Project ID: mat164

Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

2021 DOE Vehicle Technologies Office Annual Merit Review

Multiscale Development and Validation of the Stainless Steel Alloy Corrosion (SStAC) Tool for High Temperature Engine Materials

PI: Michael R Tonks
Department of Materials Science and Engineering, University of Florida
Team Members:
Simon Phillpot, University of Florida; **Adrien Couet & John Perepezko**, University of Wisconsin-Madison; **Wen Jiang**, Idaho National Laboratory; **Mark Carroll**, TENNECO

June 4, 2021

POWERING THE NEW ENGINEER TO TRANSFORM THE FUTURE

Overview

Timeline

- Project start date: Oct 1, 2018
- Project end date: Feb 28, 2022
- Percent complete: 78%

Budget

- Total project funding
  - DOE Share: $1500K
  - Cost Share: $375K
- DOE funding per budget period: $500K

Barriers

- ***Corrosion sensitization*** of valve steels at high temperature
- Lack of ***predictive modeling*** mandates conservative design

Partners

WISCONSIN UNIVERSITY OF WISCONSIN–MADISON

INL Idaho National Laboratory

TENNECO

Relevance

Barrier

- Conservative design is mandated by a lack of predictive modeling of the sensitization of stainless steels to corrosion at high temperature

Objectives

- Develop the open source ***Stainless Steel Alloy Corrosion (SStAC) tool*** for modeling corrosion of 21-2N, 21-4N, and 23-8N valve steels in an engine environment.
- Quantify the ***impact of microstructure and alloy composition on valve steel corrosion*** using laboratory and engine experiments and mesoscale modeling and simulation.

Approach:
The SStAC tool is being developed using a multiscale approach validated by laboratory and engine data

Samples
Engine testing

TENNECO

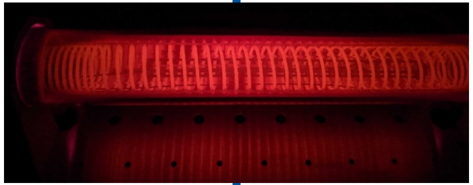
Stainless Steel Alloy Corrosion (SStAC) tool

MOOSE

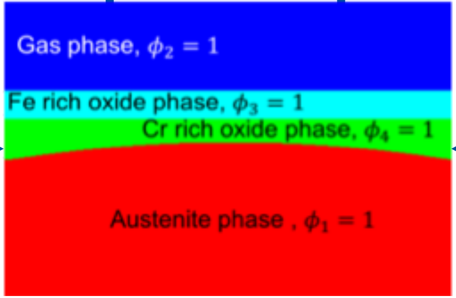
Impact of microstructure

Impact of alloy composition

WISCONSIN
UNIVERSITY OF WISCONSIN–MADISON

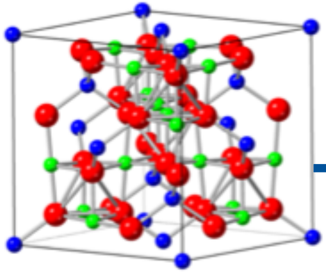


Laboratory testing



MOOSE

UF UNIVERSITY of FLORIDA



UF UNIVERSITY of FLORIDA

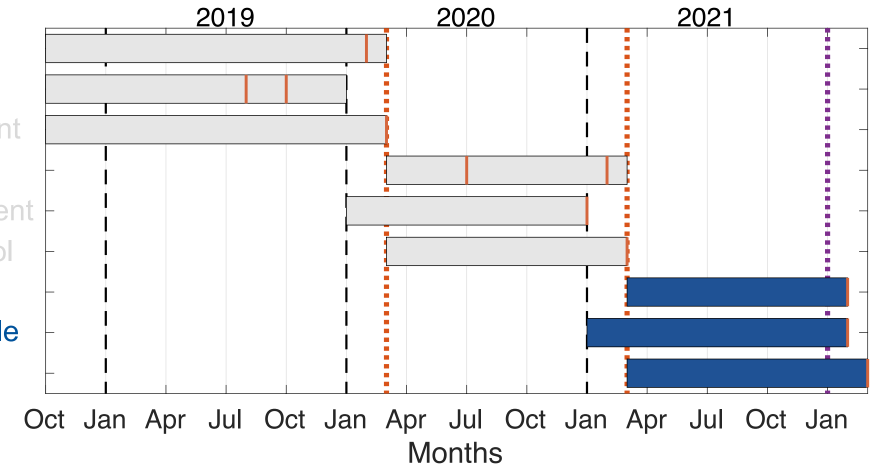
Properties
Mechanisms

Milestones:

We have completed our first six tasks and achieved our both of our Go/No-Go decisions

Tasks

1.1: 1st Experimental campaign
1.2: PF model development
1.3: Corrosion model development
2.1: 2nd Experimental campaign
2.2: Mesoscale model development
2.3: Implementation of SStAC tool
3.1: 3rd Experimental campaign
3.2: Validate and apply mesoscale
3.3: Release of SStAC tool



- BP1 Go-No Go: Corrosion model must be within 25% of experimental data
- BP2 Go-No Go: SStAC tool must function in 1D, 2D, and 3D
- BP3 FINAL: SStAC tool must predict corrosion rate with $< 10\%$ error

Technical Accomplishments and Progress: Overall Accomplishments

nanometers

Atomic-Scale Simulations

- Calculated formation and migration energies in metal and oxide phases

100's of microns

Mesoscale Simulations

- Added additional oxide phases
- Completed mesoscale tool

microns to millimeters

Lab experiments

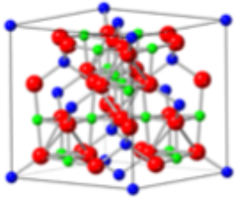
- Completed sample characterization from laboratory and engine tests

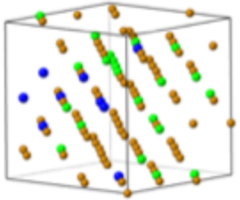
millimeters and up

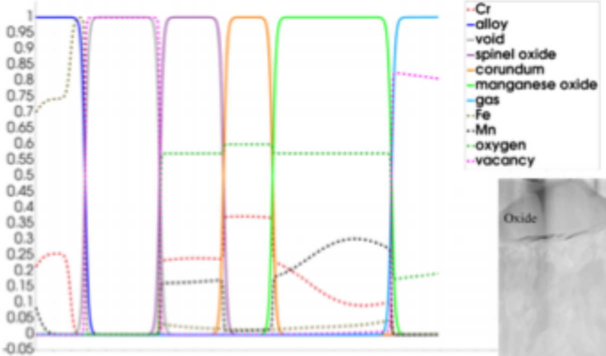
Engineering scale

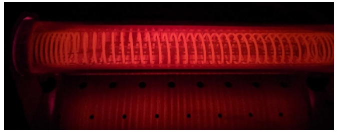
- The SStAC tool functions in 1D, 2D, and 3D

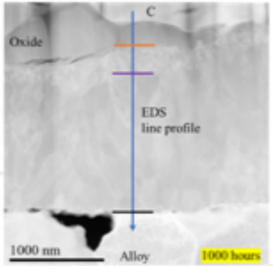
Specific properties and models are determined and passed up the scale

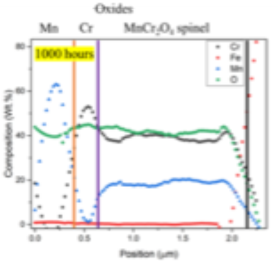


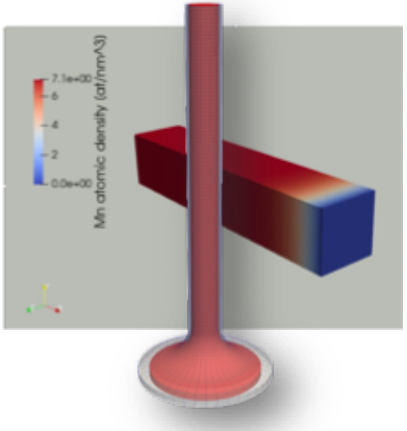






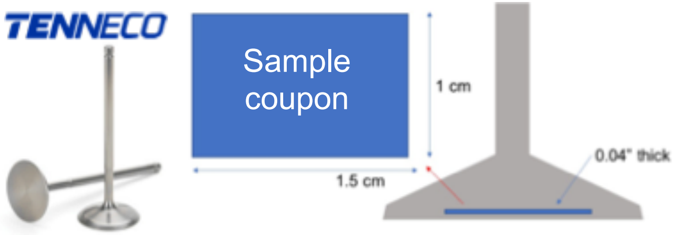




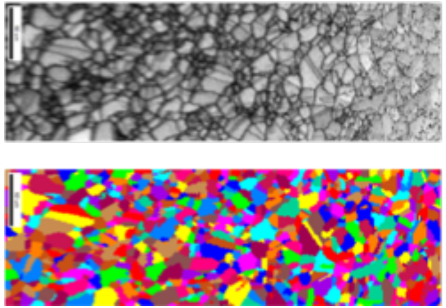


Technical Accomplishments and Progress: Review of Experimental Approach

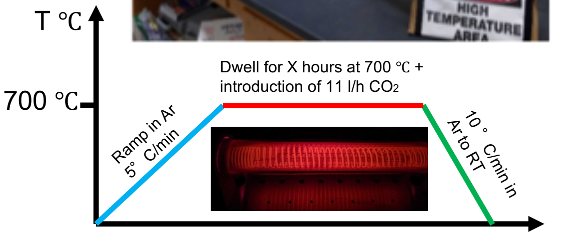
Initial Sample Preparation and Characterization



Average grain size: 9.4 μm

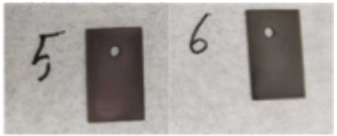


Corrosion at 700 °C for up to 1000 hours with controlled gas composition



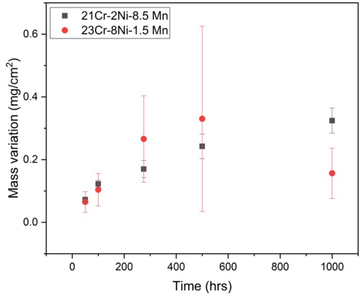
Two valve alloys are investigated:

21Cr-2Ni-8.5Mn



23Cr-8Ni-1.5Mn

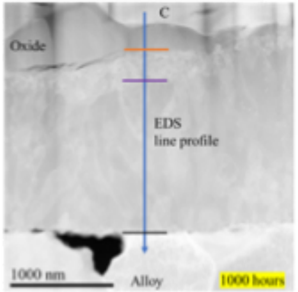
Oxidation kinetics

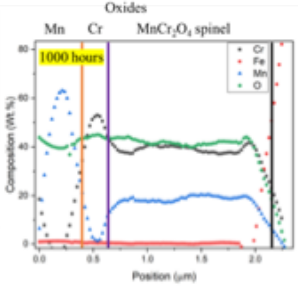


21Cr-2Ni-8.5Mn has parabolic growth but spallation observed in 23Cr-8Ni-1.5Mn

Nanoscale characterization

Oxide growth rate is limited by p-type $MnCr_2O_4$ spinel inner oxide growth



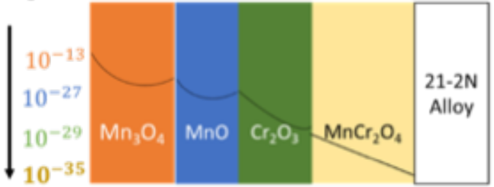


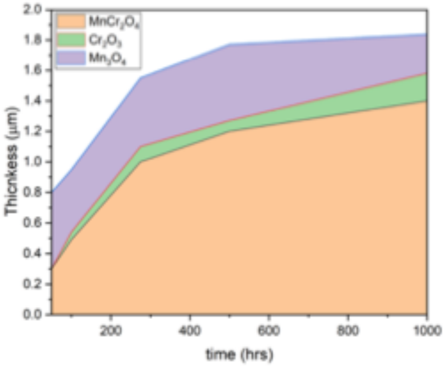
Technical Accomplishments and Progress:
21-2Ni-8.5Mn Alloy Characterization

Thermodynamic analysis

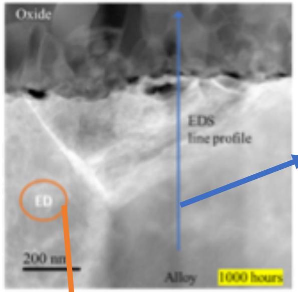
Observed oxidation progress agrees with thermodynamic data

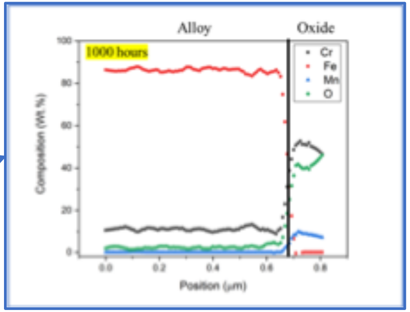
PO_2(atm) in CO2 at 700 °C ~10^{-8}

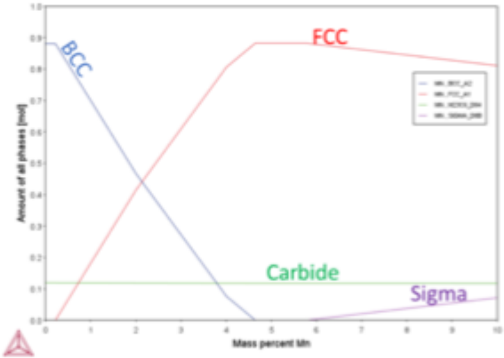




BCC transformation near metal/oxide (M/O) interface due to Mn Depletion

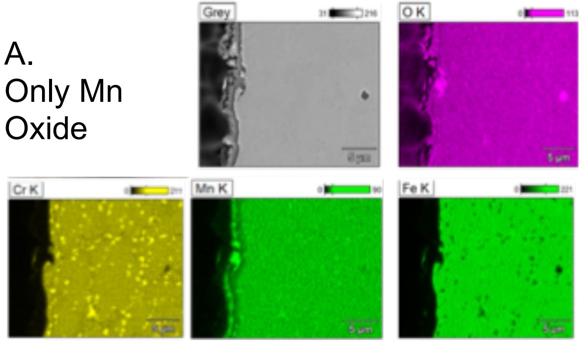




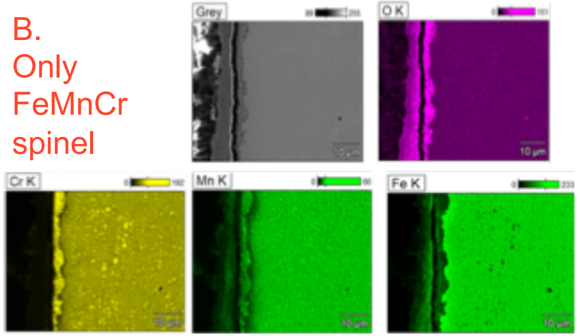


Characterization of engine-tested valves (lower temperature)

A. Only Mn Oxide

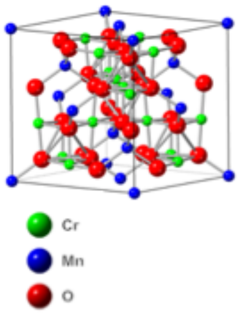


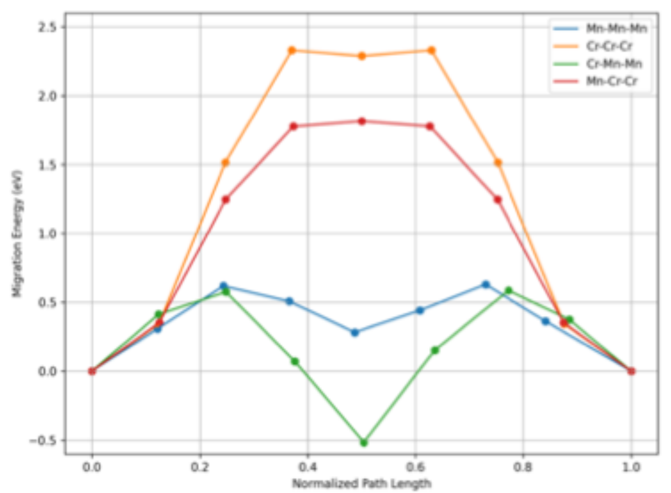
B. Only FeMnCr spinel



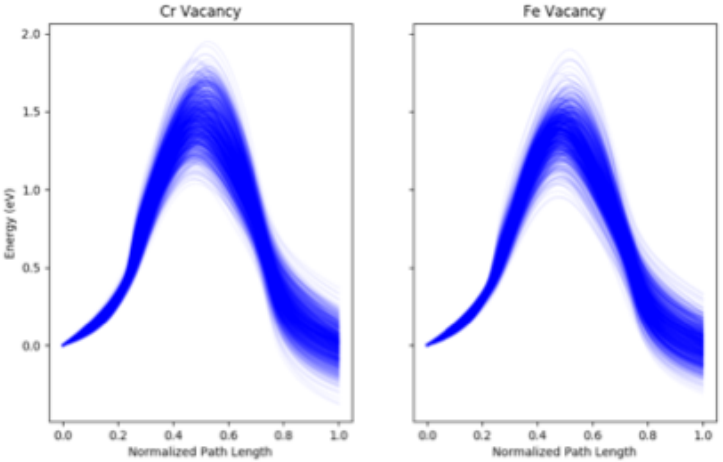
Technical Accomplishments and Progress: Atomic-Scale Simulations

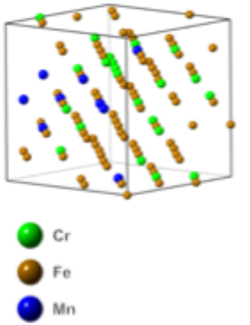
- Nudged elastic band calculations with density functional theory (DFT) and molecular dynamics (MD) are used to determine diffusion barriers
  - We have investigated the diffusivity of metallic species in both alloy and oxide phases





Vacancy and vacancy + anti-site migration profiles for cations in the $MnCr_2O_4$ spinel phase





An ensemble of Fe and Cr vacancy migration profiles in a disordered FeCrMn simulation cell

Technical Accomplishments and Progress: Mesoscale Simulation

Development

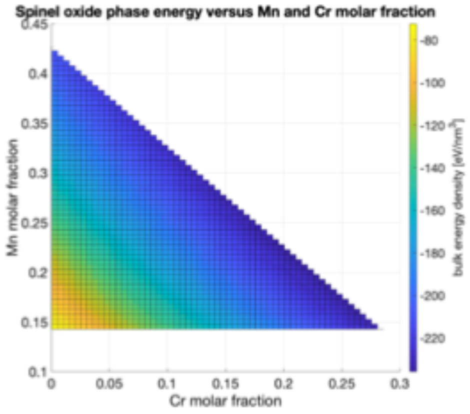
- Mesoscale model is based on CALPHAD free energies
- Diffusivities are taken from atomic simulation results

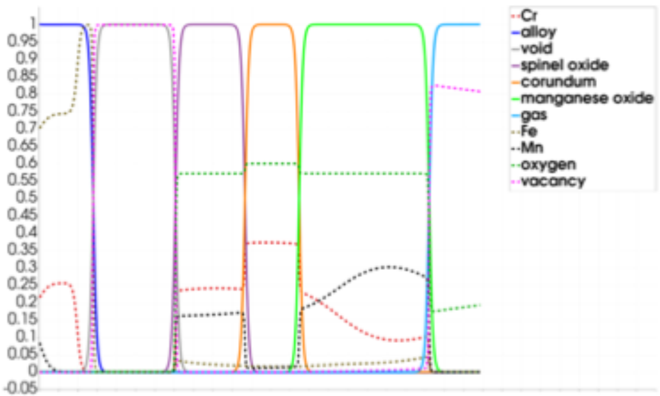
Capabilities

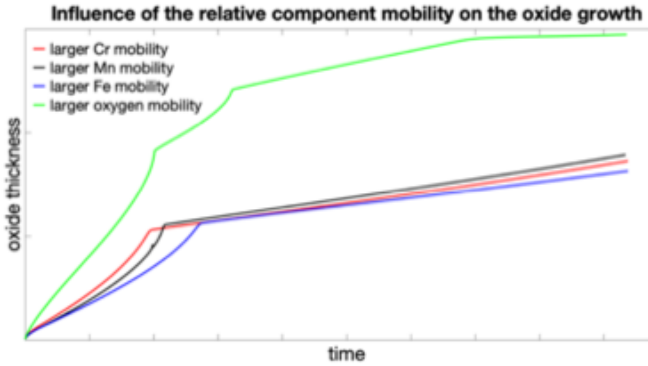
- Model predicts the growth of Cr, Mn, and Cr-Mn oxides
- Also represents vacancy transport and void growth

Results

- We have used the model to investigate mechanisms for oxide growth by comparing to experimental data







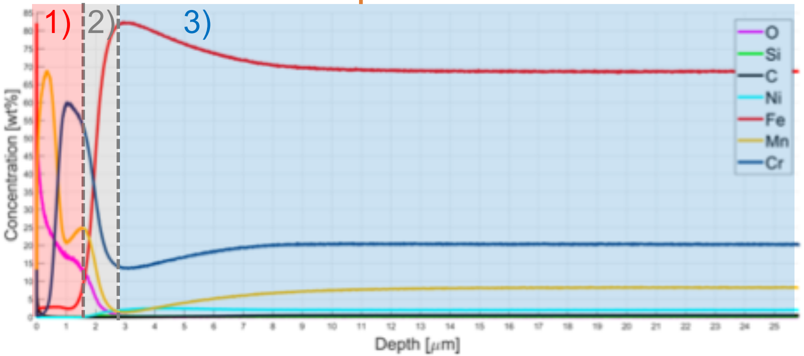
Technical Accomplishments and Progress:

Macroscale Corrosion model

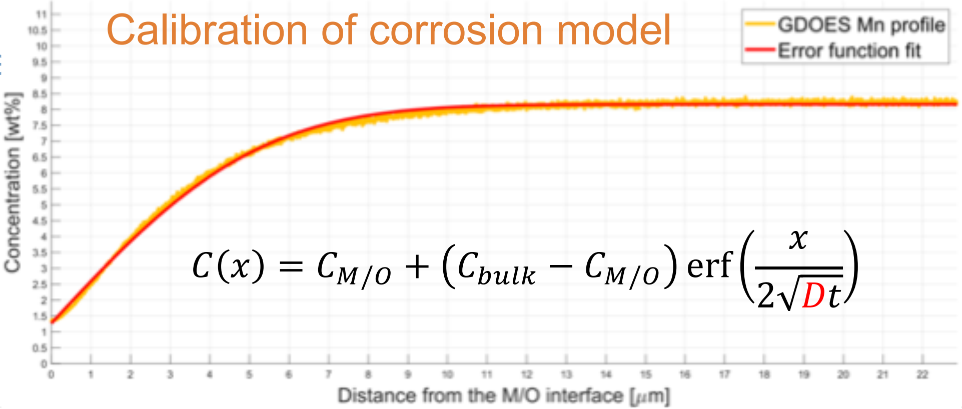
Model summary

- The model now accounts Mn depletion near the M/O interface.
- Primary assumptions:
  - Oxide formed is $MnCr_2O_4$
  - Corrosion rate is limited by Mn diffusion in the metal not in the oxide
  - Interfacial reactions are at pseudo-equilibrium
  - The Mn vacancy flux in the oxide is equal to the Mn flux at the M/O interface
- Calibrated parameters:
  - Mn/Cr diffusion coefficient D in the alloy
  - Initial concentration gradient at M/O interface

GDOES experimental data



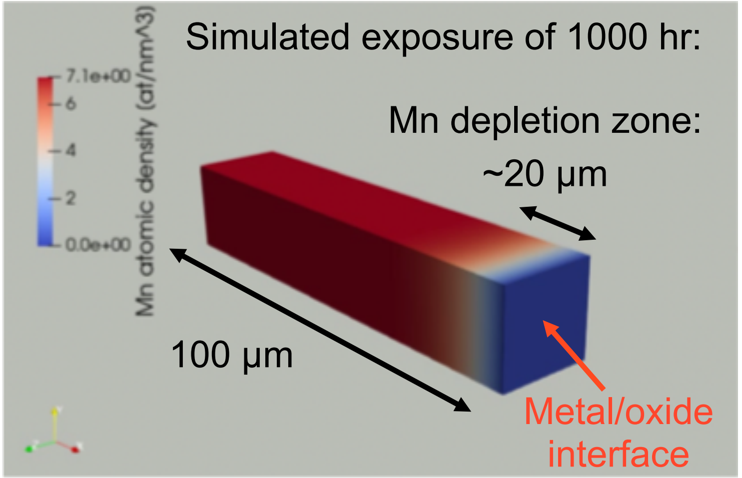
1) Oxide, 2) M/O interface, 3) Alloy

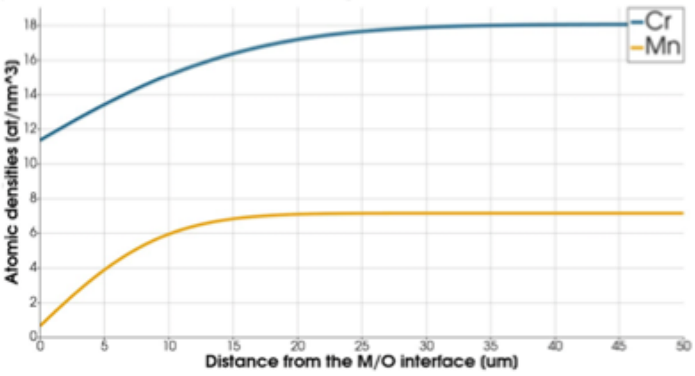


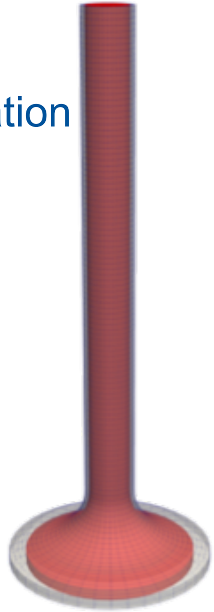
$$C(x) = C_{M/O} + \left(C_{bulk} - C_{M/O}\right)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Technical Accomplishments and Progress:
SStAC tool implementation

- SStAC tool has been created using the finite element method with the MOOSE framework to solve the corrosion model in 1D, 2D, and 3D
  - Oxide growth can be directly modeled using X-FEM
  - It can also be implied from Mn and Cr depletion for a more efficient simulation

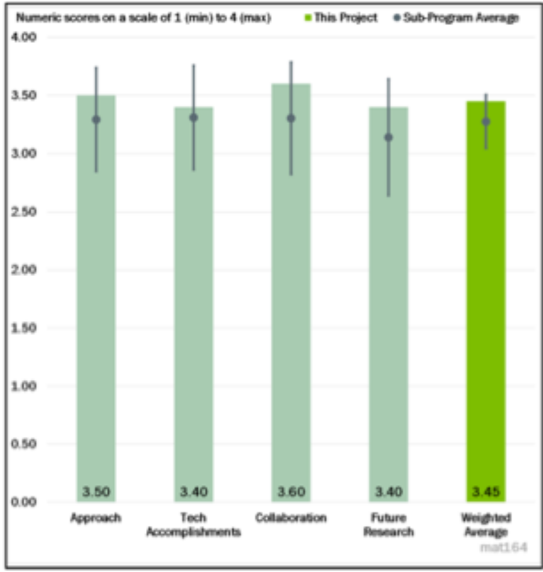






Response to previous year reviewers' comments

- The alloy systems that the team is currently working on are too simple model alloys.
  - The 21-2N and 23-8N valve steels we are considering are engineering alloys used by TENNECO and other vendors
- The experimental data to evaluate corrosion condition seem to be the mass variation only. Does the PI consider including microstructure information?
  - In addition to weight gain measurements, we have done extensive microstructure characterization using SEM, EDS and TEM
- What methodology will the project team use to validate the developed SStAC tool?
  - We will directly compare the SStAC tool predictions with data from TENNECO engine tests and from our laboratory tests.



Collaboration and Coordination with Other Institutions

WISCONSIN UNIVERSITY OF WISCONSIN-MADISON: Developing macroscale SStAC tool, carrying out laboratory corrosion experiments and analyzing corroded samples

INL Idaho National Laboratory: Providing mentorship and guidance on the application and development of MOOSE

TENNECO: Providing engine valve material, sample preparation, and carrying out engine testing

We meet monthly as a team with more frequent interactions between specific team members

Remaining challenges and barriers

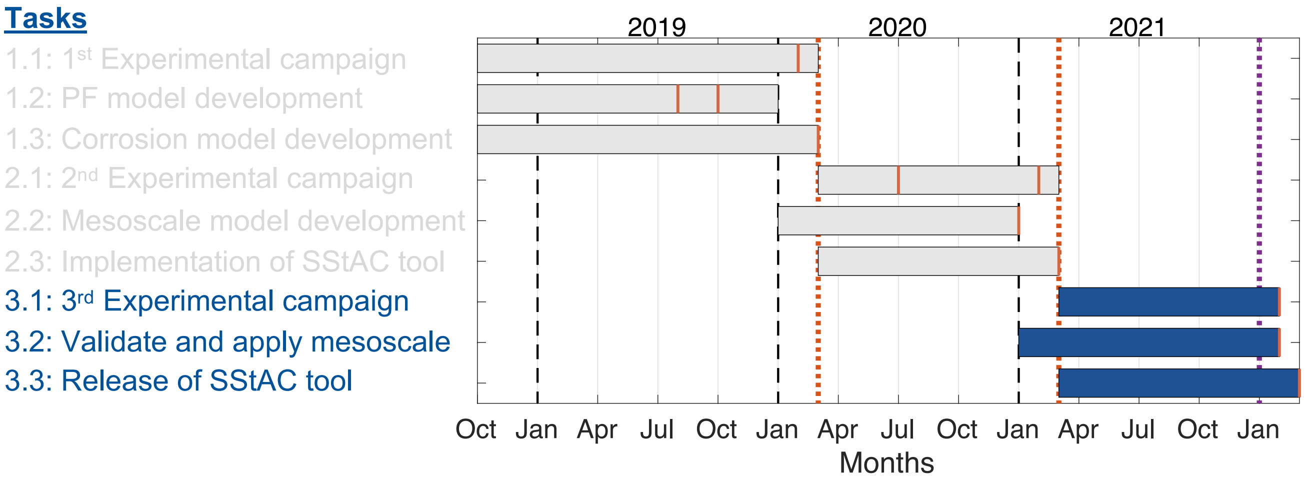
- We have not yet determined the impact of gas composition and temperature cycling on the alloy corrosion
- The SStAC tool does not yet consider the impact of microstructure and alloy composition
- The SStAC tool has not yet been validated for various alloys and engine conditions

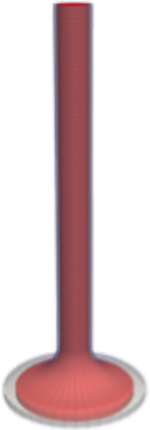
Proposed Future Research
(subject to change based on funding levels)

- **Experimental work**
  - Carry out corrosion tests with water vapor and CO2 and with temperature cycling
  - Carry out high temperature engine tests at TENNECO
  - Characterize the microstructure of all corroded samples
- **Mesoscale simulations**
  - Calculate formation and migration energies in more phases with DFT and MD.
  - Quantify the impact of microstructure and alloy composition on corrosion with the mesoscale tool
- **SStAC tool development**
  - Add capability to consider alloy composition and microstructure using mesoscale results
  - Validate against data from the literature, TENNECO, and from the project.

Summary

- The Stainless Steel Alloy Corrosion (SStAC) tool will
  - Be open-source, based on the MOOSE framework
  - Include impact of microstructure and alloy composition from lower length-scale simulations
  - Be validated using new data from laboratory and engine testing





Herbert Wertheim
College of Engineering
UNIVERSITY *of* FLORIDA

POWERING THE NEW ENGINEER TO TRANSFORM THE FUTURE