Corrosion and Oxide Layer Growth Modeling Using Deterministic and Stochastic Methods

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January 21, 2014
University of Nevada, Las Vegas (UNLV)
University of Nevada, Las Vegas (UNLV) (Cont.)

- Founded in 1957
- Student population: ~30,000 (~24,000 undergraduates, ~6,000 graduates)
- Faculty and staff: 3,100
- 220 degree programs
Outline

• Introduction
• Lead-bismuth eutectic (LBE)
• Corrosion by LBE
• Mechanisms of the oxide layer growth
• Deterministic and stochastic methods
  – Analytical solution
  – Numerical solution
  – Cellular automaton (CA) modeling solution
  – Lattice Boltzmann method (LBM) modeling solution (not included in this presentation)
  – Molecular dynamics (MD) modeling solution (not included in this presentation)
• Conclusions and Suggestions
Introduction

Next Generation of Reactors:
- **Very-High Temperature Reactor (VHTR):** a graphite-moderated, helium-cooled reactor with a once-through uranium fuel cycle
- **Supercritical-Water-Cooled Reactor (SCWR):** a high-temperature, high-pressure water-cooled reactor that operates above the thermodynamic critical point of water
- **Gas-Cooled Fast Reactor (GFR):** features a fast-neutron-spectrum, helium-cooled reactor and closed fuel cycle
- **Lead-Cooled Fast Reactor (LFR):** features a fast-spectrum lead of lead/bismuth eutectic (LBE) liquid metal-cooled reactor and a closed fuel cycle for efficient conversion of fertile uranium and management of actinides
- **Sodium-Cooled Fast Reactor (SFR):** features a fast-spectrum, sodium-cooled reactor and closed fuel cycle for efficient management of actinides and conversion of fertile uranium
- **Molten Salt Reactor (MSR):** produces fission power in a circulating molten salt fuel mixture with an epithermal-spectrum reactor and a full actinide recycle fuel cycle
Introduction (Cont.)

• The National Materials Crosscut Program (NMCP) in the U.S. expects the candidate materials meet the following design objectives:
  — Acceptable dimensional stability including void swelling, thermal creep, irradiation creep, stress relaxation, and growth
  — Acceptable strength, ductility, and toughness
  — Acceptable resistance to creep rupture, fatigue cracking, creep-fatigue interactions, and helium embrittlement
  — Acceptable chemical compatibility and corrosion resistance (including stress corrosion cracking and irradiation-assisted stress corrosion cracking) in the presence of coolants and process fluids
## Introduction (Cont.)

![Image of table and chart]

### Table: Nuclear Energy Systems Development by Country

<table>
<thead>
<tr>
<th>Country</th>
<th>Canada</th>
<th>China</th>
<th>Euratom</th>
<th>France</th>
<th>Japan</th>
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- **GFR** - Gas-Cooled Fast Reactor
- **LFR** - Lead-Cooled Fast Reactor
- **SFR** - Sodium-Cooled Fast Reactor
- **SCWR** - Supercritical-Water-Cooled Reactor
- **VHTR** - Very-High-Temperature Reactor
- **MSR** - Molten Salt Reactor

- ⬤ - Framework Signatory
- ⬤ - Expected Signatory
- ⬤ - System Signatory
- ○ - Potential Signatory
- ⬤ - Lead or Co-lead

Introduction (Cont.)

- **LFR:**
  - The LFR is a fast-spectrum reactor with the potential to meet many of the Generation IV mission interests
  - The LFR is mainly envisioned for electricity and hydrogen production and actinide management
  - Two key technical aspects of the LFR that offer the prospect for achieving the Gen-IV and GNEP goals of non-proliferation, sustainability, safety and reliability, and economics are the use of lead (Pb) coolant and a long-life, cartridge-core architecture in a small, modular system intended for deployment with small grids or remote locations
  - While options for the LFR include a range of plant ratings and sizes from small modular systems to monolithic plants, the LFR envisioned in the Gen-IV Program is the small secure transportable autonomous reactor (SSTAR) concept
  - The main mission of the SSTAR is to provide incremental energy generation to match the needs of developing nations and remote communities without electrical grid connections
  - Some technologies for the LFR have already been successfully demonstrated internationally
Introduction (Cont.)

Introduction (Cont.)

- Pb does not react readily with air, water/steam, or carbon dioxide, eliminating concerns about vigorous exothermic reactions
- It has a high boiling temperature (1,740° C), so the need to operate under high pressure and the prospect of boiling or flashing in case of pressure reduction are eliminated
- 2 land prototypes and 10 submarine reactors using lead bismuth eutectic (LBE) coolant were operated in Russia
- Corrosion of containment and structure materials present a critical challenge in the use of LBE heavy-metal cooled system
Introduction (Cont.)

• Viability of long core lifetime, passive safety, and economic performance (both capital and operating costs) will depend upon identifying materials able to meet service requirements

• Currently, a lack of systematic understanding of the scientific bases is limiting the progress of R&D

• Corrosion and oxide layer growth modeling using the deterministic and stochastic methods are continuously studied to try to understand the fundamental issues related to corrosion when LBE is used as a heavy liquid-metal nuclear coolant
Lead-Bismuth Eutectic (LBE)

- LBE: 44.8wt% (45.0 at%) Pb and 55.2 wt% (55.0 at%) Bi.

Properties:
- Low melting point: 123.5°C
- High boiling point: 1,740°C
- High heat conductivity
- No violent reactive with water or air
Lead and LBE Characteristics

Density:
\[ \rho(T)[kg/m^3] = A_\rho - B_\rho T[K] \]

Dynamic viscosity:
\[ \mu(T)[Pa\cdot s] = A_\mu \exp\left(E/R_gT[K]\right) \]

Kinematic viscosity:
\[ \nu = \mu/\rho \]

Molecular diffusivities:
\[ D_{m,Fe}[m^2/s] = 4.9 \times 10^{-7} \exp\left(-\frac{Q}{R_gT[K]}\right) \]

\[ Q = 44,100 \pm 6,300 J/mole \]

<table>
<thead>
<tr>
<th></th>
<th>( A_\rho )(kg/m(^3))</th>
<th>( B_\rho )(kg/K \cdot m(^3))</th>
<th>( A_\mu )(10(^{-4}) kg/m \cdot s)</th>
<th>( E)(J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>11,367</td>
<td>1.1944</td>
<td>4.55</td>
<td>8,888</td>
</tr>
<tr>
<td>LBE</td>
<td>11,096</td>
<td>1.3236</td>
<td>4.94</td>
<td>6,270</td>
</tr>
</tbody>
</table>


Corrosion by LBE: Corrosion Processes

• Corrosion processes
  — dissolution of the solid materials into the liquid metal
  — thermal and concentration gradients assisted mass transfer
  — redistribution of the interstitial impurities between solid and liquid
  — diffusion penetration of liquid metals into solid metals with formation of solid solution or new phase
Corrosion by LBE: Mechanism of Liquid Metal/Alloy Corrosion

Corrosion of steels in lead alloy occurs primarily through dissolution.

Two kinds of corrosion in liquid metal/alloys:
• Uniform corrosion
• Local corrosion
• Penetration
• Redistribute the impurities

Diagram of corrosion damage of metals in liquid metal/alloys media:
(a) uniform corrosion;
(b) penetration along the specific crystallographic direction;
(c) along the grain boundaries; (d) along vacancies and pores;
(e) and (f) along previous formed defects

Factors Affecting Corrosion

- Velocity

1. At low velocity, \( V \uparrow \Rightarrow \delta_m \downarrow \Rightarrow q \uparrow \)
2. When the velocity exceeds a critical value
   - the mass transfer rate is high (diffusion+convection)
   - dissolution/reaction rate controls
   - independent of \( V \)
3. For high velocities, especially in heavy liquid metals/alloys
   - high shear stress occurs
   - cavities appear
   - corrosion rates increase sharply

\[ q \]

- \( q \)
- \( V \)
- \( \delta_m \)
- Breakaway Velocity

References:

- J. S. Zhang, N. Li, J.S. Elson, “Review of Studies on Fundamental Issues in LBE Corrosion, Progress in Materials Science”
Factors Affecting Corrosion (Cont.)

• Temperature
  1. The dissolution rate, chemical reaction rate, and most of the properties are functions of temperature
  2. In a non-isothermal loop, corrosion and oxidation rates are functions of both the local temperature and the global temperature distribution

• Solubility of metals in LBE/lead

\[ \log(c_s, ppm) = A_c + B_c / T(K) \]

Oxidation of Stainless Steel in Lead/LBE

\[ \frac{1}{2} O_2(gas) \Leftrightarrow O(alloy) \quad Fe = Fe^{2+} + 2e^- \quad Fe^{2+} + 2e^- = Fe \quad 3Fe + 4O = Fe_3O_4 \quad xM + \frac{y}{2} O_2 = M_x O_y \]

Typical oxide layer structure from experiments:

<table>
<thead>
<tr>
<th></th>
<th>Pure lead (T=550°C)</th>
<th>LBE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T≤300°C</td>
</tr>
<tr>
<td>Martensitic</td>
<td>Duplex layer</td>
<td>Very thin oxide layer</td>
</tr>
<tr>
<td>Austenitic</td>
<td>Thinner duplex layer, grain boundary penetration.</td>
<td>Thin single layer spinel</td>
</tr>
</tbody>
</table>

\[ C_o = 8 \times 10^{-6} \text{ at\%} \quad T=550°C \quad t=3000 \text{ h} \quad V = 1.9 \pm 0.1 \text{ m/s} \]

Oxide layer of martensitic stainless steel in LBE

\[ T = 460 - 470°C \]

An underneath oxygen enriched layer was observed by Zhang.


Oxidation of Stainless Steel in Lead/LBE (Cont.)

Oxide layer of austenitic stainless steel in LBE

\[ T = 460 - 470^\circ C \]

- Oxide layer of austenitic stainless steel in LBE
- LBE
- Oxide Layer
- Steel
- 1.4970 steel
- single-layer Fe-Cr spinel

\[ T = 470^\circ C \quad t = 3000 \text{ h} \quad C_O = 8 \times 10^{-6} \text{ wt\%} \quad V = 1.9 \pm 0.1 \text{ m/s} \]


\[ T = 550^\circ C \quad t = 2000 \text{ h} \quad C_O = 0.03 - 0.05 \text{ wppm} \quad V = 1.9 \pm 0.1 \text{ m/s} \]

Mechanisms of the Oxide Layer Growth

- **Static molten lead/LBE**

Dissolution corrosion in unsaturated static lead or LBE

Deposition induces a single layer of (Fe,Cr)$_3$O$_4$

Duplex-layer structure without oxygen transported into the stainless steel

Corrosion ceases when dissolution is in equilibrium with deposition
Mechanisms of the Oxide Layer Growth (Cont.)

- Static molten lead/LBE

![Diagram]

- Duplex-layer structure oxide controlled by transports of iron and oxygen
  - Original surface
  - Fe$_3$O$_4$
  - (Fe, Cr)$_3$O$_4$
  - Cr, Ni enriched layer
  - O
  - New surface

- Single layer structure oxide induced by surface reaction in clean static lead/LBE
  - Original surface
  - (Fe, Cr)$_3$O$_4$
  - New surface
Mechanisms of the Oxide Layer Growth (Cont.)

- Flowing molten lead/LBE

Dissolution corrosion in unsaturated flowing lead or LBE

Corrosion and oxidation in a non-isothermal lead/LBE system with equilibrium of dissolution and deposition in total quantity.

Dissolution is in equilibrium with deposition, scale removal occurs.

Center for Energy Research (CER), Department of Mechanical Engineering, UNLV
Oxygen Control Technology

\[ \frac{1}{2} \text{O}_2 + \text{Pb} \leftrightarrow \text{PbO} \]

\[ \frac{\Delta_f G_{\text{Fe}_3\text{O}_4}^0}{2RT} \leq \ln P_{O_2} \leq \frac{2\Delta_f G_{\text{PbO}}^0}{RT} \]

\[ C_{O,s[\text{Pb}]}[\text{wt}\%] = 10^{3.2-5000/T} \]

\[ C_{O,s[\text{LBE}]}[\text{wt}\%] = 10^{1.2-3400/T} \]

\[ C_{O,\text{min}[\text{Pb}]}[\text{wt}\%] = 10^{2.1012-8048/T} \]

\[ C_{O,\text{min}[\text{LBE}]}[\text{wt}\%] = 10^{-0.2722-6508/T} \]

Experimental Facilities from LANL

DELTA Loop

A material test loop designed and established at LANL

Valentina Tcharnotskaia, Curtt Ammerman, Keith Woloshun, *Results from the Initial Operation of the LANL DELTA Loop.*
Deterministic Method

• A deterministic model is one in which every set of variable states is uniquely determined by parameters in the model and by sets of previous states of these variables

• Numerical models in microscopic viewpoints
  — elements, physical and chemical reactions, corrosion environment, diffusion and transportation

• Microscopic points of view (~nm)
  — Complex: as they are all involved in a deterministic
  — Time consuming: simulation of the corrosion process is lengthy

• Accurate boundary conditions are required

• Commonly use continuity equations, Navier-Stokes equations, energy equation, species transport equations, and chemical reaction equations

• Two-dimensional analytical solutions have been successfully obtained

• CFD has been used to solve for those governing equations with specified boundary conditions
Stochastic Methods

• A stochastic model, randomness is present, and variable states are not described by unique values, but rather by probability distributions

• Better computational efficiency than the previous way

• Provide the accurate results similar to the deterministic approaches

• Emphases on the randomness of corrosion (neglected in the deterministic models)

• Cellular automaton (CA) and lattice Boltzmann method (LBM) have been successfully developed and used to study corrosion and oxide layer growth

• Needs less well-defined boundary conditions

• Obtain good agreements with experimental results
Corrosion Model Processes: Deterministic Modeling Diagram

- Oxide growth model
- Surface kinetics
- Equation in the mass transfer boundary layer
- Transport equation in the bulk flow
- Simplifying assumptions
- Kinetic corrosion for simple loop at steady state. Solutions for corrosion product concentration and corrosion/deposition rate
- Incorporate geometry variations
- Model for multi-modular loop

Ongoing:
- Dissolution faster than mass transfer
- System corrosion kinetics model

Finished:
- Model transient process

Starting Point (corrosion product transport)
Corrosion and Oxidation Model Processes

1. In flowing liquid lead/LBE media
   • Mass transfer boundary layer: convection + diffusion
   • Beyond the boundary layer: convection

2. In the oxide layer (duplex layer)
   • Surface reactions (ionization and oxidation)
   • Ionic iron diffuses outwards
   • Oxygen transports inwards (unclear mechanism, effective diffusion)
   • The oxide layer follows the Wagner’s theory and Tedmon’s equation if scale removal occurs
     \[
     \frac{d\delta}{dt} = \frac{K_p}{2\delta} - K_r
     \]
Corrosion and Precipitation in Non-isothermal Liquid Lead or LBE systems

Methodology:

1. For the analytical solutions
   - Fourier expansion, coordinate transformation and similarity solution

2. For the numerical model
   - CFD commercial software: FLUENT
   - Corrosion product transport equation was solved numerically with considering the effect of turbulent diffusivity (expression from Malang, UDFs have been coded and coupled)
   - 3-D, steady-state, structured mesh, segregated solver, standard k-ε model, finite volume method

\[ D_t = \begin{cases} 
0 & 0 < y^+ \leq 5 \\
\nu(y^+ / 5 - 1) & 5 < y^+ \leq 30 \\
0.005\nu \text{Re}^{0.875} & 30 \leq y^+ 
\end{cases} \]

\[ K_D = \frac{D_t}{D_m} = \begin{cases} 
0 & 0 < y^+ \leq 5 \\
0.750 & 5 < y^+ \leq 30 \\
27808 & 30 < y^+ 
\end{cases} \]

S. Malang, 1984
For the dissolution process, the surface iron concentrations equal their saturated concentration

\[
\log(C) = \log(C_s) = A_1 + B_1 / T
\]

By using oxygen controlled technique, a protective oxide film can be built up at the interface of liquid metals as a barrier. The reaction reaches equilibrium state at the interface

\[
Fe_3O_4 \leftrightarrow 3Fe + 4O
\]

The equilibrium concentration of iron can be obtained

\[
\log(C_{eq}) = A_2 - B_2 / T - \frac{4}{3} \log(C_O)
\]

Boundary condition for the corrosion product at the wall are

\[
C_w = \min(10^{6.01-4380/T}, C_O^{-4/3} 10^{11.35-(12844/T)})
\]
2-D Theoretical Corrosion Model

Assumptions:
- Mass transfer controlled corrosion
- Steady state, fully developed turbulent
- Reaction on the wall is at equilibrium
- Schmidt number $\gg 1$ ($\delta_m < \delta_h$)
- Buffer zone is neglected
- Reaction term is neglected in the flow
- Bulk flow velocities and physical properties stay constant in x-dir
- Smooth wall surface

With Fourier expansion, the solutions for the concentration of corrosion product in the laminar sub-layer $c_l$, bulk concentration in the turbulent core region $c_b$, and the surface corrosion/precipitation rate $q$

$$c_l(\xi, \eta) = a_0 + \sum_{k \neq 0} \frac{a_k}{Ai(0)} Ai \left( \left(2\pi ki\right)^{1/3}\eta \right) e^{2\pi ki\xi}$$

$$c_b(\xi) = \frac{D\gamma L}{V_b (R - \delta)} \sum_{k \neq 0} \frac{ia_k}{\pi k Ai(0)} Ai(1, (2\pi ki)^{1/3} \gamma \delta)(2\pi ki)^{1/3} e^{2\pi ki\xi} + a_0$$

$$q(\xi) = \left( \frac{\lambda \pi D^2 V_b^2}{3\nu L} \right)^{1/3} \frac{1}{Ai(0)\Gamma(1/3)} \sum_{k \neq 0} Q_k e^{2\pi ki\xi}$$

Theoretical modeling of corrosion rate based on DELTA loop at the Los Alamos National Laboratory.

Loop/pipe length is 29.92 m, hydraulic diameter is 0.0525 m, kinematic viscosity of LBE is $1.5 \times 10^{-7}$ m$^2$/s, Liquid LBE velocity is 0.5 m/s, oxygen concentration in LBE is 0.01 ppm, and the diffusion coefficient is taken as $10^{-9}$ m$^2$/s.
Results – Numerical vs. Analytical

1. Same tendency in both solutions
2. Numerical solutions have large maximal corrosion/precipitation rates
3. Differences increase with temperature differences
4. The solutions are in the same order

\[ \Delta T = 50 \, ^\circ \text{C} \]

\[ \Delta T = 200 \, ^\circ \text{C} \]

\[ \Delta T = 350 \, ^\circ \text{C} \]

\[ C_0 = 0.01 \text{wppm} \]
\[ V = 0.5 \, \text{m/s} \]
Results – Numerical vs. Analytical vs. Experimental

1. Models were benchmarked with a pure lead loop
2. Both solutions agree well with the experimental data
3. Numerical solution has large maximal corrosion/precipitation rates

The Diffusion Controlling Oxidation Model

In oxide phase:

For \( C_{O_0} > C > C_{OM} \) (or \( \delta_{\text{tot}}(t) > x > 0 \))

\[
\frac{\partial C}{\partial t} - D_{Ox} \frac{\partial^2 C}{\partial x^2} = 0
\]

In metal phase:

For \( C_{MO} > C > 0 \) (or \( L(t) > x > \delta_{\text{tot}}(t) \))

\[
\frac{\partial C}{\partial t} + V_{Me} \frac{\partial C}{\partial x} - D_{Me} \frac{\partial^2 C}{\partial x^2} = 0
\]

\[
m = \frac{wp + r - rw}{r} \rho_{Me} + w(1 - p) \rho_{out} \approx \frac{B}{r} \quad \text{(simple case)}
\]

w: weight ratio of M in metal materials

p: ratio of the inner reacted atoms (M) to the total reacted atoms (M)

In metal phase:

\[
r = \frac{xM_M}{yM_O + xM_M}
\]

Pilling-Bedworth ratio \( B = \frac{\rho_{Fe}}{\rho_{Fe_3O_4}} \)
Non-dimensional Form and Coordinate Transformation

\[ C^* = \frac{C}{C_{00}} \]

\[ x^* = \frac{x}{L_0} \]

\[ t^* = \frac{tD_{Me}}{L_0^2} \]

\[ V_{Me}^* = \frac{V_{Me}L_0}{D_{Me}} \]

\[ \frac{\partial C^*}{\partial t^*} - \frac{D_{Ox}}{D_{Me}} \frac{\partial^2 C^*}{\partial x^*2} = 0 \quad \text{for } 1 > C^* > C_{OM}^* \quad \text{(or } L^* (t^*) > x^* > \delta_{tot}^* (t^*)) \]

\[ \frac{\partial C^*}{\partial t^*} - V_{Me}^* \frac{\partial C^*}{\partial x^*} - \frac{\partial^2 C^*}{\partial x^*2} = 0 \quad \text{for } C_{Mo}^* > C^* > 0 \quad \text{(or } \delta_{tot}^* (t^*) > x^* > 0) \]

\[ V_{Me}^* = \left(1 - \frac{1}{m}\right)V_{OM}^* - \frac{K_r^*}{m} \quad \left( V_{OM}^* = \frac{V_{OM}L_0}{D_{Me}} \quad K_r^* = \frac{K_rL_0}{D_{Me}} \right) \]

Coordinate Transformation

\[ y = \begin{cases} 
\frac{1}{m} \left(1 + \frac{K_r^*}{V_{OM}^*}\right)x^* & \text{for } \delta_{tot}^* (t^*) \geq x^* \geq 0 \\
x^* - \left(1 - \frac{1}{m}\right)\delta_{tot}^* (t^*) + \frac{K_r^*}{m} t^* & \text{for } L^* (t^*) > x^* > \delta_{tot}^* (t^*) 
\end{cases} \]

\[ y(\delta_{tot}^* (t^*)) = y(\delta_{tot}^* (+t^*)) = y_{OM}^* (t^*) = \frac{1}{m} \delta_{tot}^* (t^*) + \frac{K_r^*}{m} t^* \quad \text{y}(x^* = L^* (t^*)) = 1 \]

\[ \frac{\partial C^*}{\partial t} - D^* \frac{\partial^2 C^*}{\partial y^2} = 0 \]

\[ D_{Ox}^* = \frac{1}{m^2} \left(1 + \frac{K_r^*}{V_{OM}^*}\right)^2 \frac{D_{Ox}}{D_{Me}} \]

\[ D_{Me}^* = 1 \]
Boundary Conditions

- At $x^* = 0$

\[ C^* = 1 \text{ at } y = 0 \ (x^* = 0) \]

- At the interface of the oxide and the metal regions

\[ C^* = C_{OM}^* \text{ at } y(x^* = \delta_{tot}^*(t^*)) = \frac{1}{m} \delta_{tot}^*(t^*) + \frac{K_r^*}{m} t^* \]

\[ C^* = C_{MO}^* \text{ at } y(x^* = \delta_{tot}^{++}(t^*)) = \frac{1}{m} \delta_{tot}^{++}(t^*) + \frac{K_r^*}{m} t^* \]

- At the far end of the specimen

\[ y(x^* = L^*(t)) = 1 \]

\[ -\frac{\partial C^*}{\partial y} = 0 \text{ at } y(x^* = L^*(t)) = 1 \]

\[ \begin{align*}
  -D_B \frac{\partial C}{\partial x} \bigg|_{\delta^+} &+ D_A \frac{\partial C}{\partial x} \bigg|_{\delta^-} + (C_{AB} - C_{BA})(V + \delta(t)) = 0 \\
  L(t) &= L_0 + V_{Me} t
\end{align*} \]
Benchmark 2 and 3

For pure titanium

Distribution of oxygen concentration at time $t=0.5h$ ($Kr=2 \times 10^{-9}$ m/s for the scale removal model)


For stainless steel in LBE


$V = 1.9 \pm 0.1 \text{ m/s}$

$K_r = 7.0 \times 10^{-13} \text{ m/s}$

$C_D = (1 - 2) \times 10^{-6} \text{ wt%}$
Numerical Simulation of Duplex Layer Growth

$$w=0.9$$

$$K_r=1e^{-10}m/s$$

$$p=0.8$$

Cellular Automaton (CA) Model on Oxidation Mechanism

- It can be derived through finite difference formulations of the underlying governing equation.
- CA is a method that describes the discrete spatial and temporal evolution of complex systems by applying local deterministic or probabilistic transformation rules to the cells of a lattice.
- These rules determine the state of a lattice point as a function of its previous state and the state of the neighboring sites.
- After each time interval, the variables at each site are updated synchronously based on the local rules.

Schematic of CA model on corrosion/oxidation of stainless steel in LBE, considering interstitial sites.

A global random walk method is included to characterize the diffusion process of iron and transport of oxygen.


IMO CA Model adding New Scale Removal (NSR) Model

- Improved CA model
  - Added parameter: $P_{kr}$
    - Scale removal effect

Walker:
ionic metal site (partial $Fe_3O_4$ and Fe ion) can diffuse in the oxide layer in any random direction

Structure of CA Model

- Modified Moore neighborhood model
  - 8 neighbor lattices (in lattice)
  - 4 interstitial sites (in boundary of lattice)

Corrosion Model Processes: Stochastic (CA) Modeling Flow Chart

1. Diffusion of Oxygen
   Give initial value for lattices and interstitial sites

2. Reaction of Metal/Walker
   Reaction Probability: $P_{\text{act}}$
   Chromium content: $C_{\text{cr}}$
   Transportation rate: $K_d$
   Scale Removability: $P_{kr}$
   Yes
   No

3. Scale Removal Effect

4. Data output
   Yes
   No

Total Time Steps: $N_t$
   Yes
   No
   End of Simulation

- Oxygen concentration: $C_{\text{oxy}}$ = 0.2
- Chromium content: $C_{\text{cr}}$ = 10%, 30%
- Transportation rate: $K_d$ = 2, 4
- Scale Removability: $P_{kr}$ = $10^{-4}$
- Total Time Steps: $N_t$ = 20k, 200k
Grid System of CA Model (at time=0)

Oxidation simulation

Give initial value for lattices and interstitial sites

1. Diffusion of Oxygen

2. Reaction of Metal/Walker

3. Scale Removal Effect

4. Data output (t=200000)

Yes

No

O step > K_d

Yes

No

3. Scale Removal Effect

4. Data output (t=200000)

No

time > t

Yes

End of Simulation

Square lattices:
A site which will be occupied by metal or oxide in solid phase/LBE in liquid phase (In LBE, the oxygen concentration is kept constant and the oxygen distribution is uniform)
Diffusion of Oxygen

1. Diffusion of Oxygen
   - Give initial value for lattices and interstitial sites

2. Reaction of Metal/Walker
   - O step > \( K_m \)
   - Yes
   - No

3. Scale Removal Effect

4. Data output (t=200000)
   - Yes
   - No

End of Simulation

In each oxygen transport step, the atomic oxygen transports randomly in four possible directions along the interstitial edge of the lattices in the oxide layer or the metal zone.

Interstitial sites (in LBE): routes for oxygen to occupy and transport

Interstitial sites (in oxide layer): routes for oxygen to occupy and transport
Walker: a whole lattice with ionic metal overlapping with any oxide lattice site

Walker can diffuse in the oxide layer in any random direction
Oxidation & Ionization at Inner Interface of Oxide/Metal

If at least one of the eight neighbor sites is oxide, the oxidation reaction of metal occurs immediately with a probability, $P_{act}$.

The site of metal disappears and an overlapping site of oxide and ionic metal (walker) substitutes. Then a walker was formed. Reaction speed is assumed to $\gg$ diffusion speed of oxygen. One of the oxygen sites is chosen randomly from the nearest interstitial sites for reaction and disappears.
Oxidation at Outer Interface of Oxide/LBE

When a “walker” meets LBE, oxidation occurs immediately, since it is assumed the oxygen diffuses very fast in LBE.

- Oxidation simulation
- Give initial value for lattices and interstitial sites
  - 1. Diffusion of Oxygen
    - 2. Reaction of Metal/Walker
      - Yes
        - O step > $K_d$
          - Yes
            - 3. Scale Removal Effect
              - 4. Data output (t=200000)
                - No
                  - time > t
                    - Yes
                      - End of Simulation
The Ratio of Transport Steps

- Oxidation simulation
  - Give initial value for lattices and interstitial sites
    - 1. Diffusion of Oxygen
    - 2. Reaction of Metal/Walker
      - O step > $K_d$
        - Yes
        - 3. Scale Removal Effect
          - 4. Data output (t=200000)
            - No
            - time > t
              - Yes
              - End of Simulation
            - Yes
            - No

$K_d = \frac{\text{Diffusion rate of oxygen}}{\text{Diffusion rate of ion}}$

Usually the transport rate of oxygen is faster than the diffusion of ionic metal.
Scale Removal – Erosion

1. Diffusion of Oxygen
   - Give initial value for lattices and interstitial sites
   - O step > K_d
   - 1. Reaction of Metal/Walker

2. Reaction of Metal/Walker
   - 2. Reaction of Metal/Walker

3. Scale Removal Effect

4. Data output (t=200000)
   - Yes
   - No

5. End of Simulation
   - No
   - time > t
   - Yes

Flow direction

5 of 17 kinds of morphology

The flow direction of LBE is assumed from left to right.

The morphology and roughness of the oxide/flow interface do influence on scale removal effect.
Simulation Results of CA Model

Output data:
1. coordinate of state of each lattice and interstitial sites
2. thickness of oxide layer
Oxidation Process Using CA Simulation

\[ N_t = 10,000 \]
Oxidation Process Using CA Simulation (Cont.)

\[ N_t = 10,000 \]

\[ \delta_{N,in} = \frac{1}{N} \sum_{i=1,N} (Y_0 - Y_{Ox_{Min}}(i)) \]

\[ \delta_{N,out} = \frac{1}{N} \sum_{i=1,N} (Y_{Ox_{Max}}(i) - Y_0) \]

\[ C_{wa,j} = \frac{1}{N} \sum_{i=1,N} IW_{i,j} \]

\[ IW_{i,j} = \begin{cases} 1 & \text{if } Lat_{i,j}(t) = Lat_5 \\ 0 & \text{if } Lat_{i,j}(t) \neq Lat_5 \end{cases} \]

\[ C_{Oxy,j} = \frac{1}{N + 1} \sum_{i=0,N} IO_{i,j} \]

\[ IO_{i,j} = \begin{cases} 1 & \text{if } Inte_{i,j}(t) = Inte_1 \\ 0 & \text{if } Inte_{i,j}(t) = Inte_0 \end{cases} \]
Parametric Study on Oxide Layer Growth

For $P_{act} = 0.0005$

For $P_{act} = 0.5$

Center for Energy Research (CER), Department of Mechanical Engineering, UNLV
Oxidation of Inconel 625 Superalloy in Supercritical water

- Major elements: Ni, Cr
- Duplicated oxide layer structure

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
<th>C</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percent %</td>
<td>5.0</td>
<td>58.0</td>
<td>20.0</td>
<td>8.0</td>
<td>3.15</td>
<td>0.40</td>
<td>0.40</td>
<td>0.10</td>
<td>0.50</td>
</tr>
<tr>
<td>max</td>
<td>max</td>
<td>min</td>
<td>~23.0</td>
<td>~10.0</td>
<td>~4.15</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
</tr>
</tbody>
</table>

- Inner oxide layer (270 nm)
- Outer oxide layer (590 nm)
- Cr depleted layer
Simulation of Thickness of Oxide Layer (OL)

- Simulation of case 1 for 2000 hours vs. Inconel 625 Superalloy in 600°C, 24.8 MPa supercritical water for 24, 100, 300, 600, 1000 hours

- Thickness of OL for 2000 hours = 1,831 nm predicted by mesoscopic CA model

Alloy Material with Chromium (Cr)

- Cr is an important alloying element (10%~30% shown in literatures) added in stainless steels and nickel based alloys which have been proposed to be used in advanced nuclear reactors.

- The oxide layer is composed of a brittle external magnetite layer of Fe$_3$O$_4$ and a compact internal Fe-Cr spinel oxide layer.

- The cellular automaton (CA) model: potential and economic to study the behavior of corrosion and oxidation process thoroughly.
Conclusions and Suggestions

- Deterministic and stochastic methods on studying corrosion and oxide layer growth modeling have been successfully developed.
- Reasonable analytical and numerical results have been obtained with good agreements compared with available experimental measurements.
- Multiscale method including deterministic and stochastic approaches are currently under developing to study fluid mechanics coupled with erosion, corrosion, and oxide layer growth. The successful development will be able to predict the material life span under the flow conditions.
- The final goal of our numerical approaches is to accomplish and satisfy the National Materials Crosscut Program (NMCP) in the U.S. and to find out:
  - Acceptable dimensional stability including void swelling, thermal creep, irradiation creep, stress relaxation, and growth.
  - Acceptable strength, ductility, and toughness.
  - Acceptable resistance to creep rupture, fatigue cracking, creep-fatigue interactions, and helium embrittlement.
  - Acceptable chemical compatibility and corrosion resistance (including stress corrosion cracking and irradiation-assisted stress corrosion cracking) in the presence of coolants and process fluids.
Thank you for your attention!