Development of a Functionally Graded Composite Alloy for Corrosion Resistance in Pb-Bi Environments: NERI Project

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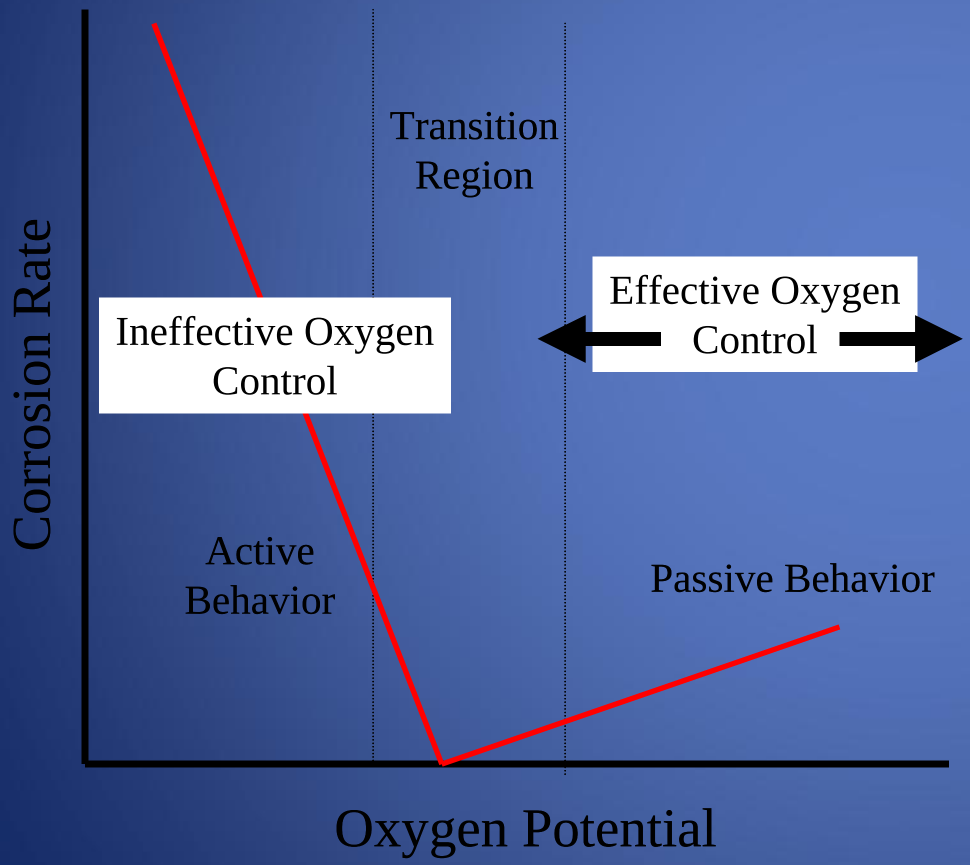
MIT Center for Advanced Nuclear Energy Systems
H. H. Uhlig Corrosion Laboratory

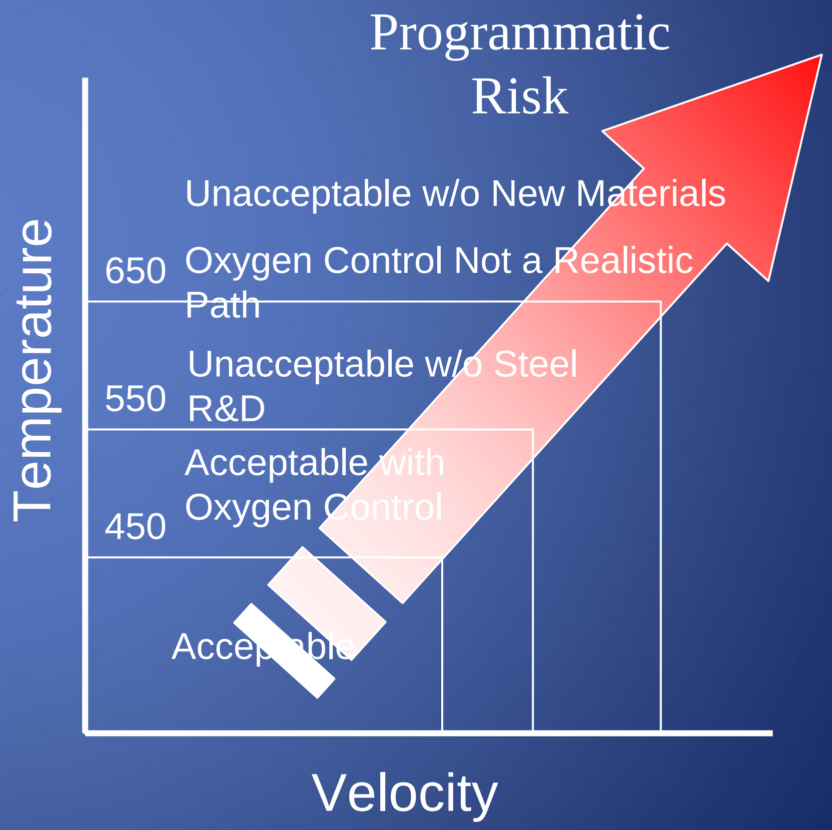
Pb-Bi Systems

- For Pb-Bi, Dose will be very high
  - Swelling, Embrittlement
  - Significant Reduction in Ductility
- New Materials Requited for T > 500°C
- Key Issues
  - General Corrosion
  - Fuel & Cladding (Radiation Damage)

Corrosion Issues: Pb-Bi

- Key Variables: Temperature, Velocity, O_2 Potential
- Location of "Transition" Region a Function of Material System



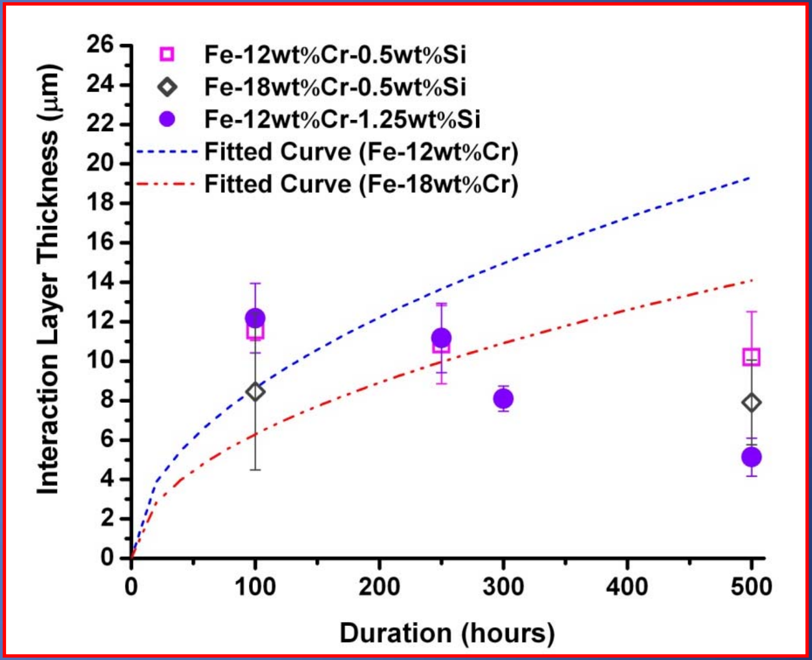


Performance Requirements

- Resistance to Corrosion in Pb and Pb-Bi Eutectic at Temperatures up to 650°C
- Resistance in BOTH Oxidizing (w.r.t iron oxide potential) and Reducing Potentials. (Avoids Fe-Oxide Phase Transformation Issues)
  - *Protection Scheme Must be Self-Healing in Oxidizing Environments*
  - *Low Dissolution Rates in Low (or zero) Oxygen Concentration Regions*
- High Temperature Strength: $\sigma_Y \geq 210$ MPa @ 650°C
- Adequate Creep Rupture Strength
- Microstructural Stability
  - Adequate In-Core Performance
- Fabrication Using Current Technology
  - *Suitable as Structural Material & Cladding Material*

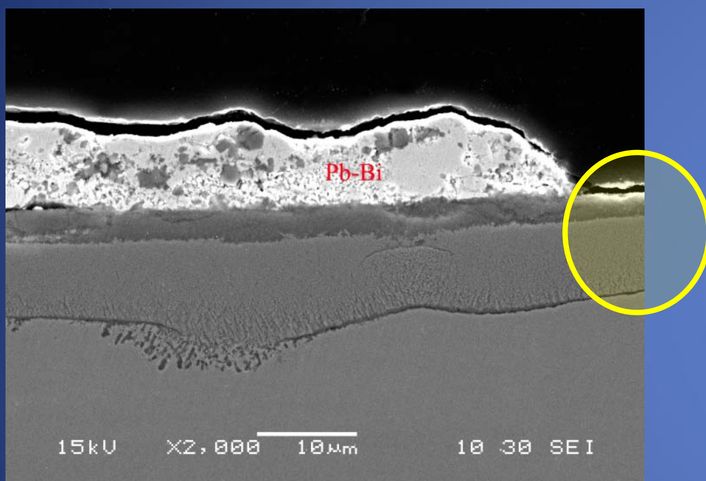
Effect of Silicon

- Fe-Cr-Si alloys (>12% Cr)
  - Actual reduction in the interaction layer thickness
  - Effect of Si
    - Time-delayed behavior → slow growth of Si-oxide
    - Effective diffusion barrier for further oxidation

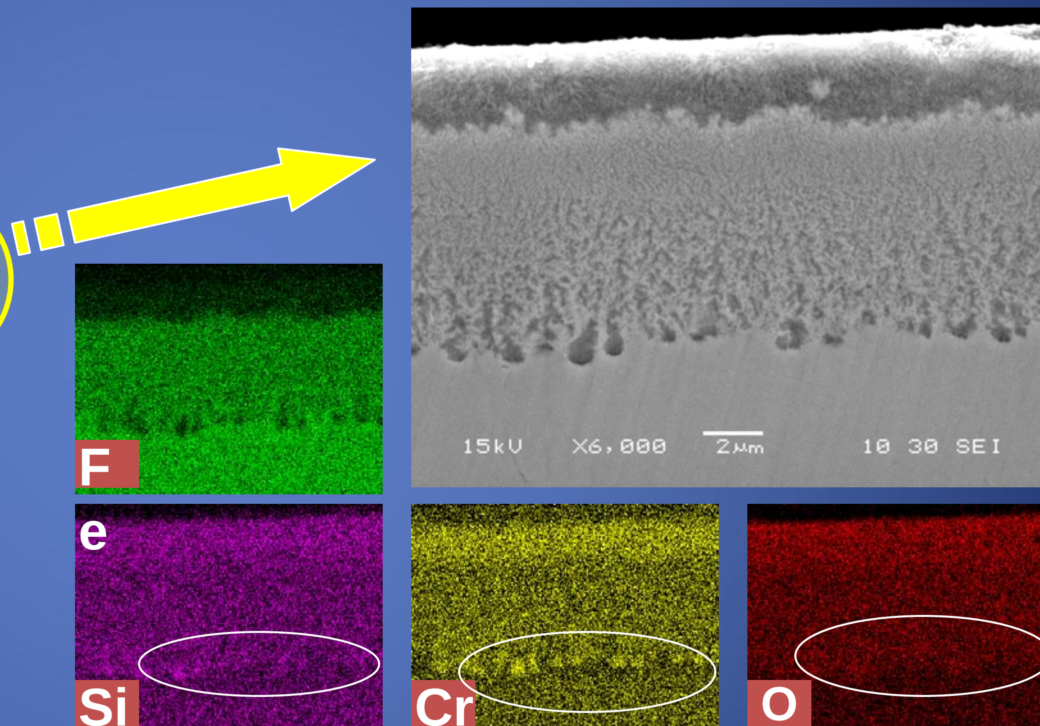


Fe-Cr-Si with Higher Cr

- Fe-12%Cr-1.25%Si: Sufficient Cr for continuous Cr-rich oxide layer

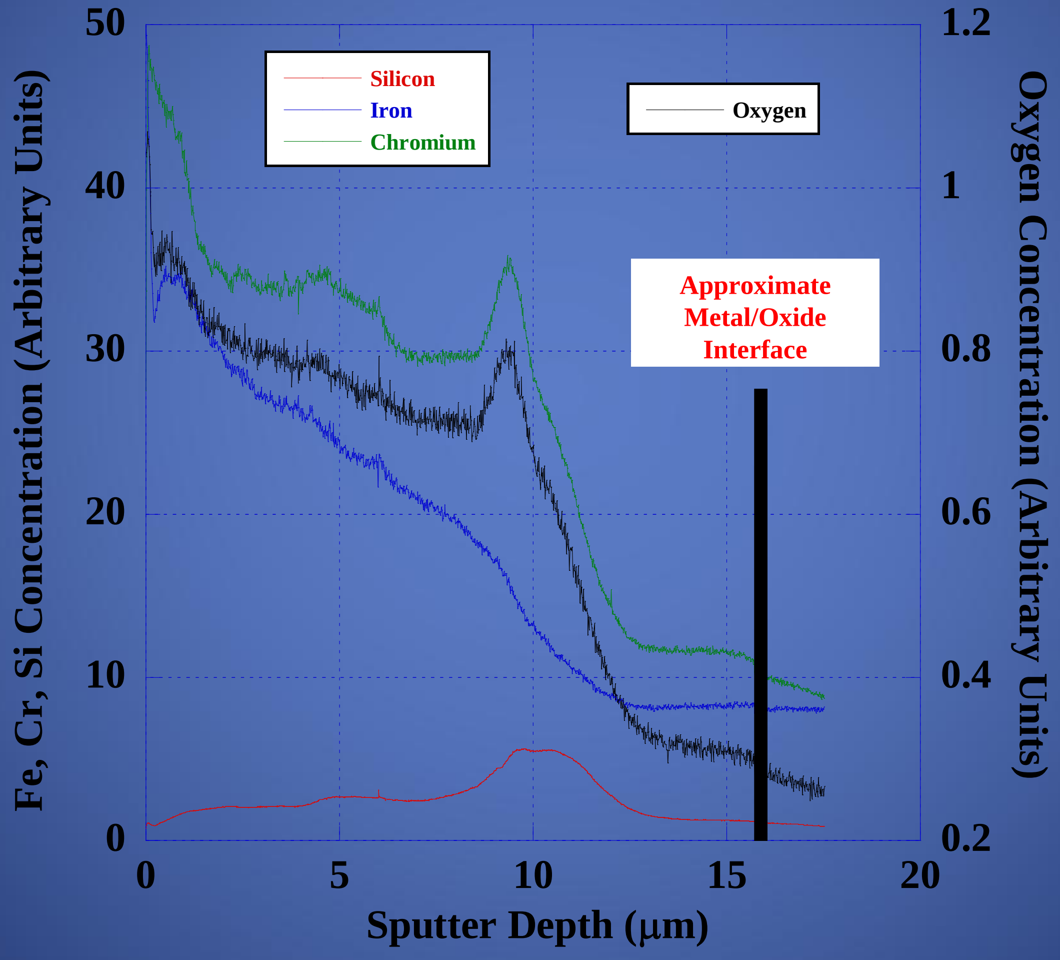


Exposure at 600°C for 250 hours



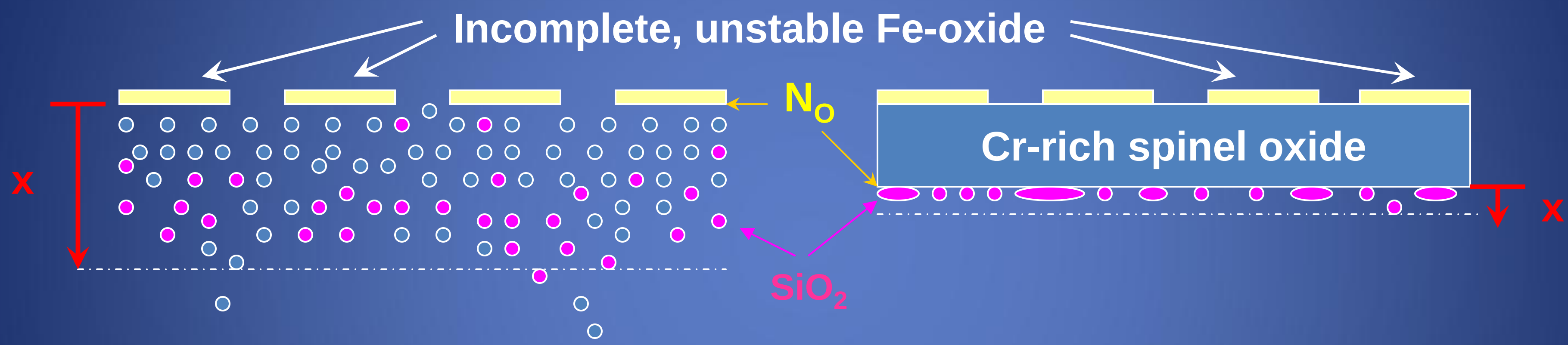
→ Enrichments of Cr and Si at the interface of oxidation zone/the base metal

SIMS data for Fe-12Cr-1.25Si exposed @ 600°C/500 Hours



Si with Low Cr vs. High Cr

- Fe-Cr-Si with low Cr
- Fe-Cr-Si with high Cr

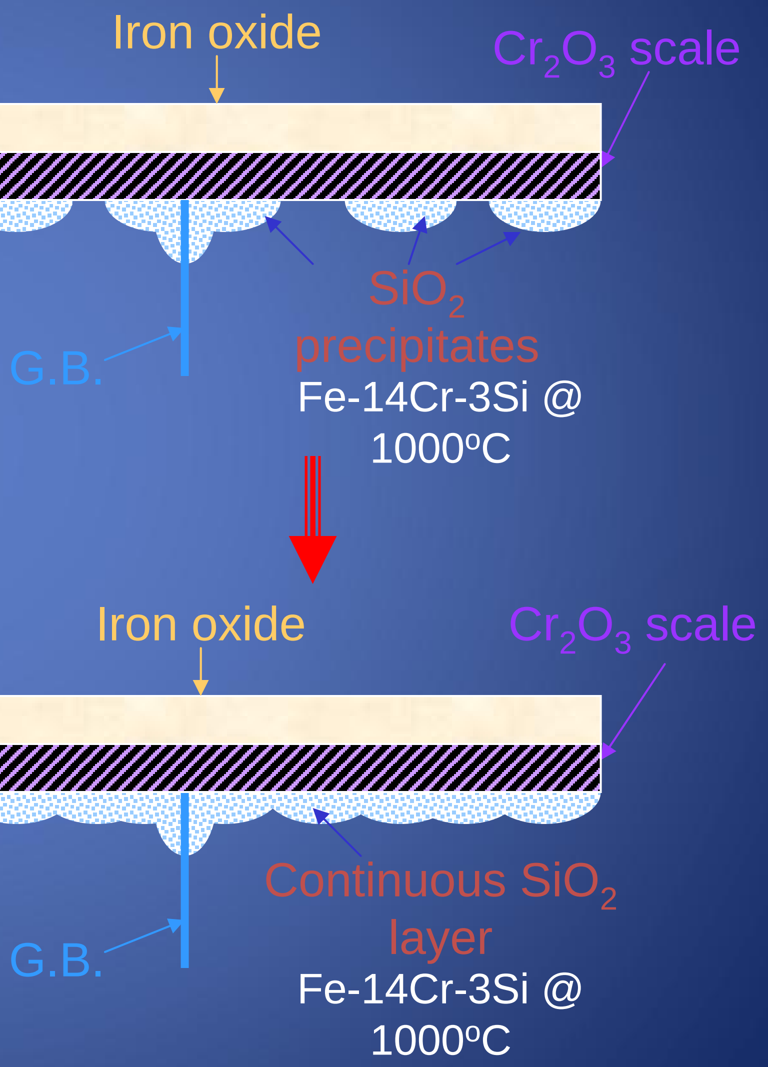


Internal oxidation depth: $X \propto (N_O)^{0.5}$
(N_o: oxygen concentration, $\propto$ **$[P(O_2)]^{1/2}$**)

→ Fast formation of <u>continuous Cr-rich oxide</u> lowers the oxygen concentration at the oxide/alloy interface, which reduces the internal oxidation depth of Si and localizes SiO_2 formation near the Cr-rich oxide layer.

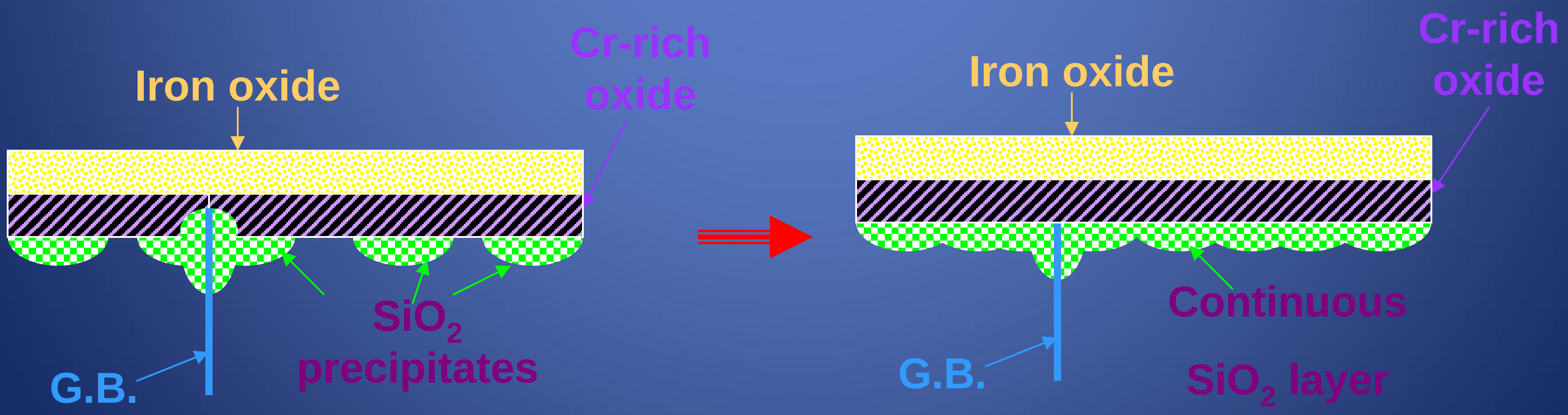
Silicon as an Alloying Element

- Oxides Formed on Fe-Cr-Si alloy Under Oxidizing Conditions
  - Multiple layer structure
    - Outer iron oxide scale
    - Inner Cr_2O_3 scale
    - SiO_2 at scale/alloy interface
  - Synergistic Effect of Cr and Si
- THE BAD NEWS
  - Radiation Embrittlement



Summary: Effectiveness of Si

- Fe-Cr-Si alloy under oxygen controlled environment
  - General multi-layer structure (if iron oxide is stable)
    - Outer iron oxide, inner Cr-rich oxide
    - SiO_2 formation below Cr-rich oxide
  - SiO_2 precipitates: an effective diffusion barrier, retarding the further diffusion of Fe and Cr into oxide, eventually hindering dissolution.
  - Effectiveness of Si addition is achieved with adequate Cr concentration



Issues

- Microstructural Stability
  - Laves/Sigma Precipitation
- Inter-Layer Diffusion
  - Influence on Structural Layer Properties
- Oxide Layer Stability
  - Thermal Cycling
    - Phase Change During Cycling
    - Differential Thermal Expansion

Advanced Alloy "System" Options

- Composite Structural Material System
  - Fe-Based ODS or FM (>9Cr) Structural Layer
    - Other Materials?
  - General Corrosion Resistant Layer Exposed to Coolant
    - > 25Cr (Cr-Based Scale Forming)
    - Si/Al-Based Scale Forming

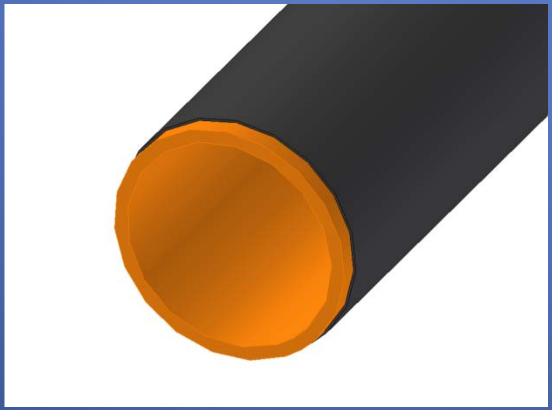
- REMEMBER-You Have to Actually BUILD it!!
  - Eliminates "Lab Scale" Processing

U-NERI Program: Purpose & Tasks

- Purpose
  - Development of a functionally graded composite product that will be both corrosion resistant in Pb and Pb-Bi alloys as well as structurally adequate up to a temperature of 650°C or higher.
- Tasks
  - **Task 1: Cladding/Piping Product Procurement**
    - ***<u>Weld Overlay Product Development and Procurement</u>***
    - ***<u>Quenched & Tempered Steel Based Product Production</u>***
  - **Task 2: Corrosion Testing**
    - **Static (MIT), Flowing (MIT-Harp, LANL-Pumped Loop)**
  - **Task 3: Diffusion Testing**
    - **Weld & Overlay Dilution**
  - **Task 4: Mechanical Properties Testing**

U-NERI Program: Concept

- Functionally Graded Composite
  - High Strength, Radiation Damage Resistant Structural Component
    - Q&T System (T91)
  - Fe-Cr-Si Surface Layer for Corrosion Resistance
    - 2wt% Si



Advantages of FGC System

- Allows for Tailoring of Properties
- Avoids Radiation Damage Issue (Si)
- Complete Metallurgical Compatibility Between Layers
- Joining Issues Minimized (Hi Si Alloy Weld Wire)
- Processing Issues Minimized

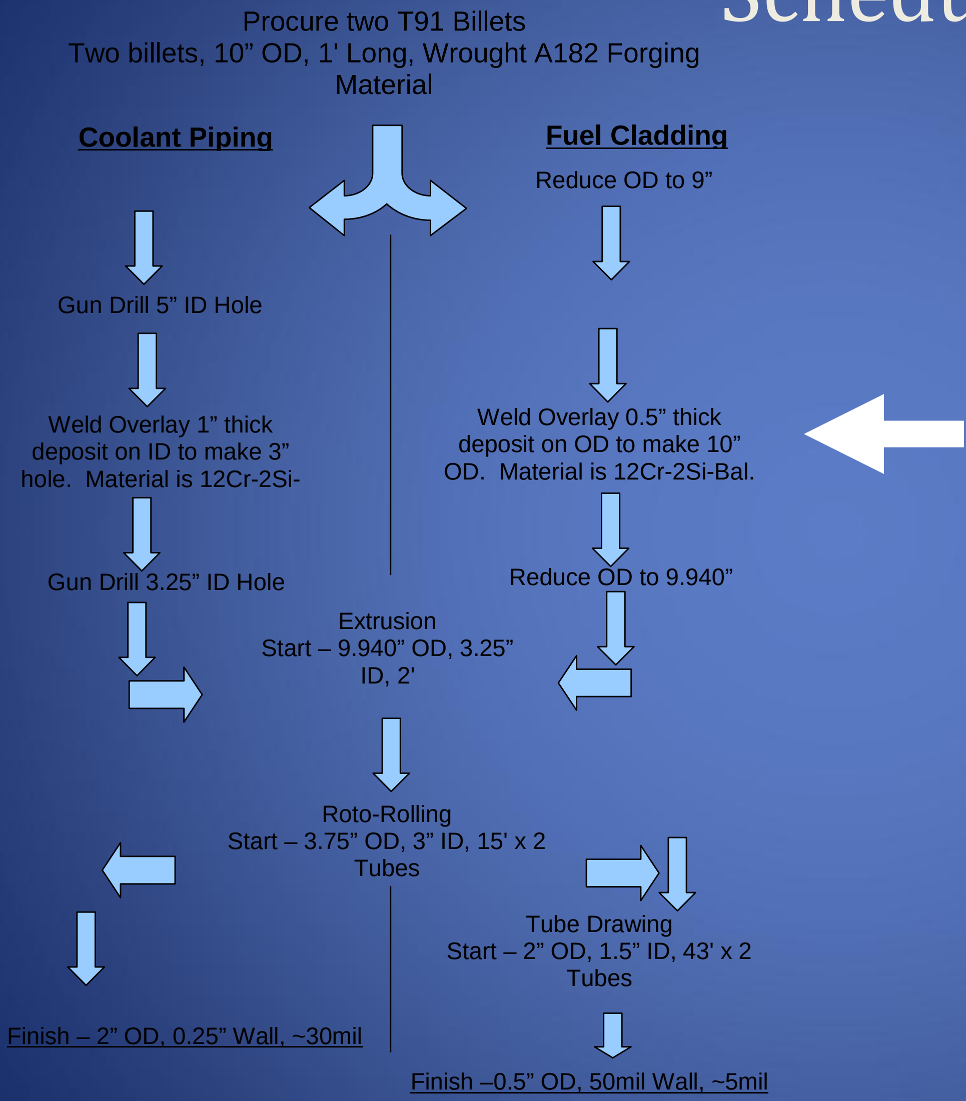
Disadvantages/Challenges of FGC System

- Processing
  - Q&T Structural Layer with Non-Heat Treatable (soft) Layer
    - Hot Extrusion
    - Cold Pilgering/Drawing
- Dilution of Si
  - Weld
  - Overlay (also a weld in our case)

Q&T Material

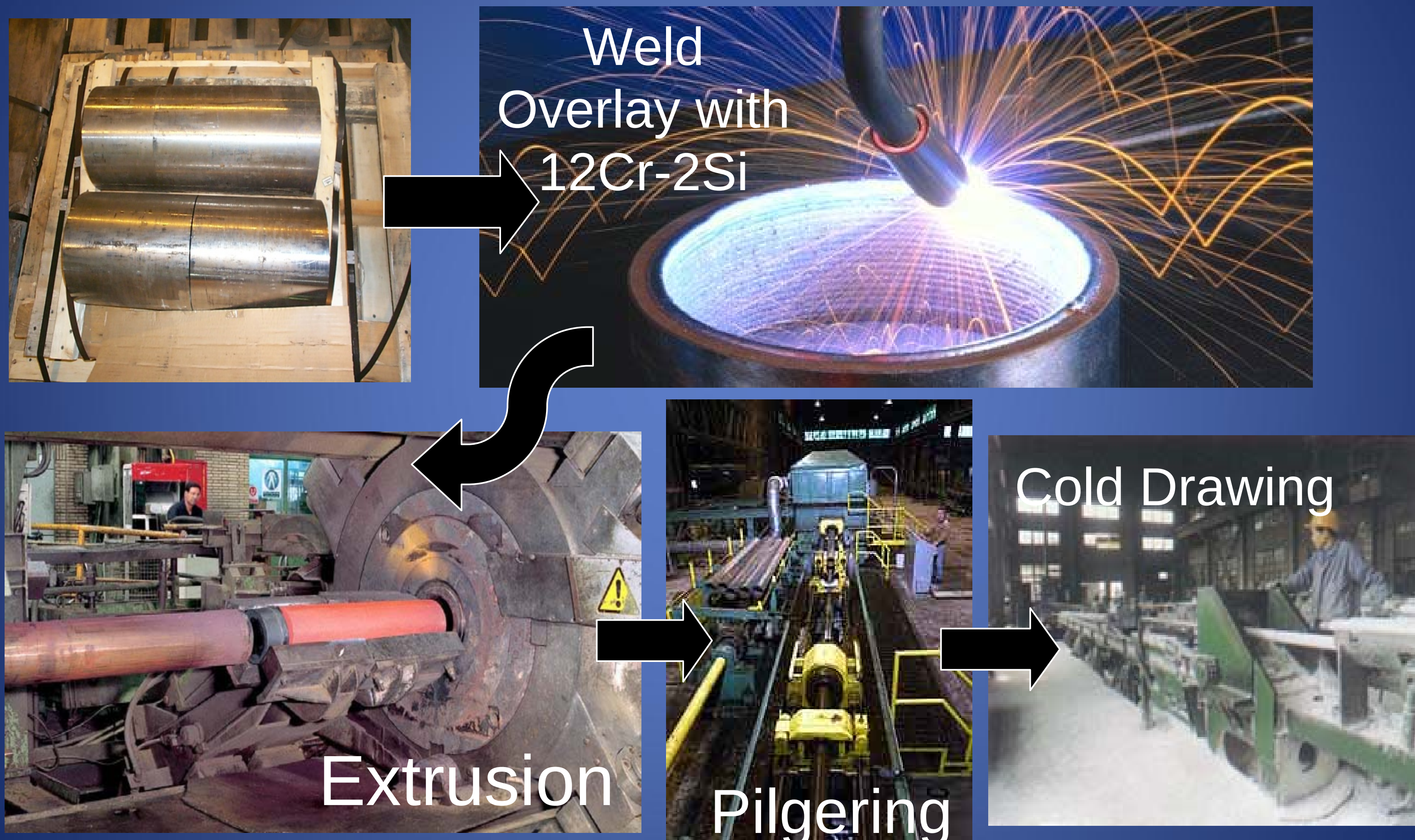
- Good Radiation Damage Resistance
- Adequate Strength to ~ 650ºC
- Processing Issues Less Than for ODS
- Joining Issues Less Than for ODS
- Commercially Available-Very Significant

Product Form Processing Schedule



Weld Wire Has Similar Processing Schedule

Processing Schedule



Current Status

- Processing Schedule Complete
- Forging Billets Obtained
- Extrusion Billets Pre-Machined
- Weld Wire Rod Fabricated
- Diffusion Studies in Progress
- INL Collaboration Established
  - Cladding Production

Extrusion Billets

Weld Wire Rod

Weld Wire Billet

Weld Wire Rod

Diffusion Studies

- Composite will have different Si content in each layer (T91, 0.2-0.5wt%), Clad Layer (~2 wt%)
- Weld overlay process will result in dilution of Si concentration
- In-Service diffusion between layers may compromise the system
- Need to study diffusion of Si in the actual material.
- No data available for diffusion of Si in T91

Test Program

- Use “Clean” system-no weld dilution
- Hot Isostatic Pressed (HIP) samples
- Measure concentration profile with exposure time & temperature
- Infer mass transport coefficient for Si in T91
- Estimate amount of thermal dilution with time
  - Extrapolate short time data to long time
- Test as-fabricated product

Initial HIP-Based Program

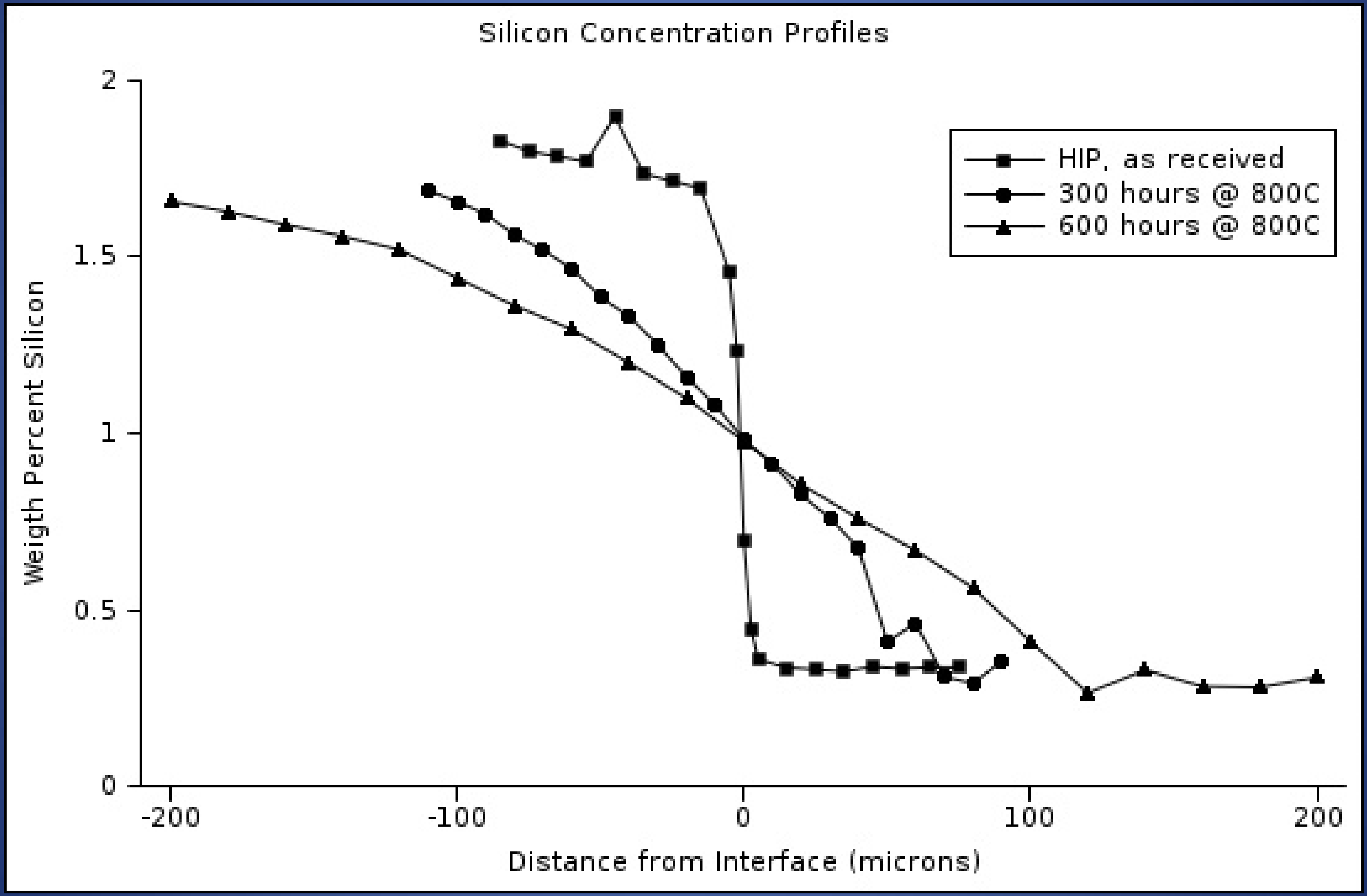
- T91/Fe-12Cr-2Si Samples
- HIP Processed @ 1065°C/4 Hours/20,000 psi
- Samples Aged @ 800°C for 300, 600, 1000 hours
- Electron microprobe analysis (EMPA) on a JEOL JXA-733 electron microprobe with a 1.2 μm spot size calibrated to elemental samples of Cr, Mo, Si and Fe.

Typical HIP Boundary

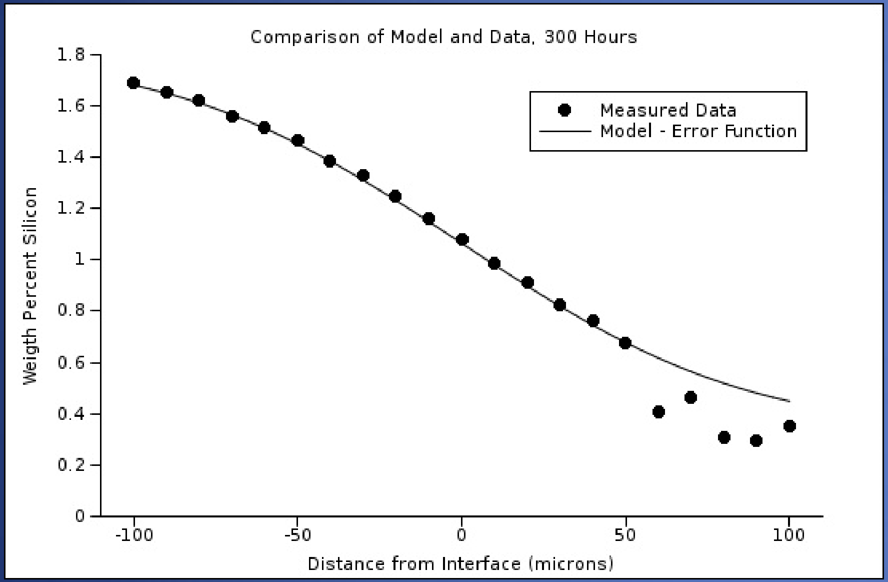
T91

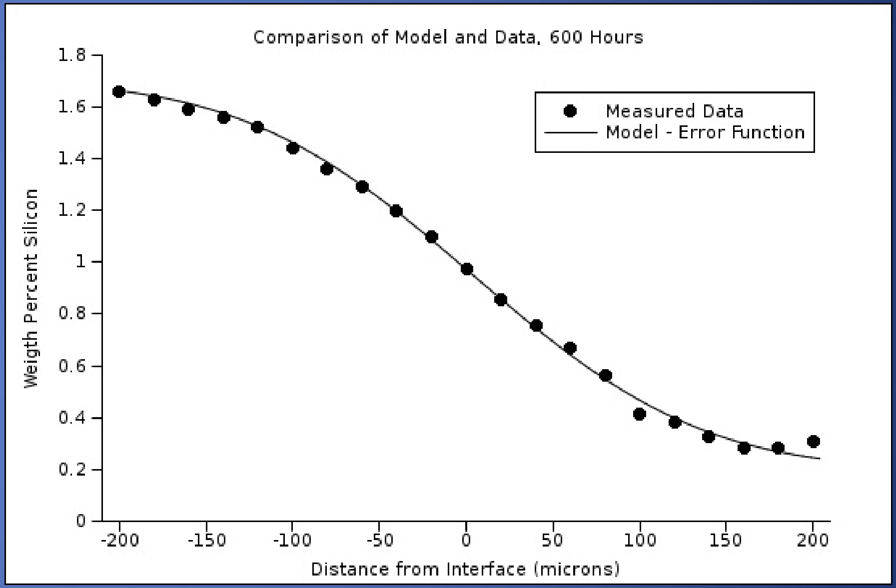
Fe-12Cr-2Si

Results


Silicon Concentration Profiles
2
1.5
1
0.5
0
Weigth Percent Silicon
-200
-100
0
100
200
Distance from Interface (microns)
HIP, as received
300 hours @ 800C
600 hours @ 800C

Results (Cont.)

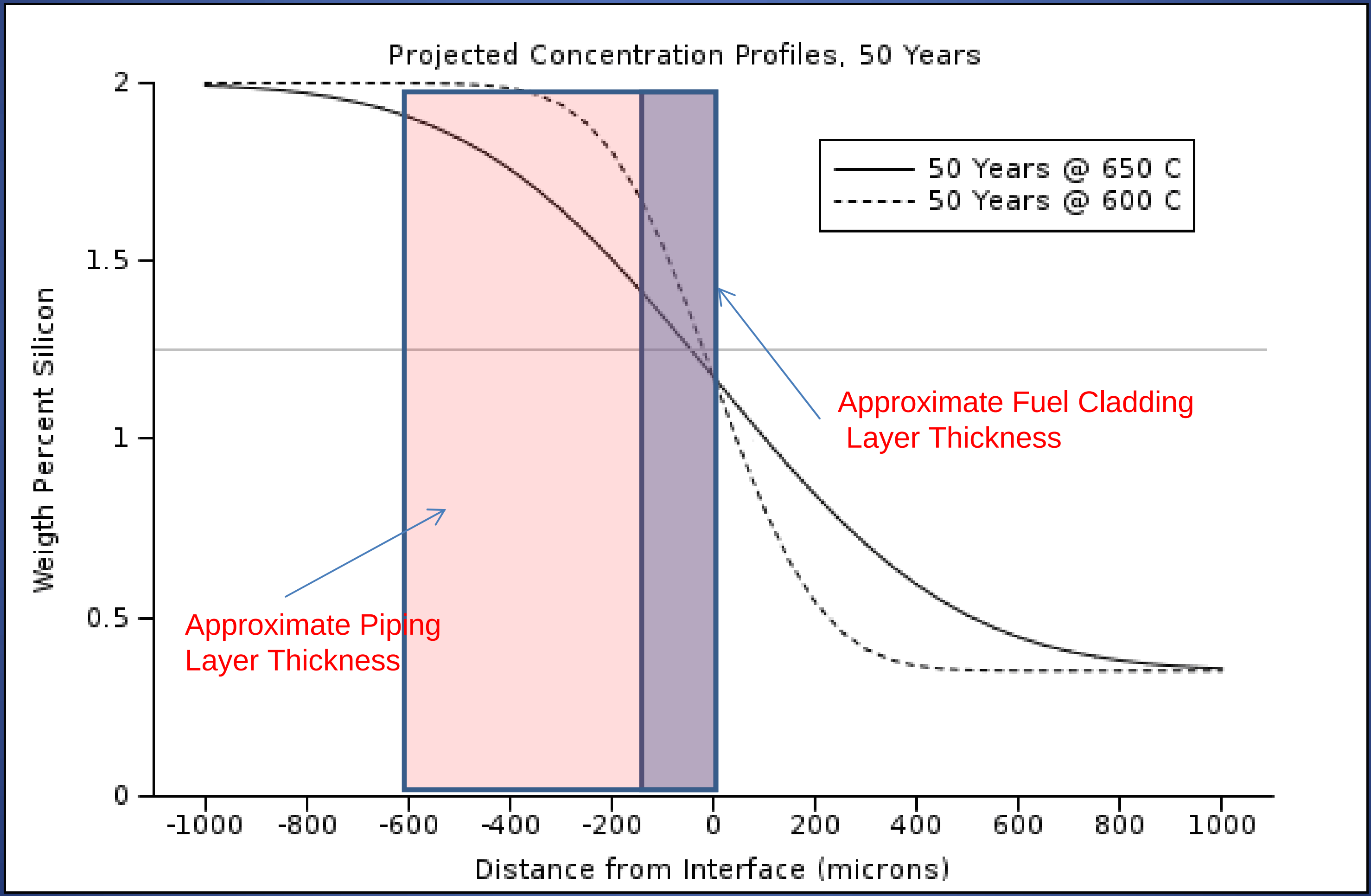




$$D_{Si} = 1.24 \frac{cm^2}{s} \times \exp\left(\frac{-25420}{T}\right)$$

.Comparable to J. Borg, D. Y. F. Lai, "Diffusion in alpha-Fe-Si Alloys" *Journal of Applied Physics*, Vol. 41, No. 13, p. 5193-5200 (1970)

Extrapolation in Time @ 650°C



Early Conclusions-Dilution

- Dilution unlikely to be a show stopper
- Studies using actual article will hopefully confirm

Path Forward

- Process Wire Rod into Weld Wire
- Overlay Billets (ID, OD)
- Extrude
- Process to Pipe and Cladding Product Forms
  - Product forms shipped to INL, LANL for testing
- Testing
  - Corrosion
  - Mechanical Properties
  - Dilution-real article