \frac{1 + \nu}{1 - \nu} \varepsilon^{00} \quad \text{(inside)} \quad \varepsilon_r = -\frac{2}{3} \frac{1 + \nu}{1 - \nu} \frac{a^3}{r^3} \quad \text{(outside)}
\]

Deviatoric stress is large near the interface outside.

Need a thermodynamically consistent phase-field model for plasticity
A New Phase-Field Plasticity Model: Preliminary Results: Spherical Dilatational Inclusion in an Infinite Elasto-Perfect Plastic Matrix

3% isotropic volume change is assumed in the inclusion.

Same Young’s modulus and Poisson’s Ratio for matrix and inclusion. Yield strength for the matrix is set to be 1/10 of the inclusion.

Good agreement with analytical solution in stress components and plastic zone size

Analytical solution by J. Lee, Y. Earmme, H. Aaronson, K. Russell 1980
Preliminary Results: Prediction of coherent to incoherent transition based on energetics

\[ \varepsilon^0_{ij} = \begin{bmatrix} 0.02 & -0.01 \\ -0.01 & -0.01 \end{bmatrix} \]

Pure deviatoric eigenstrain

\[ \Delta G \sim 4\mu\delta^2 \cdot \frac{4\pi r^3}{3} + 4\pi r^2 \cdot \gamma \]

Porter & Easterling’s model

![Graph showing energy and particle radius relationship](image-url)
Preliminary Results: Coherent precipitate with both dilatational and deviatoric eigenstrain

\[
\varepsilon_{ij}^0 = \begin{bmatrix} 0.03 & 0 \\ 0 & 0 \end{bmatrix} = \begin{bmatrix} 0.01 & 0.01 \\ 0.01 & 0.01 \end{bmatrix} + \begin{bmatrix} 0.02 & -0.01 \\ -0.01 & -0.01 \end{bmatrix}
\]

Dilatational + deviatoric

Von Mises stress and hydrostatic stress distribution with a coherent interface
Preliminary Results: Incoherent precipitate with both dilatational and deviatoric eigenstrain

\[
\varepsilon_{ij}^0 = \begin{bmatrix} 0.03 & 0 \\ 0 & 0 \end{bmatrix} = \begin{bmatrix} 0.01 & 0.01 \\ 0.01 & -0.01 \end{bmatrix} + \begin{bmatrix} 0.02 & 0 \\ 0 & -0.01 \end{bmatrix}
\]

Von Mises stress and hydrostatic stress distribution with an incoherent interface: hydrostatic stress could not be completely removed in the precipitate!

Porter and Eastering’s model needs to be reconsidered as they assumed elastic strain energy can be completely removed after loss of coherency.
Summary and Outlook

• Developed a *simulation capability* based on Phase-Field Method to simulate external oxidation in simple systems.

• *Further development* is on-going to develop an internal oxidation modeling capability that will eventually be able to simulate the transition from internal to external oxidation.