High Performance, High Temperature Materials to Enable High Efficiency Power Generation: June 2022 Project Update

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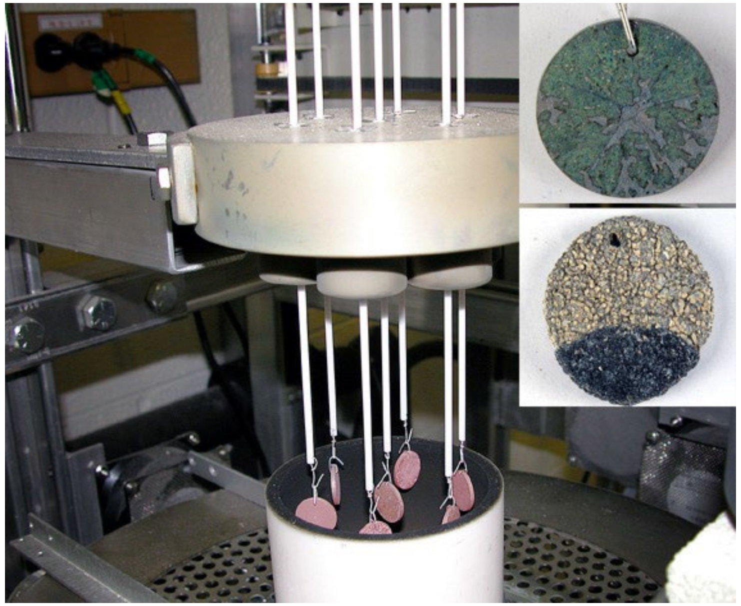
Oak Ridge National Laboratory

June 2022

Corrosion Science & Technology Group Mission:

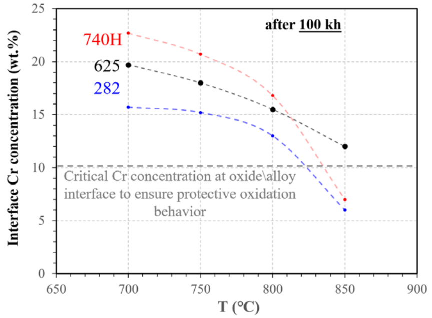
Develop corrosion solutions for all forms of power generation and transportation

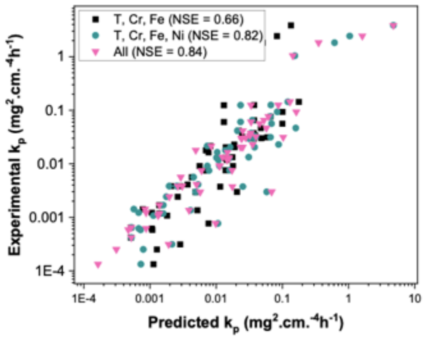
Thermal convection loops determine compatibility in flowing salts or liquid metals



Thermal cycling simulates turbine and automotive duty cycles to evaluate new alloys or coatings

Unique: cycling in controlled gas up to 1500°C





Machine learning and thermo-kinetic models being employed to predict performance

Field & engine tests to validate performance models (e.g. Capstone 65kW microturbine)

- Expertise covers aqueous and high temperature corrosion
- Solutions include material selection, lifetime modeling, process modification and new alloy or coating development

CST Group has broad expertise solving corrosion issues

- Experience with a range of environments
  - Aqueous
    - Transportation
    - Nuclear reactors
  - High temperatures
    - Steam, air+H_2O (exhaust)
    - Mixed gases (H, O, C, S)
    - Supercritical CO_2
    - He
  - Biomass
    - Wide range of feedstocks
  - Molten salts
    - Nuclear & concentrated solar
  - Liquid metals
    - PbLi, Li and Sn for fusion
    - Previously Pb, Hg and Na

- ❑ Provide better understanding and prediction of materials performance
- ❑ Aid in materials development and selection
- ❑ Advance a technology
- ❑ Solve a particular industrial problem
- ❑ Not in competition with private industry

3-year DOE CHP project : Higher Performance/ Temperature & Lower-Cost Materials To Increase CHP System Efficiency

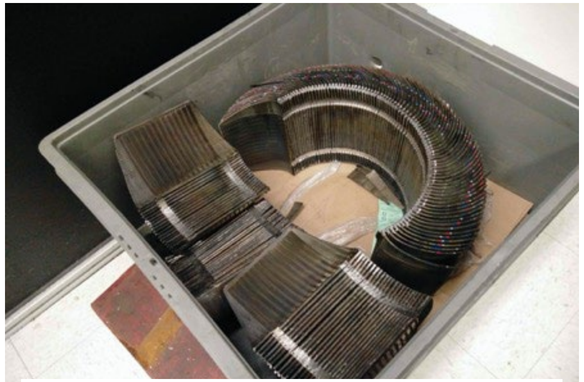
Alloy Selection & Development

Degradation mechanisms Lifetime models

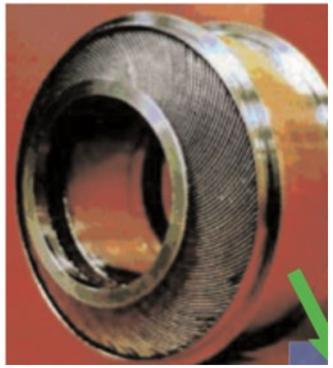
Mechanisms / Models validation

- Alumina forming austenitic (AFA) Fe- and Ni-based alloys
- High performance, lower cost austenitic alloys
- Corrosion- and fatigue-resistant coatings

- Cyclic oxidation and mechanical testing
- Mechanical testing in relevant environments
- Engine exposures
- Predictive lifetime models



Rainbow recuperator

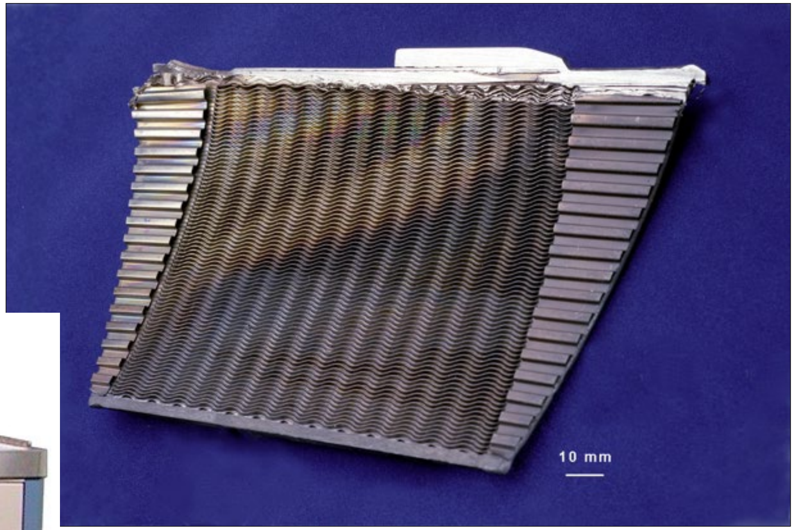


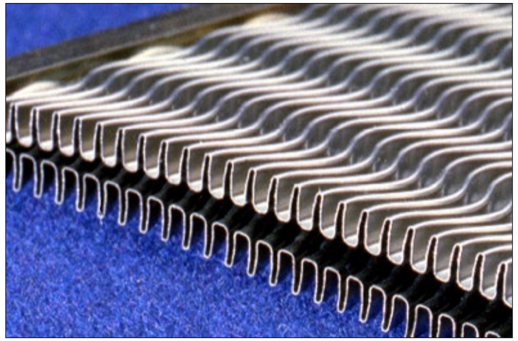
Project Tasks Related to Different Components & Material/Coating Needs

- **Task 1: Lifetime modeling & alloy evaluations for high-temperature thin-wall components**
  - *Primary surface recuperator (heat exchanger) and combustor liner*
  - *Comparison of laboratory and field exposures for model validation*
- **Task 2: Investigation of materials for ≥100°C temperature increase**
  - *Higher temperature heat exchangers and combustor liners*
  - Commercialization of wrought Ni-based alumina-forming alloy
- **Task 3: High performance corrosion-resistant coatings for prime movers**
- **Task 4: Advanced characterizations for CHP Materials and Coatings (ANL)**

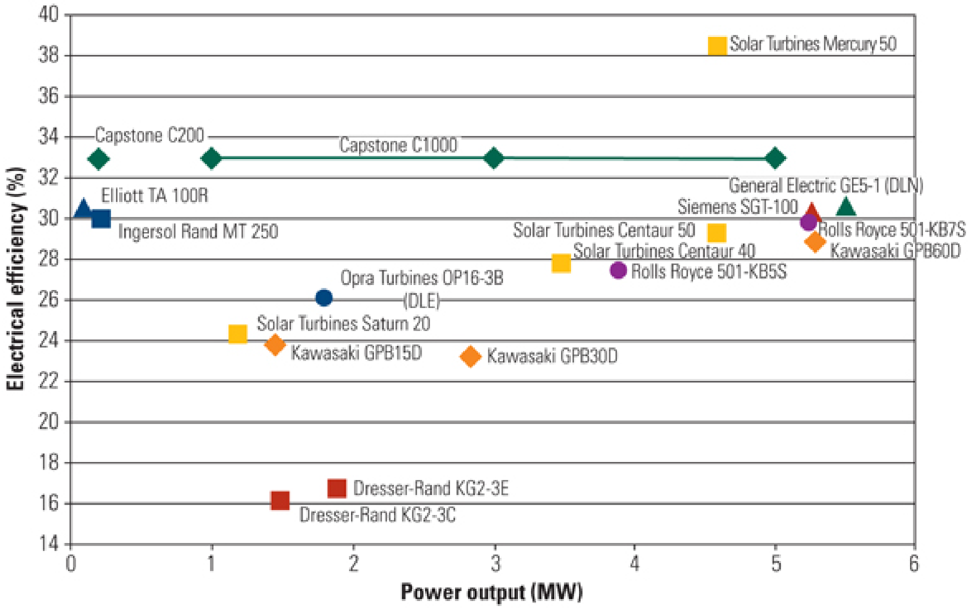
Recuperators Are Compact Heat Exchanges that Significantly Boost the Efficiency of Microturbines (2005 slide)

Capstone 200 kW Microturbine





Primary Surface Recuperator (PSR), annular configuration



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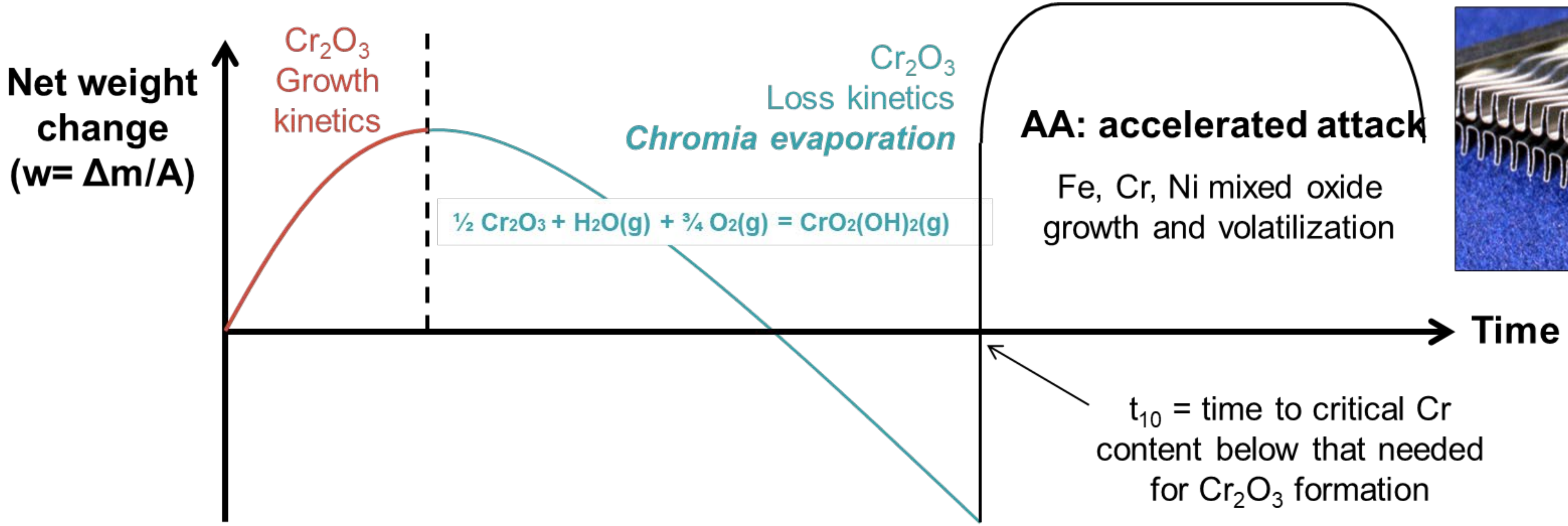
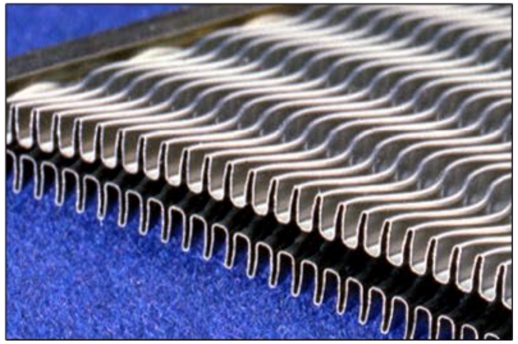
Task 1: Long-term recuperator performance: what are we modeling ?





Net weight change = **Weight of metal oxidized** – **weight of scale vaporized**

Time < t_{10}
1: Cr_2O_3 formation

$$\frac{dw}{dt} = \frac{d}{dt}\left(\left(\frac{1}{a1}\right) w_{m1}\right) - \frac{d}{dt}\left(w_{ox,ev1}\right)$$

Update
Time > t_{10}
2: Mixed oxide formation

$$\frac{dw}{dt} = \frac{d}{dt}\left(\left(\frac{1}{a2}\right) w_{m2}\right) - \frac{d}{dt}\left(w_{ox,ev2}\right)$$

Mass transfer theory for laminar flow over a rectangular plate

$$w_{ox,ev} = 0.664\left(\frac{p^{(i)}p^{(0)}}{RT}\right)\left(\frac{D^4}{\nu}\right)^{\frac{1}{6}}\left(\frac{u}{l}\right)^{1/2} M_{Cr}$$

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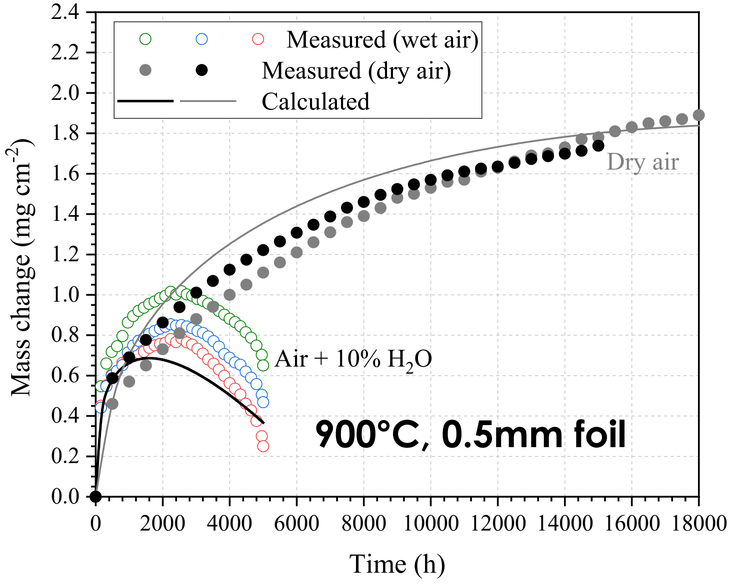
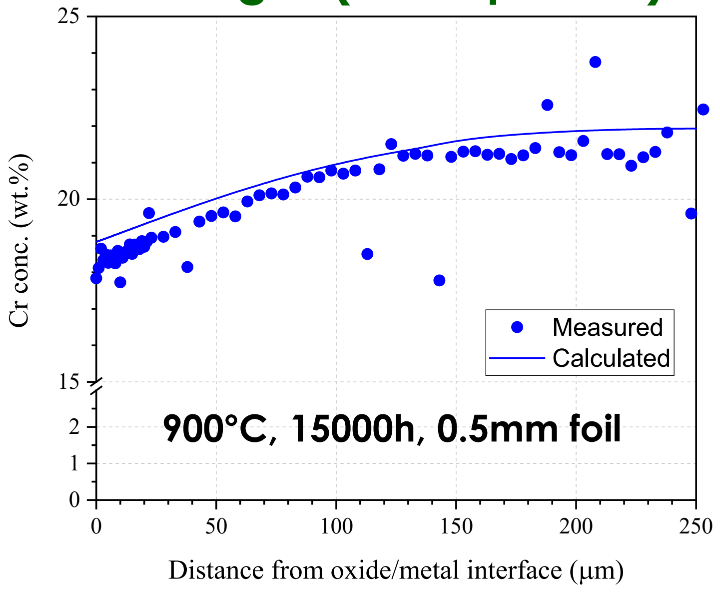
Task 1. Modeling Approach/Development

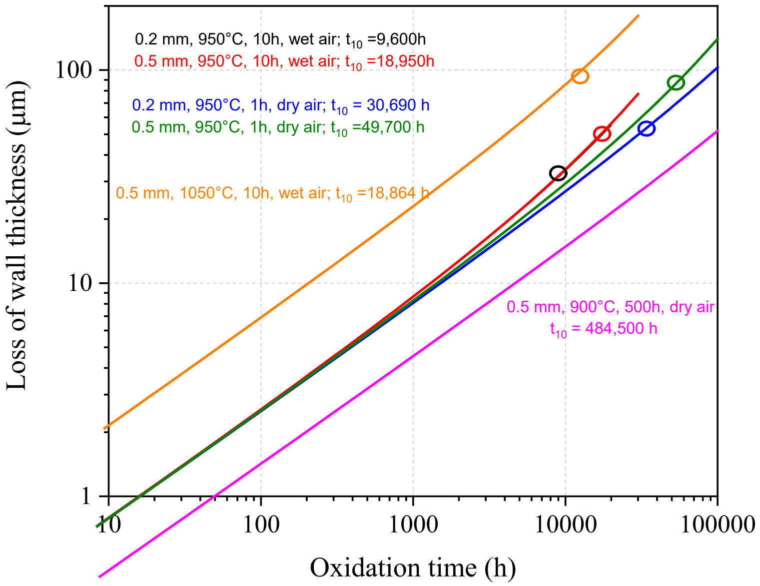
Predict oxidation kinetics



Predict compositional changes (Cr-depletion)



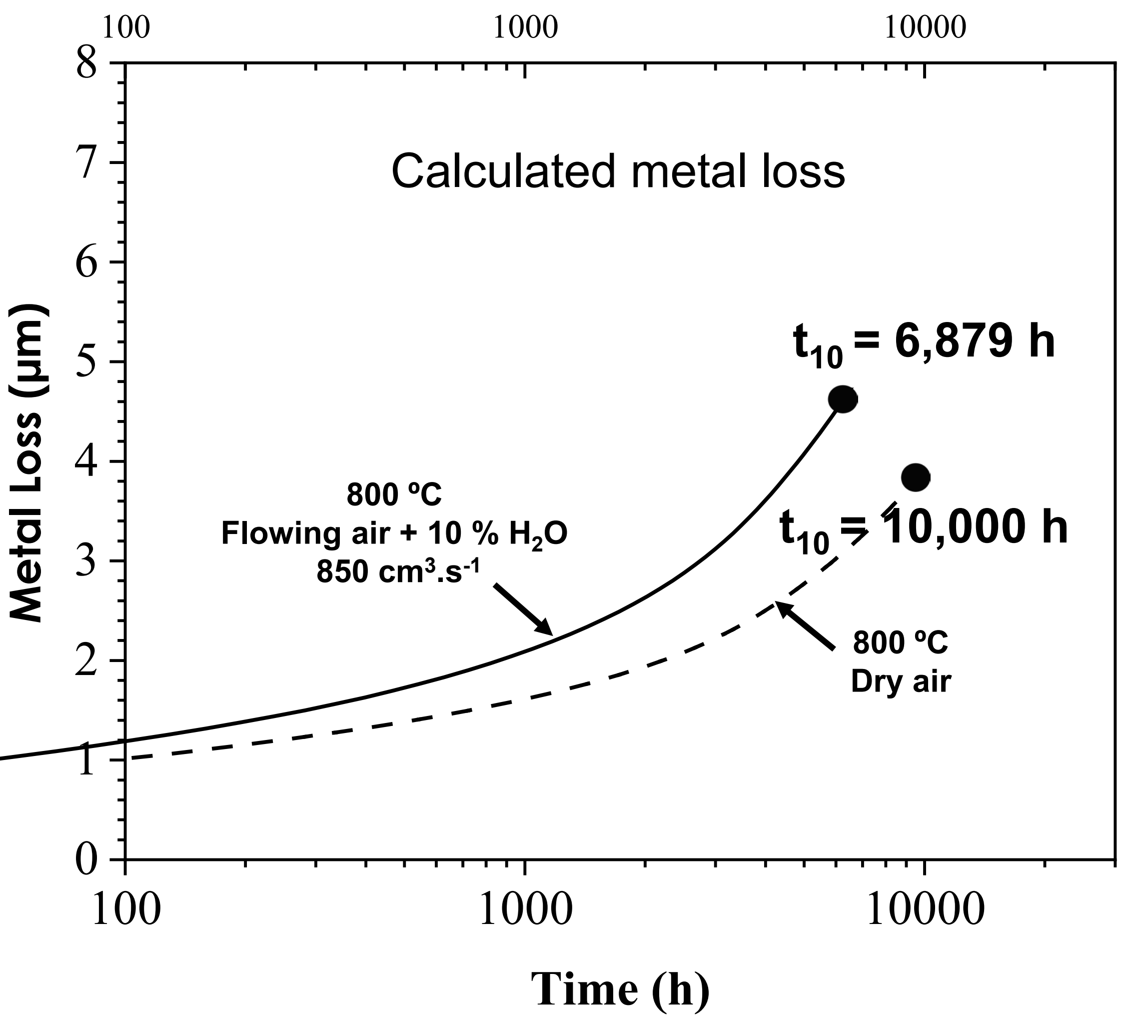
Oxidation lifetime diagram



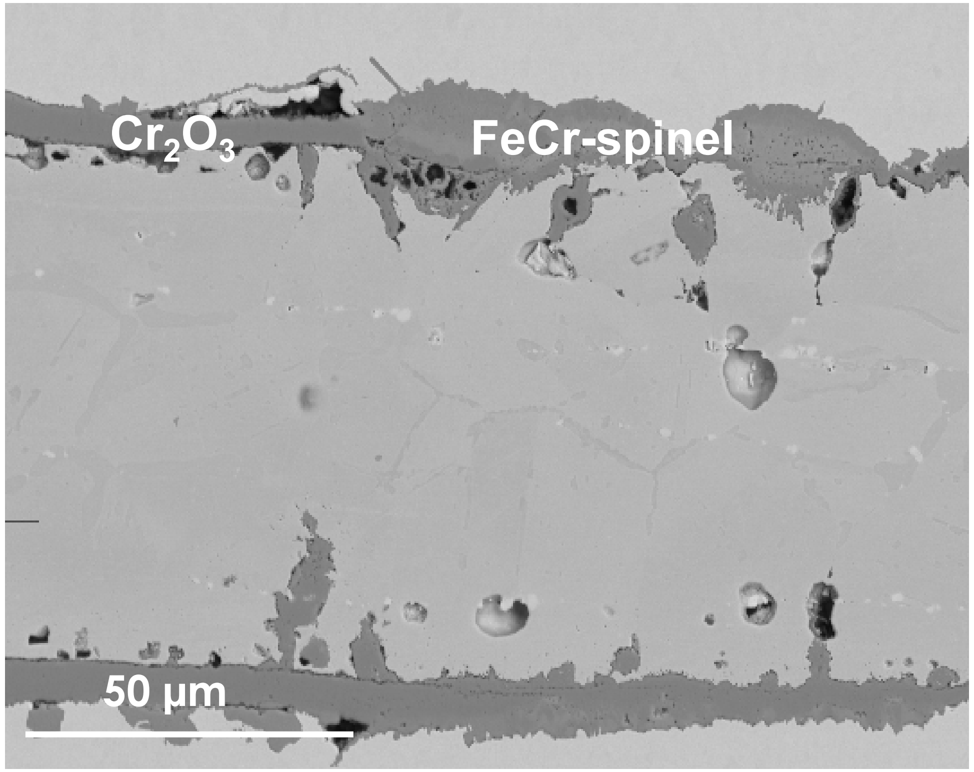
- Predict
  - oxidation kinetics
  - compositional changes (time to 10 wt.% concentration of Cr at scale\alloy interface, critical concentration)
  - loss of wall thickness

as a function of time, temperature, specimen thickness, thermal cycle duration and atmosphere

Alloy HR120 (25Cr-35Ni): Cr_2O_3 breakdown in dry and wet air



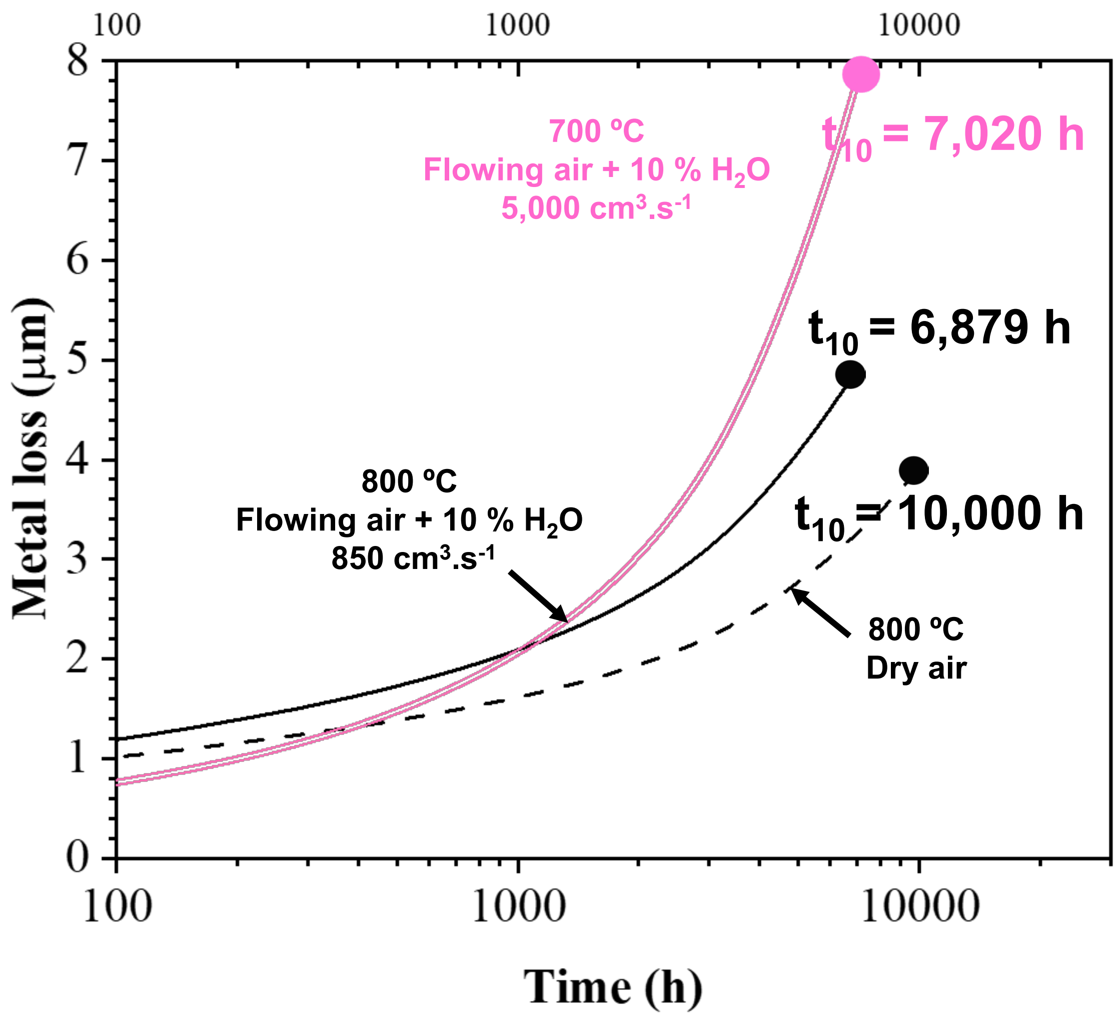
Dry air
10,000 h at 800 ºC

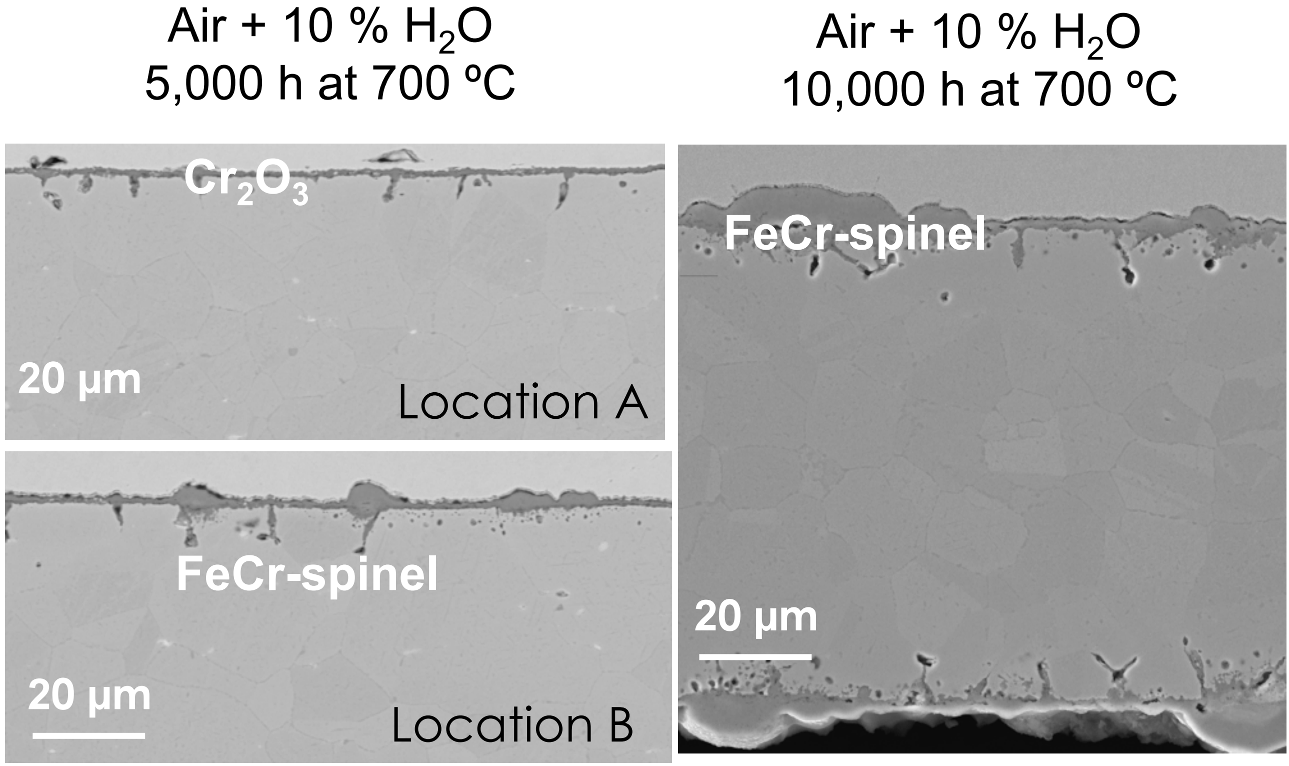


✓ Cr_2O_3 breakdown/ t_{10} was predicted before 7,500 h in wet air

✓ t_{10} was predicted after 10,000 h and coincides with localized formation of FeCr-spinel in dry air

Alloy HR120 (25Cr-35Ni): Cr_2O_3 breakdown in dry and wet air





✓ Cr_2O_3 breakdown/ t_{10} was predicted before 7,500 h in wet air

✓ t_{10} was predicted after 10,000 h and coincides with localized formation of FeCr-spinel in dry air

✓ Cr_2O_3 breakdown/ $t_{10}$was predicted at 700 ºC and higher flow rate in wet air

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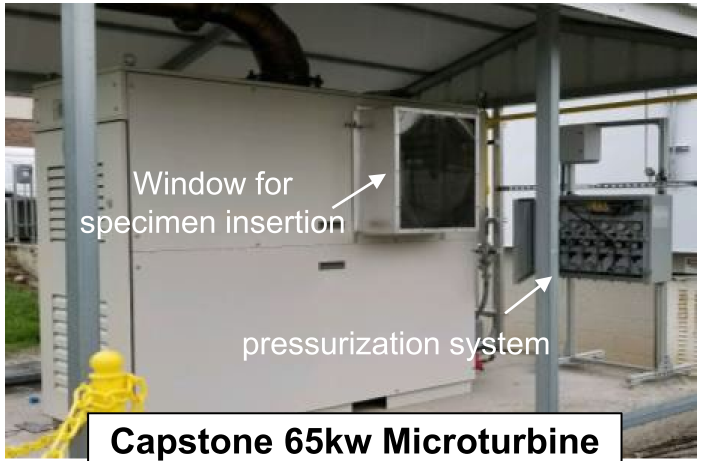
Data collection: laboratory tube furnace, ORNL microturbine & field - 65kW Capstone Microturbine provides prototypic results

- Microturbine has been modified in collaboration with Capstone to allow for higher temperature operation i.e. turbine exhaust temperature (TET) of 690°C
- Engine tests: rainbow recuperator made of AFA (Fe-14Cr-25Ni-3.6Al-2.5Nb), 120 (Fe-38Ni-25Cr) and 310 (Fe-20Ni-25Cr) alloy foils has been tested for :

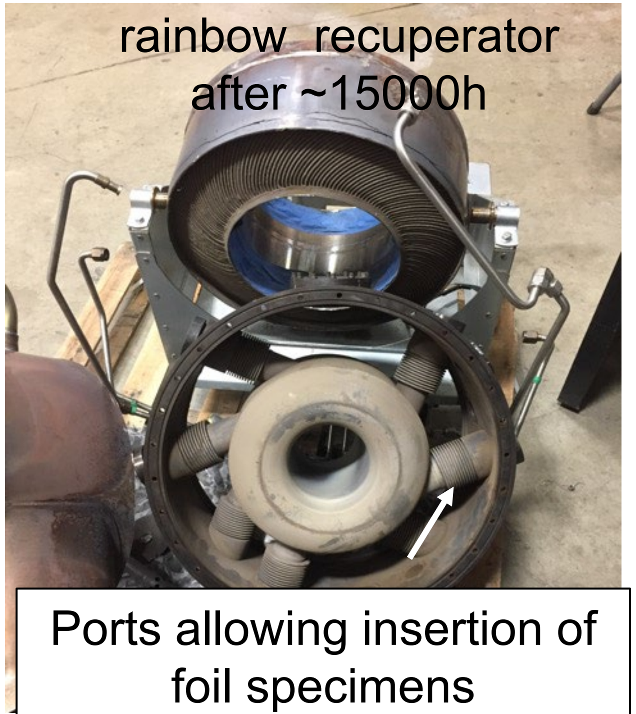
- 3350h in normal operation (65kW, TET~633 ºC)

- 15,000h at higher temperature (TET~690 ºC.)

- Microturbine is also used as a test facility with possibility to insert pressurized probes for material evaluation



Capstone 65kw Microturbine



Ports allowing insertion of foil specimens

Welded Foils, 3000h of exposure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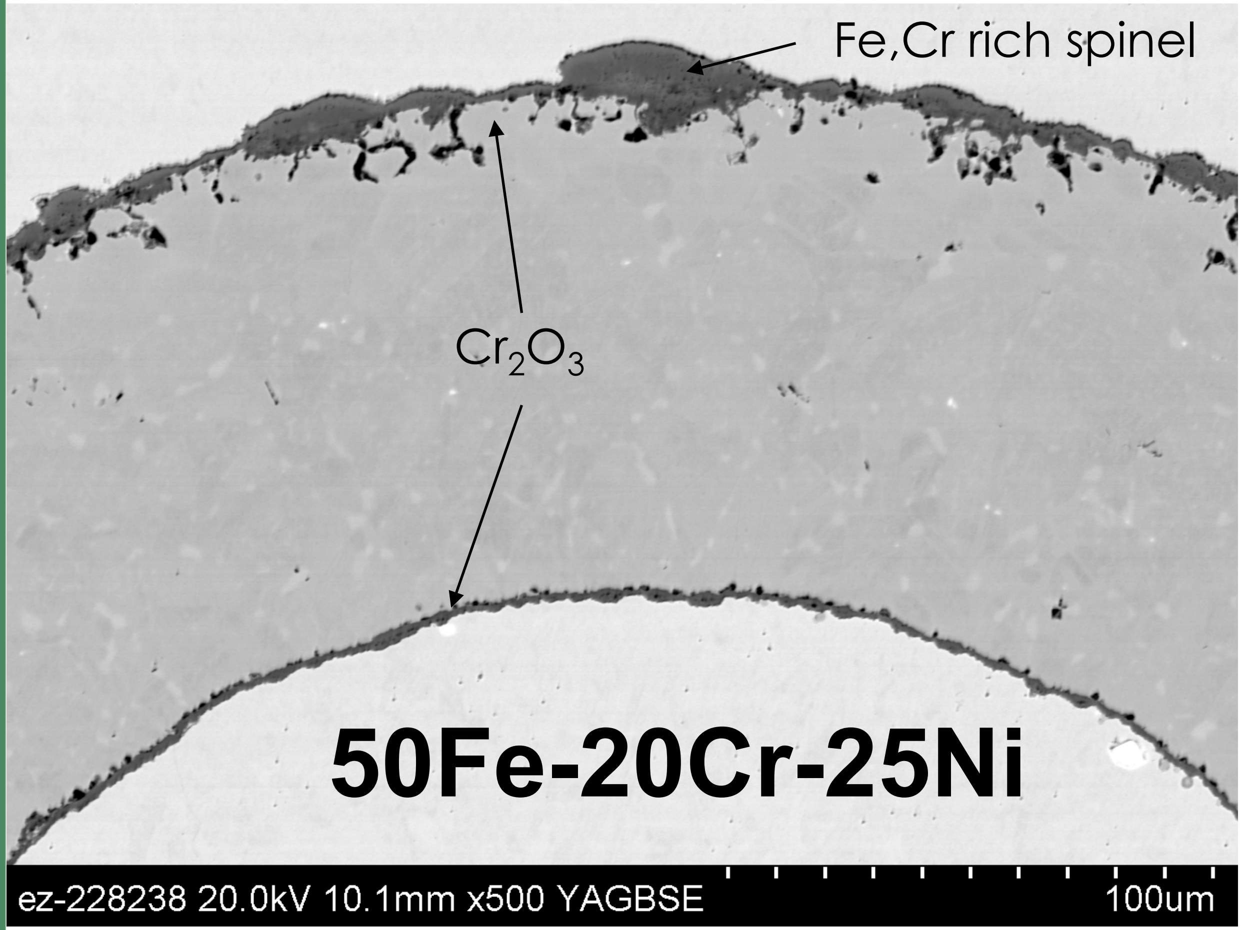
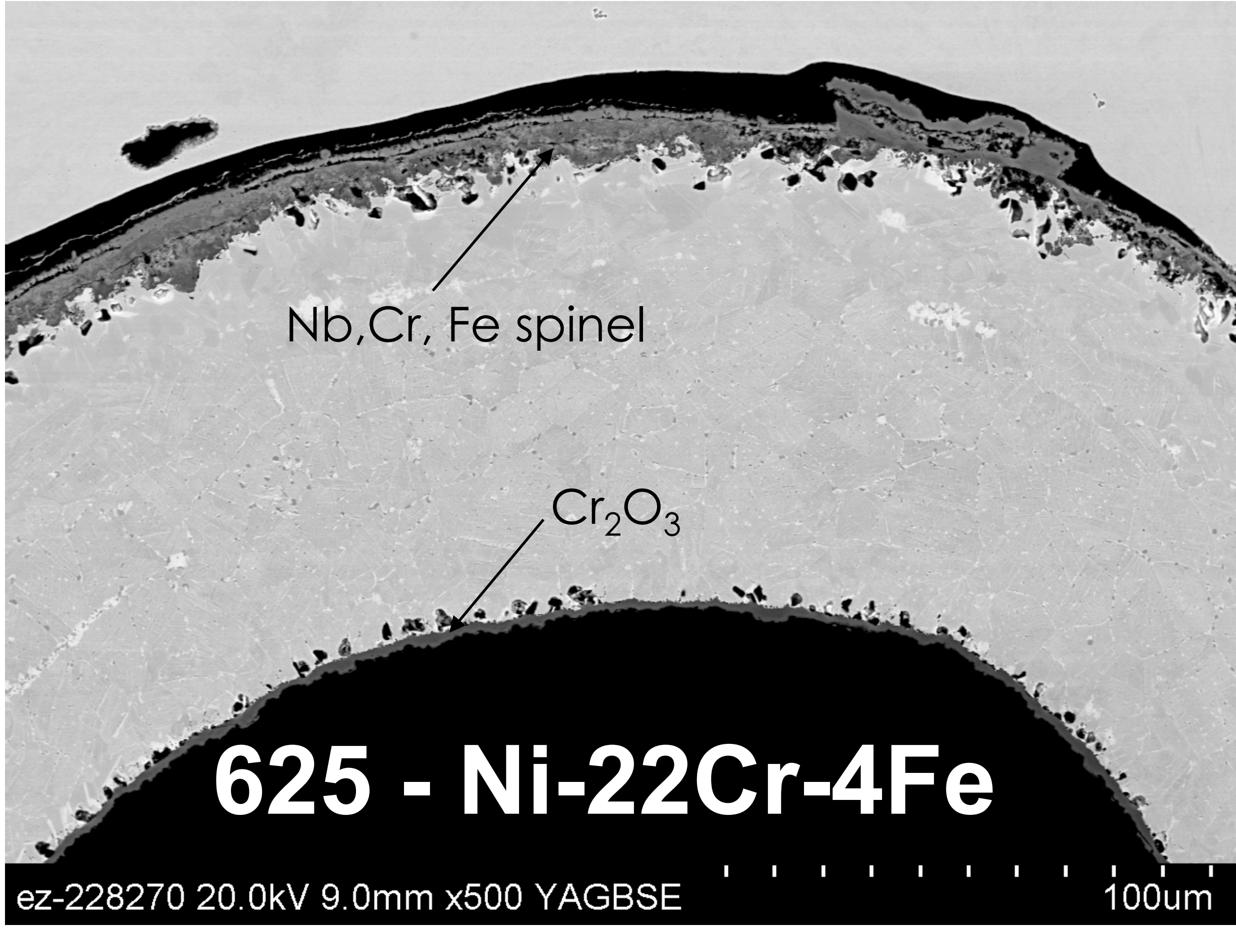
Task 1. Field exposures from Mercury 50 (4.6MW)

643 °C, air + 4-7% H_2O, 10-20 m/s (lab ~2 cm/s)

106,000 h: ~10 times longer than laboratory exposures





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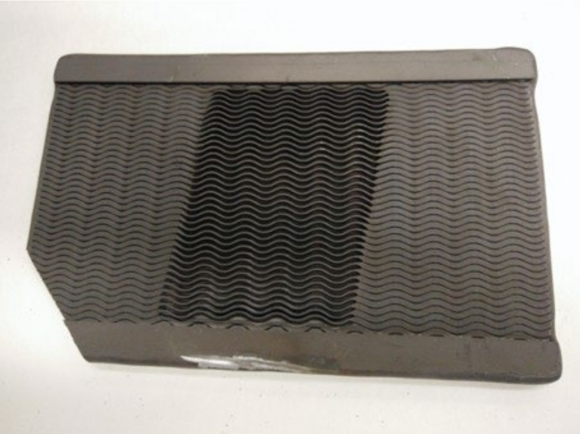
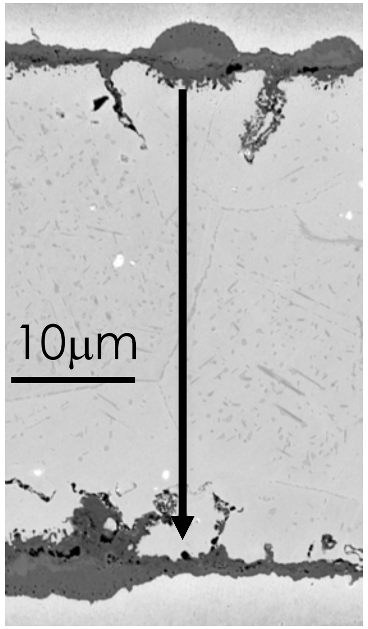
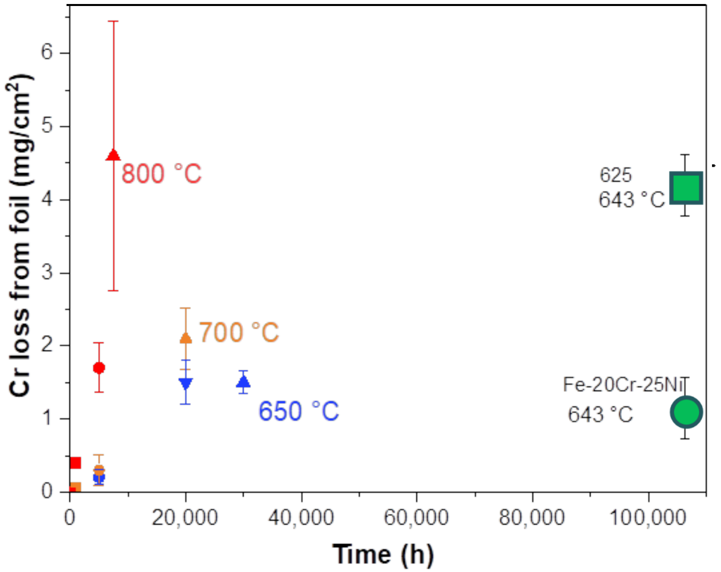
Field results: Model validation using Solar Turbine's Mercury 50 engine test for up to 106,360 h at ~643°C

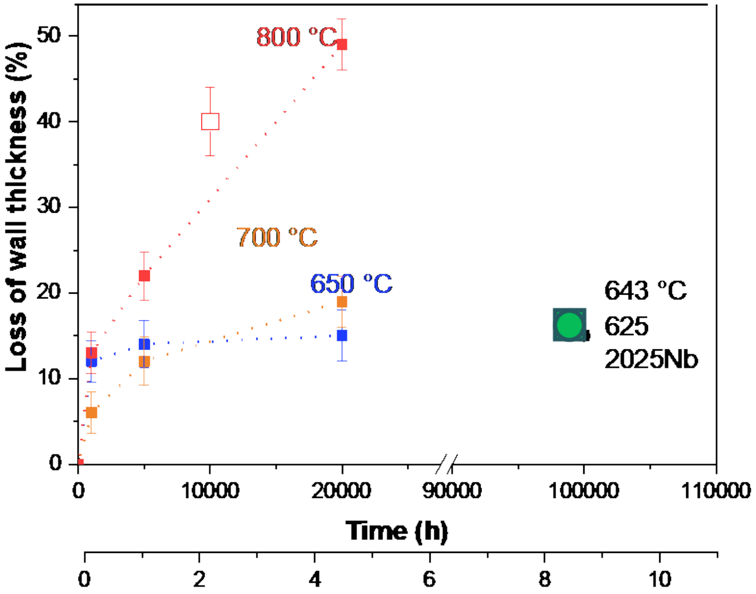
2025Nb panel



Measurement of Cr concentration over the entire foil + final foil thickness to

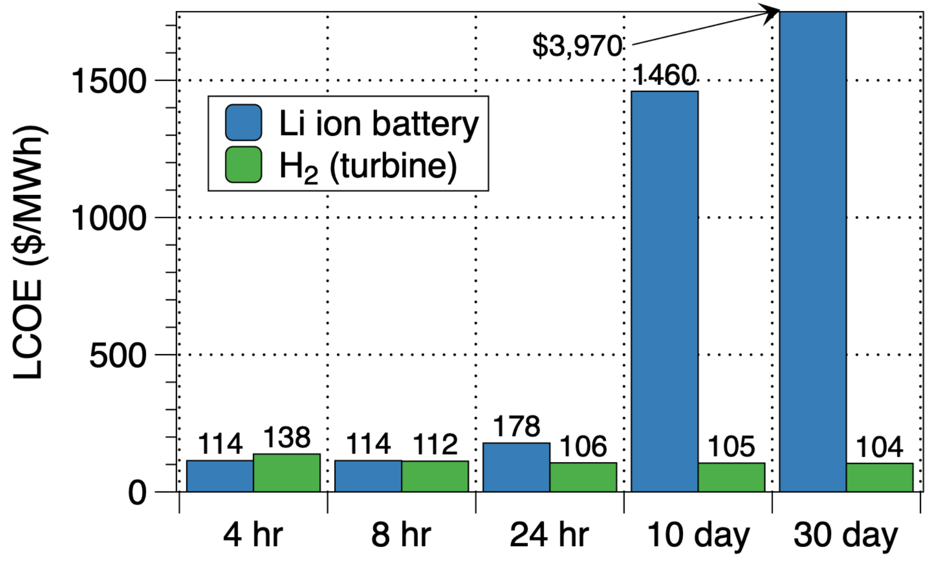






“Green” hydrogen is quickly becoming reality
Extreme environment of H_2 transportation, generation and combustion

- Project for 1GWh storage in Utah (operation in 2025)
- Japan already demonstrating 1MW 100% H_2-fired turbine
- Hydrogen current choice for long-term economical energy storage
- Match with distributed generation/CHP to avoid H_2 distribution cost/issues



Hydrogen attractive for long term storage

- Materials issues with:
  - Combustion – AM design to prevent flashback
  - Turbine* – higher flame temperature & higher H_2O exhaust issues
    - opportunity to use modeling to predict, followed by validation
  - Electrolyzer – improve efficiency & durability of H_2 production
  - Other areas: fuel cells, reciprocating engines, pipelines (transport)

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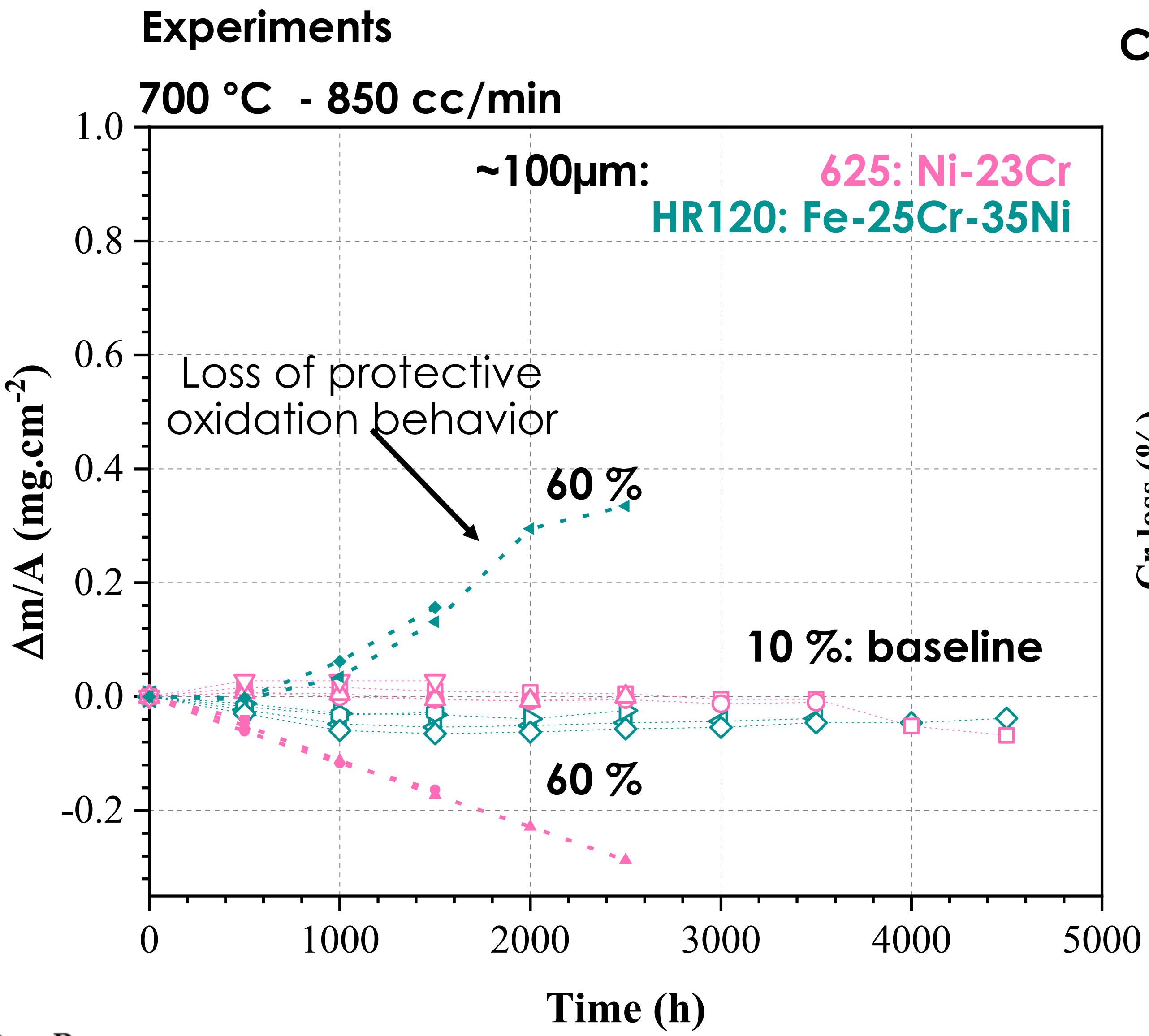
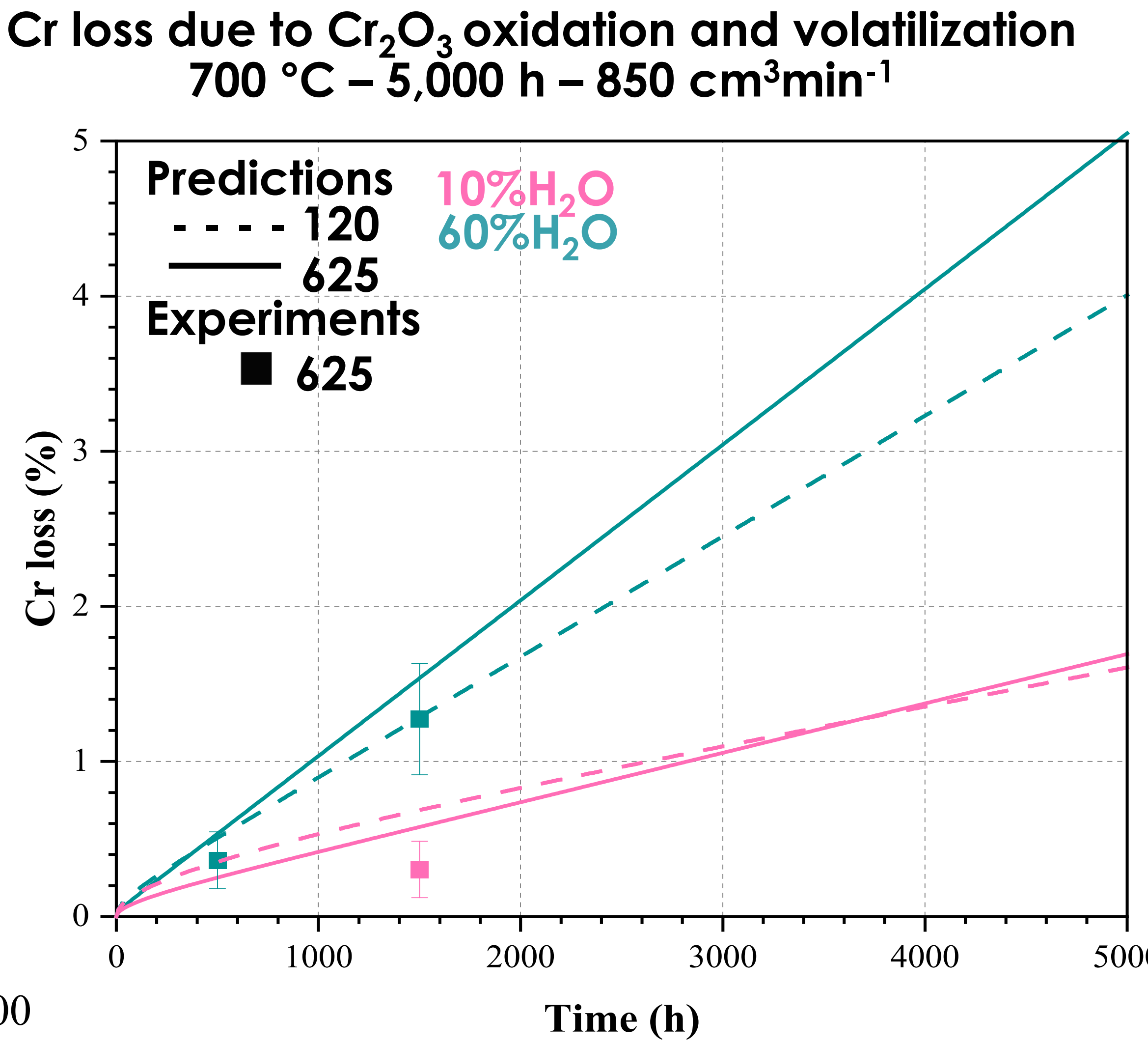
* EPRI report

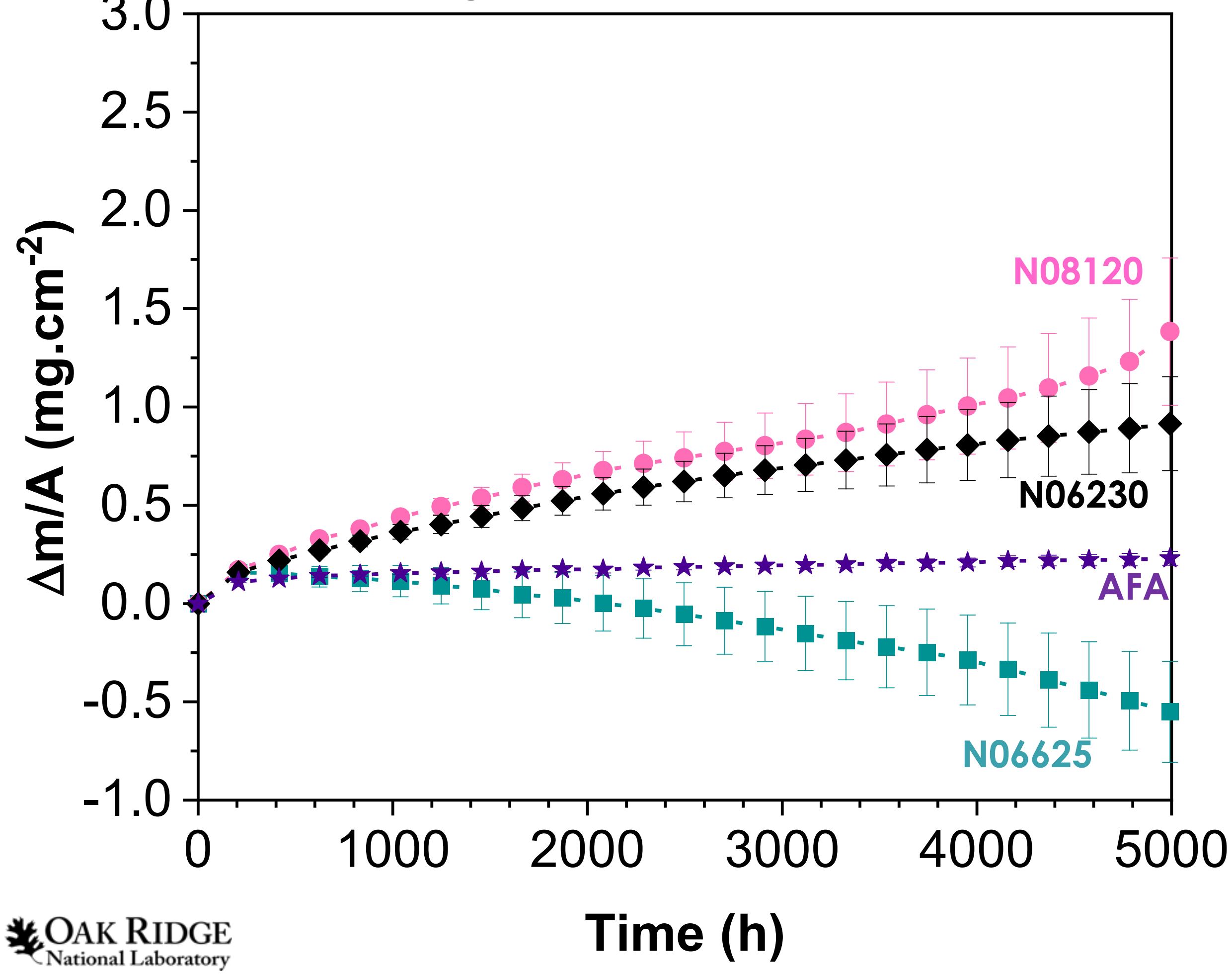
Burning H_2: validating model for higher H_2O levels





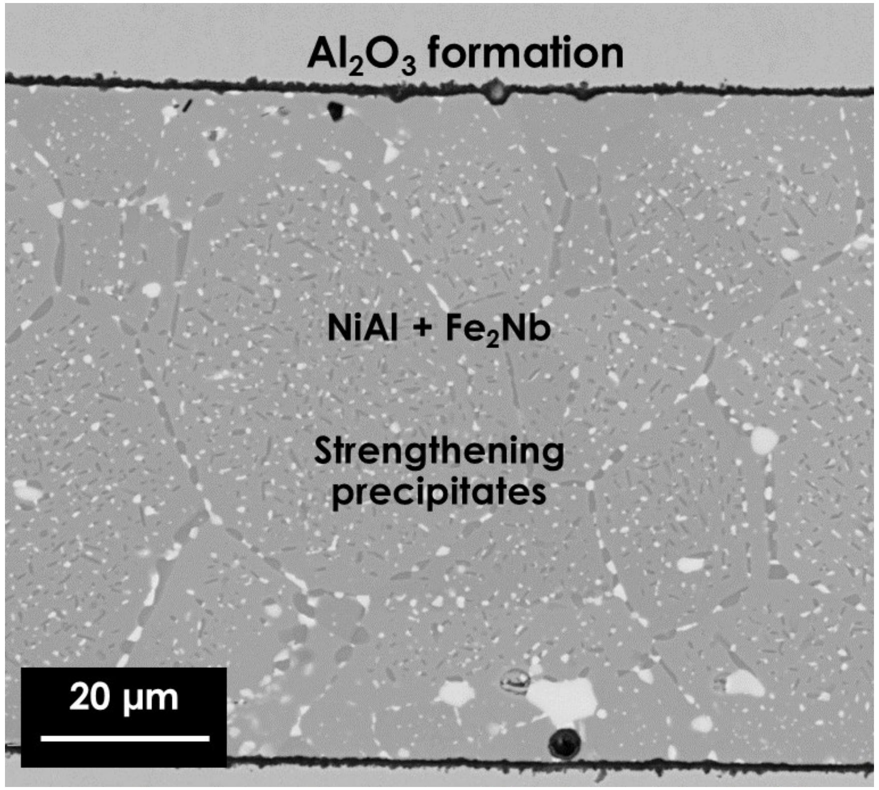
Task 2: >100°C higher temperatures
Alumina-forming austenitic steels at 850°C in wet air
- Al_2O_3 less affected by H_2O than Cr_2O_3

850°C- 100 h cycle
Mass change

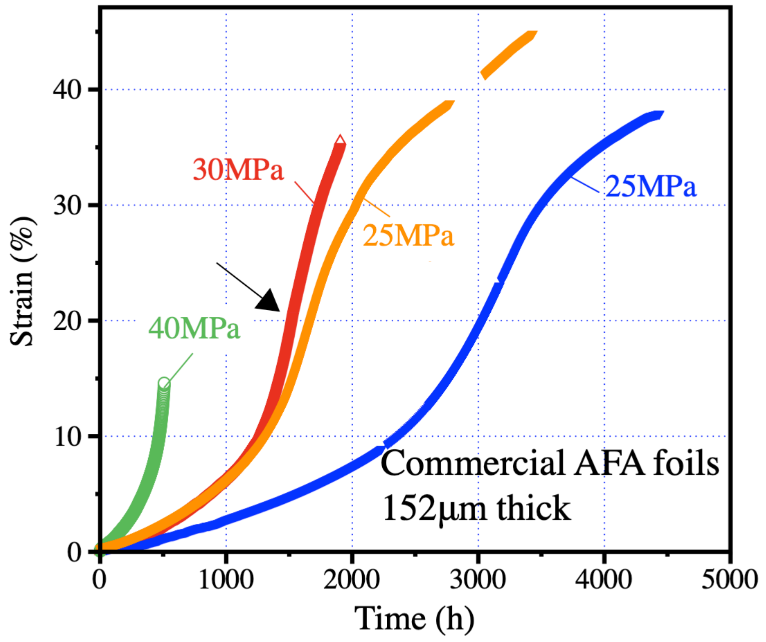


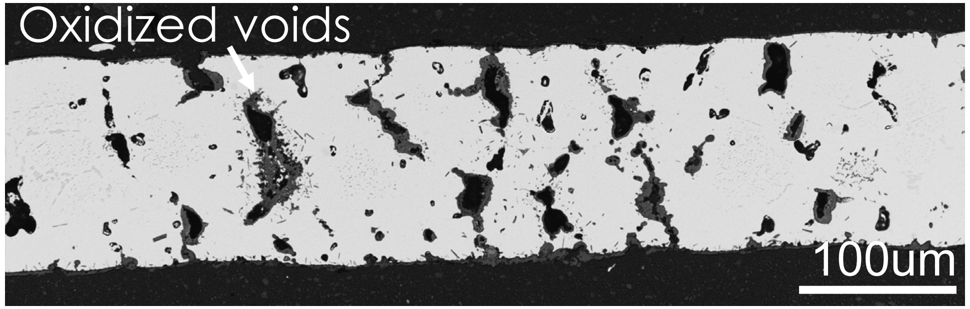
BSE image

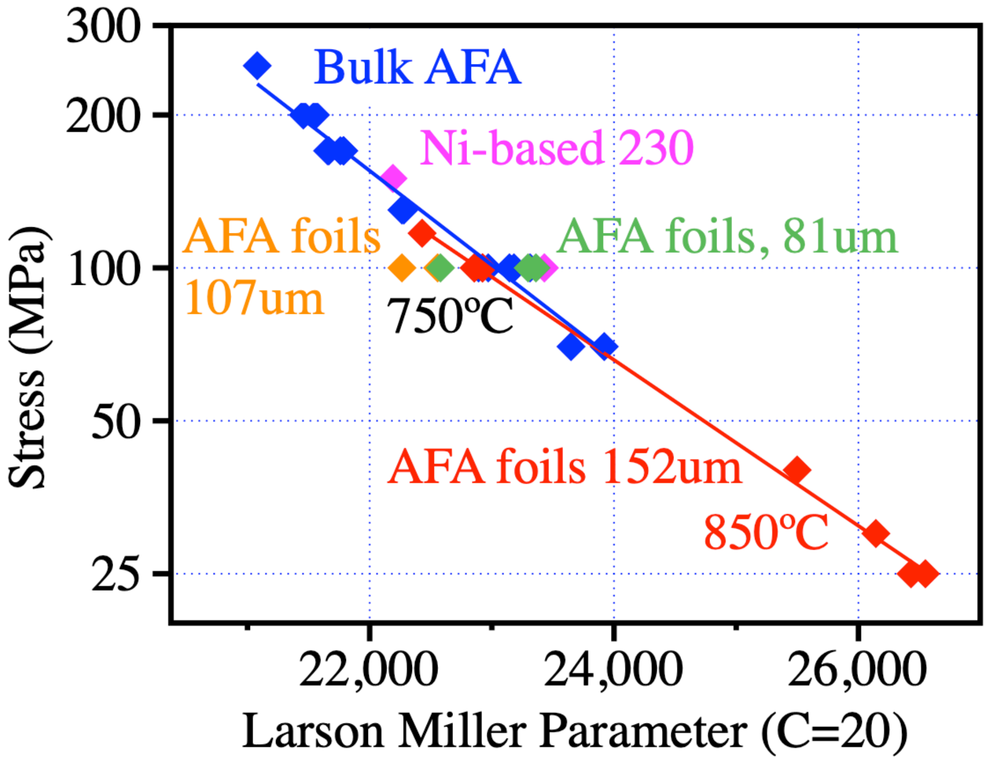
AFA – after 3,000 h at 850°C in wet air



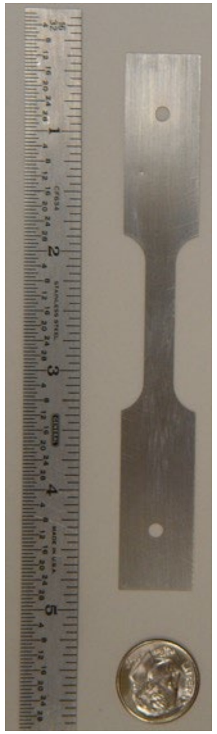
Task 2: Evaluated AFA Foil Creep properties at 850°C







$LMP=T(\log(t_r)+C)$



dime

Experiments allow designers to size components for 750°-850°C applications

Similar creep results for bulk and foil AFA steels but void formation for foils

More expensive Ni-based alloy foils have similar creep properties

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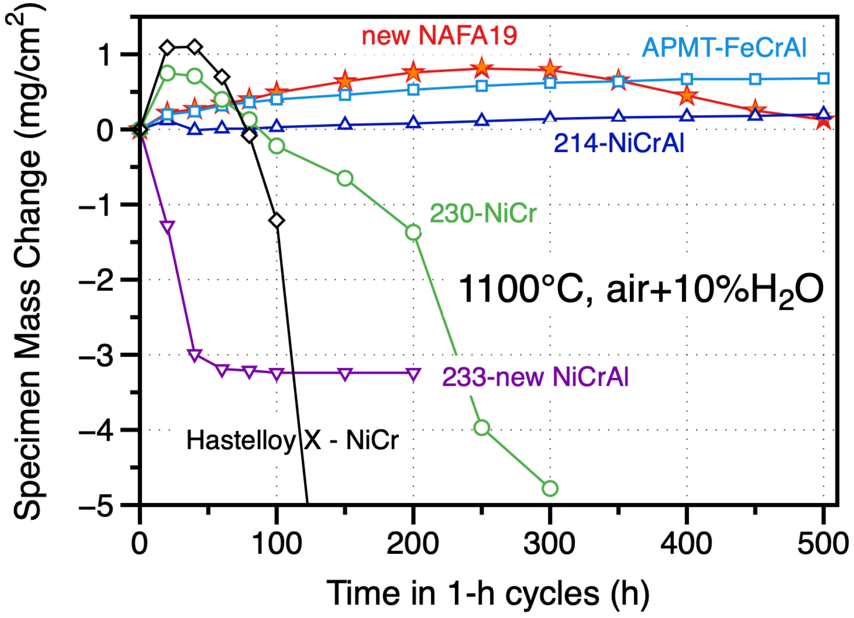
New Ni-based alumina-forming alloy developed at ORNL

- Target >1000°C components such as combustor liners
- Patents awarded
  - Alumina-forming, high temperature creep resistant Ni-based alloys, US Patent 10,174,408 issued January 8, 2019
  - US Patent 10,745,781 issued August 18, 2020 (broader composition award)
  - Excellent combination of creep strength and oxidation resistance
- Scale-up: 23 kg heat produced
  - Homogenized and rolled to plate
    - Characterization completed
  - Specimens machined
    - Verify tensile, creep and fatigue properties
    - Goal is to generate database for end users
      - Mechanical testing delayed
  - Oxidation testing at 1100°C in wet air



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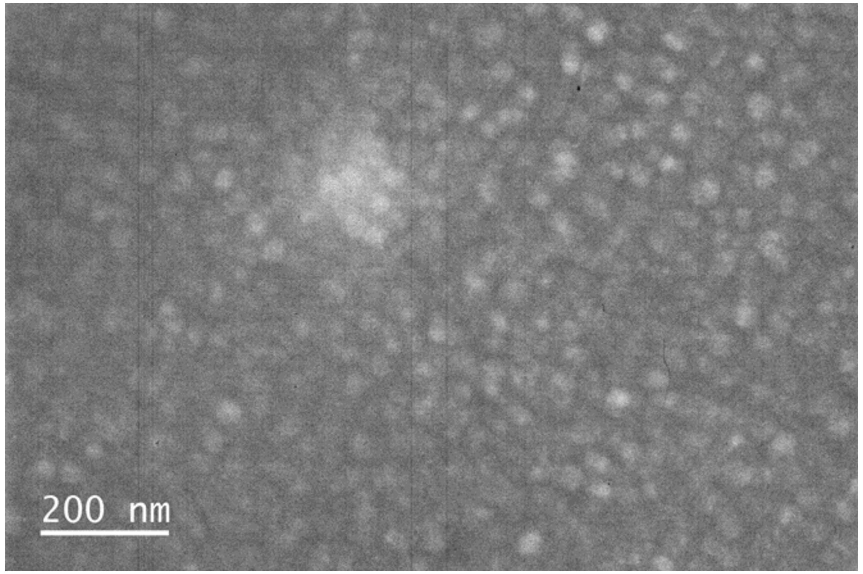
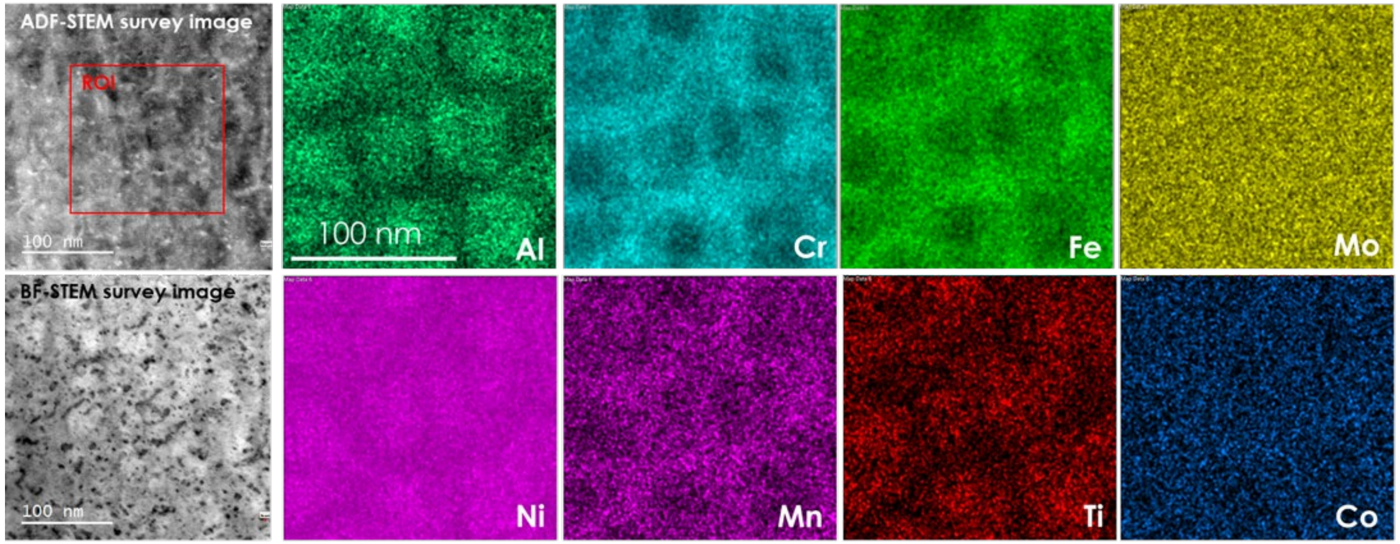
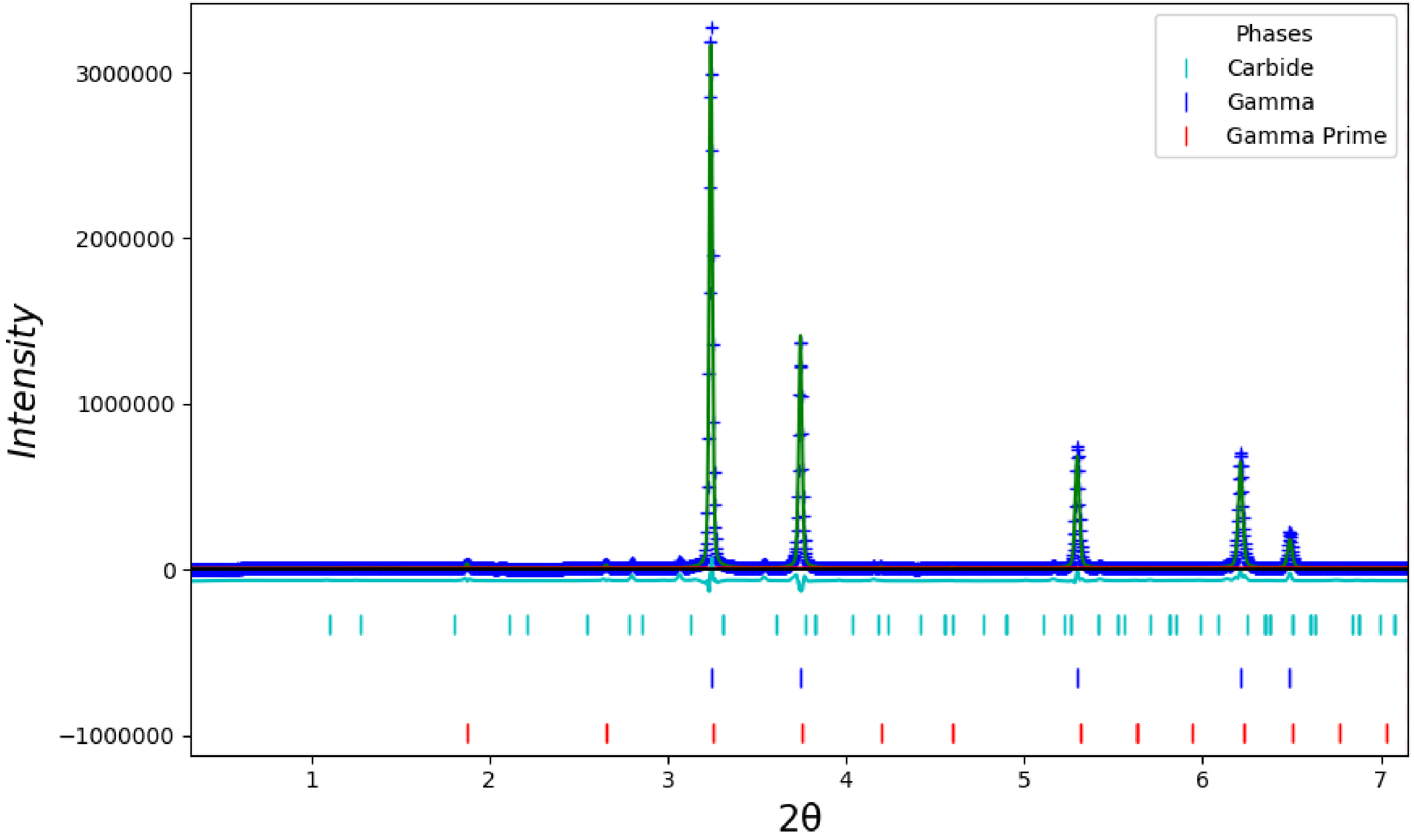
Larger heat of NAFA: Transmission Electron Microscopy confirmed presence of fine γ' precipitates rich in Al & Ti





Task 4: High-energy synchrotron x-ray diffraction conducted at ANL Advanced Photon Source to study new NAFA alloy



ANL: L. Xiong, D. Singh
11-ID beamline: 105.7 keV
500 × 500 μm: mm-scale depth

Specimen from 23 kg casting

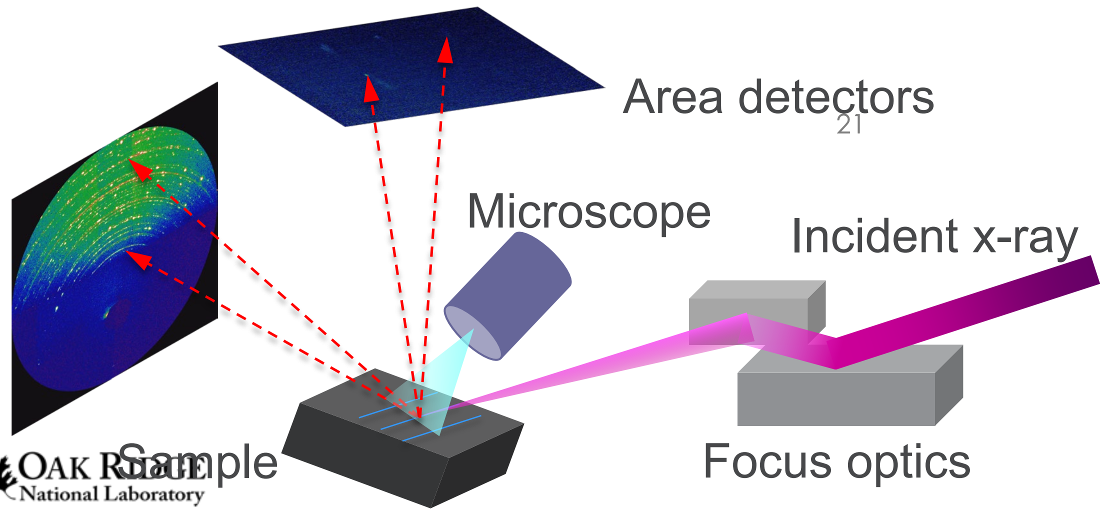
Results can be used to calculate γ-γ´ misfit to compare to other superalloys

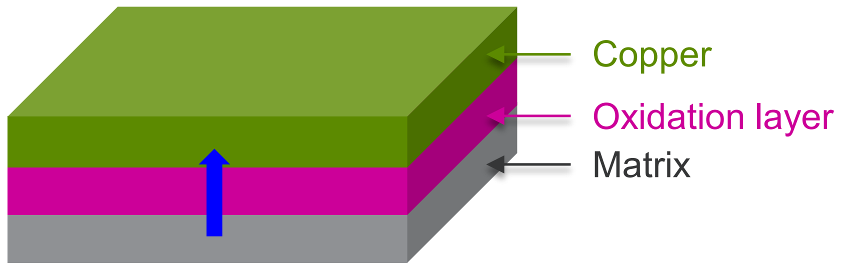
Example: aged 0.5h/1121°C+4h/800°C: 92.5% γ phase, 7.4% γ´ & 0.002% $M_{23}C_6$

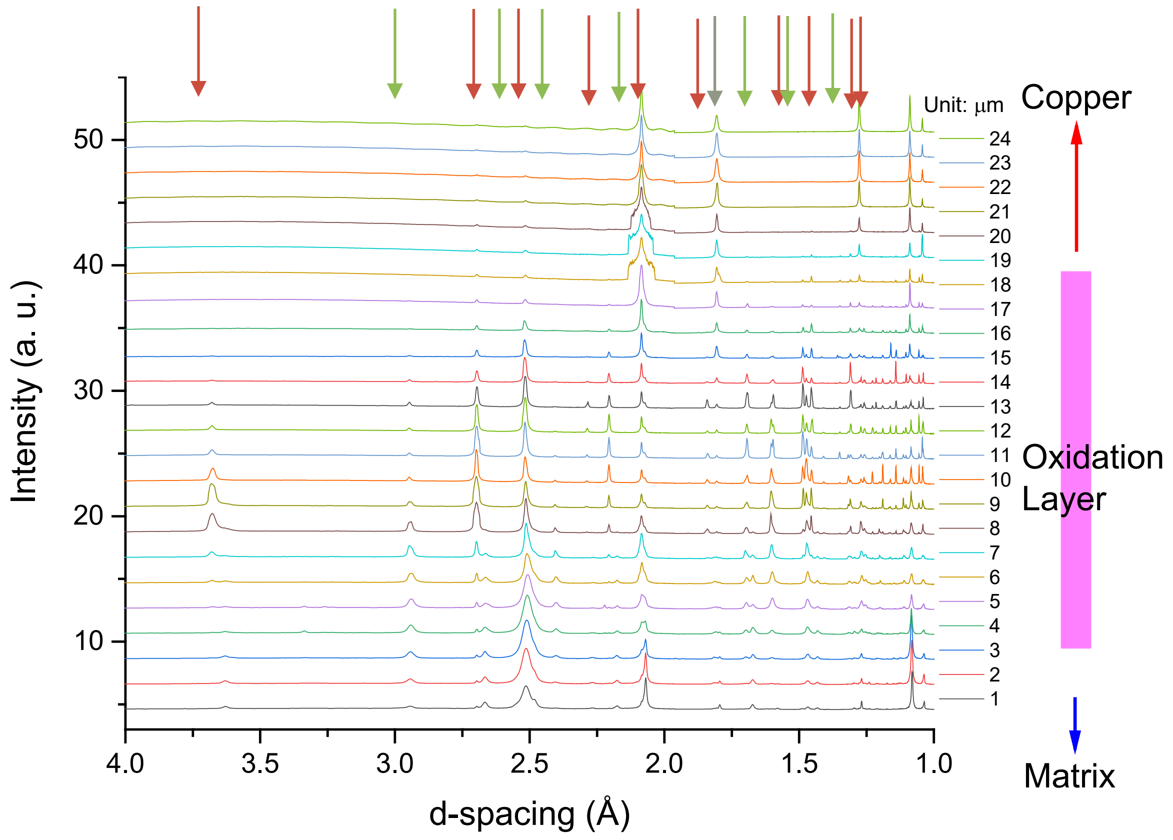
Task 4: ANL task studying Fe-rich oxides on AL2025Nb

- **Synchrotron Microdiffraction:**
  - Beam: 250 nm (FWHM), 10 & 20 keV
  - Sample: 200μm (8 mil) 700°C 15 & 26 kh
  - High-precision line scan
    - Step size 1 μm
    - d-spacing 1-4 Å
- Phases
  - Trigonal: Cr_2O_3, Fe_2O_3
  - Cubic: spinel type $Ni(Cr,Fe)_2O_4$
  - Orthorhombic: $NiFe_2O_4$

Beamline schematic

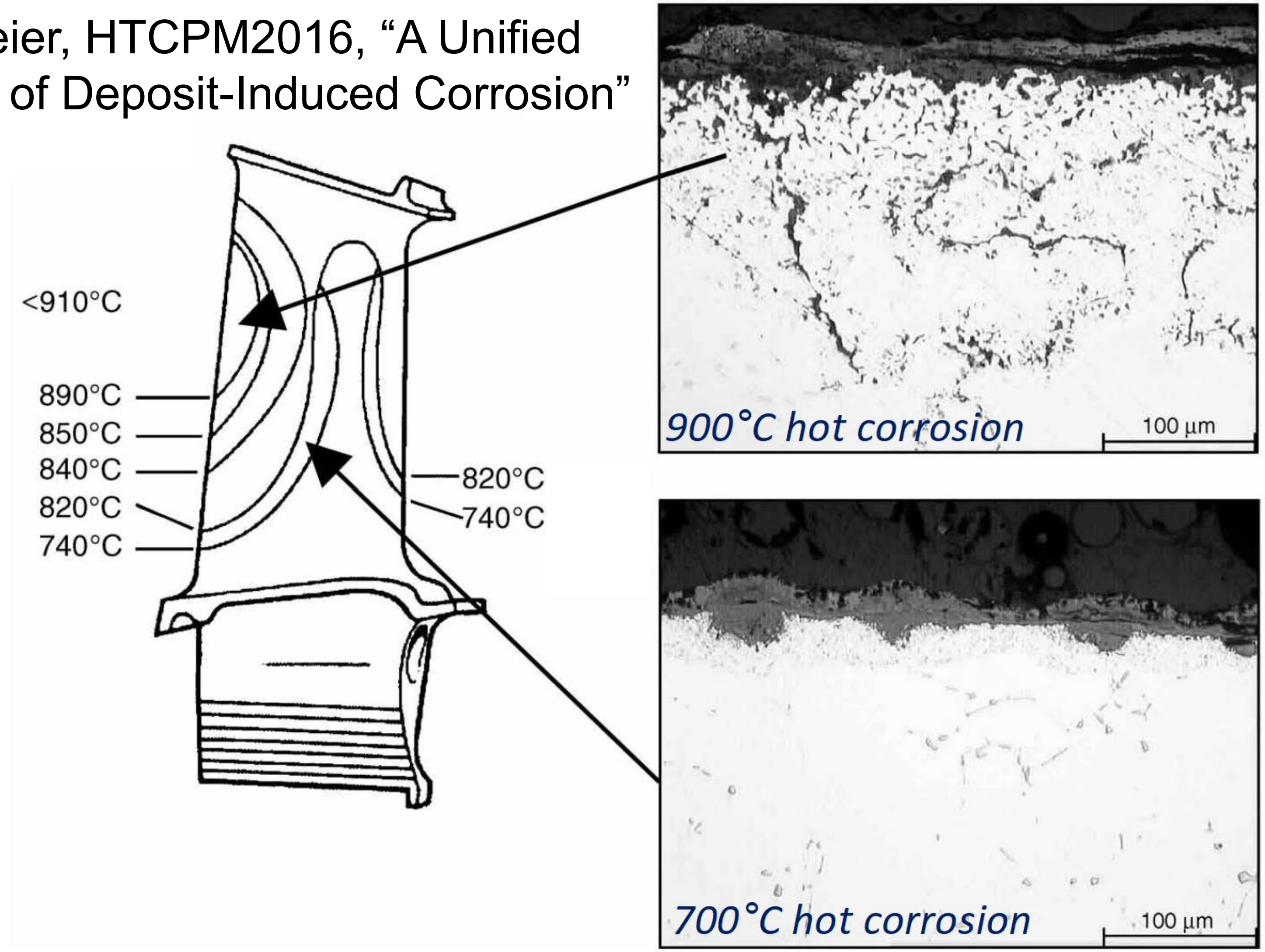






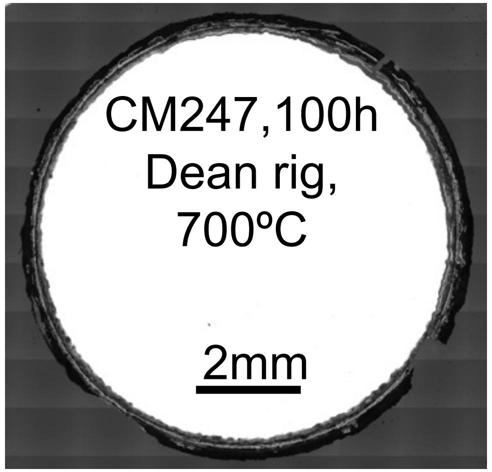
Task 3 Background: Significant Blade Degradation Due to Hot Corrosion in Gas Turbines

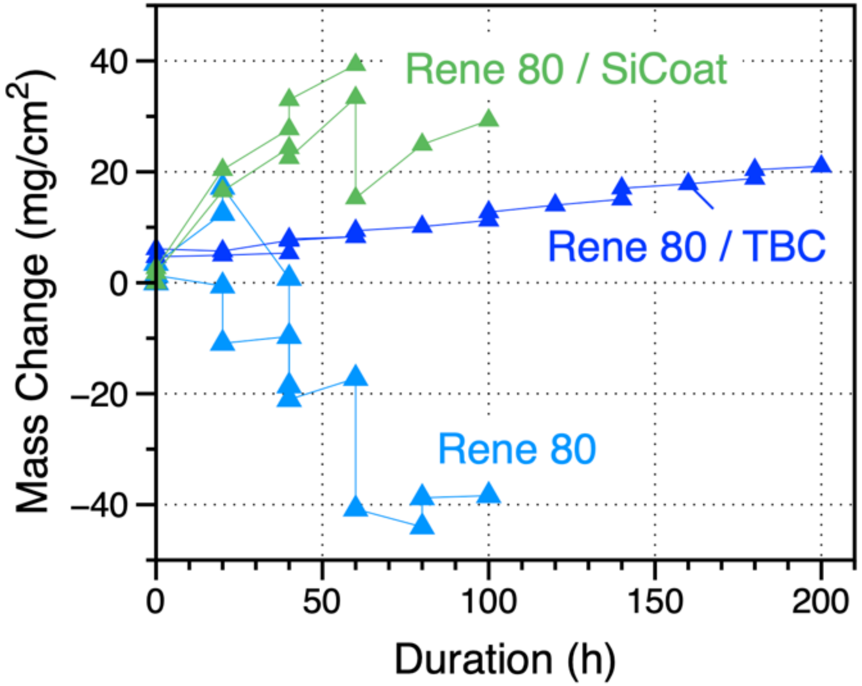
J. Meier, HTCPM2016, "A Unified View of Deposit-Induced Corrosion"

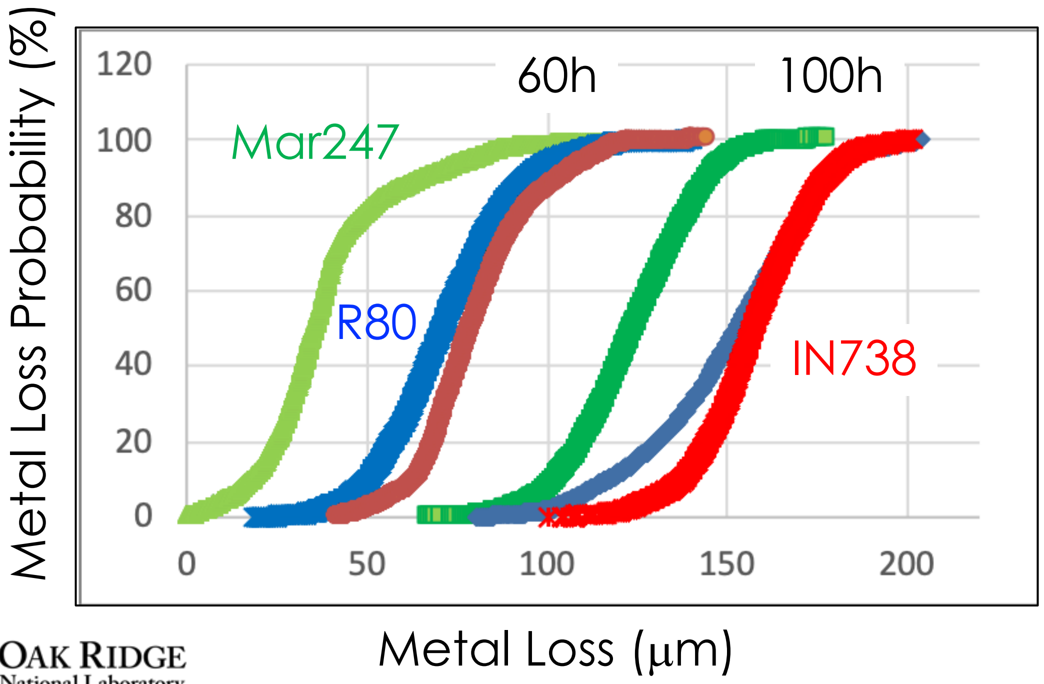


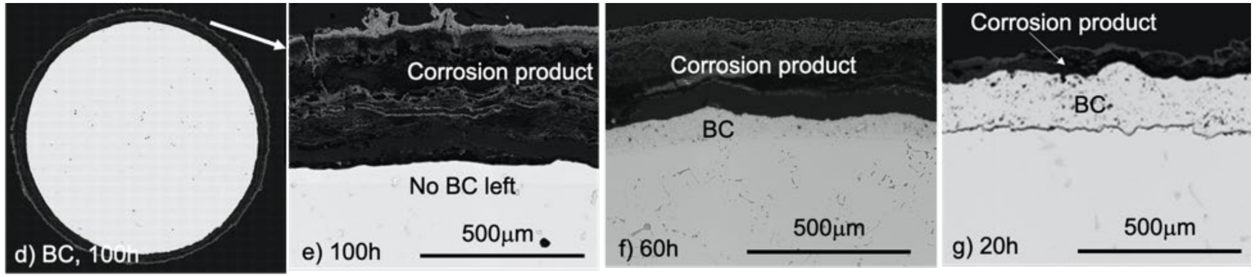
- **Significant issue for both aerospace and industrial gas turbines**
- **Higher temperature is key to improve gas turbine efficiency and reduce CO_2 emission**
- **Increasing issue for disk alloys at >700ºC**
- **Common issue with burning opportunity fuels**

Task 3. Common to evaluate coatings in hot corrosion Dean Rig testing of Siemens and TN Tech's Coatings









- Python program developed to quantify metal loss
- Full TBC performs better than Bond Coat only

Unique Rig Commissioned to Conduct Low Cycle Fatigue in Corrosive (SO_2+Molten Salt Deposit) Environment

5” button head fatigue specimens

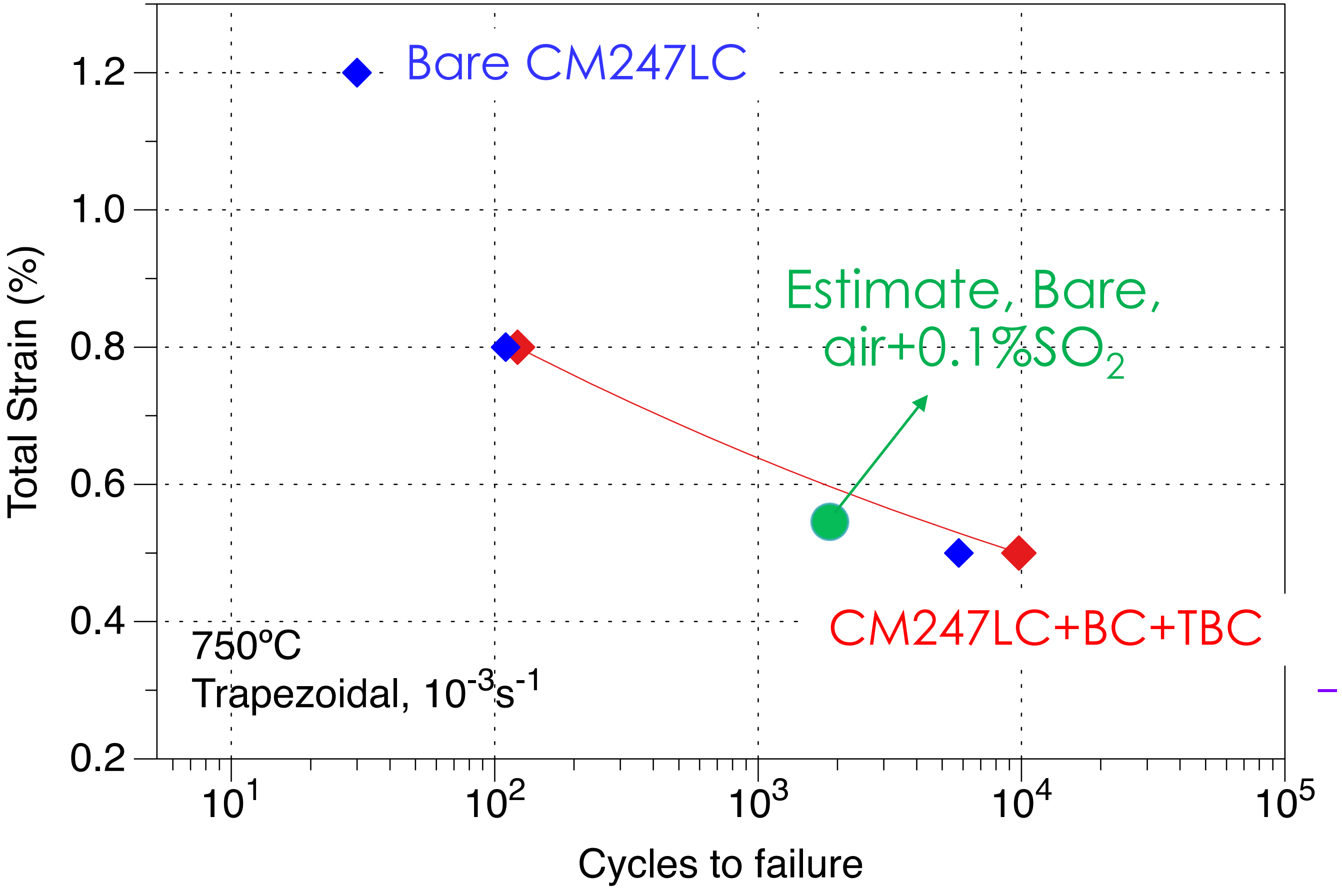
Sealed chamber with bellows to accommodate displacement

Enclosure connected to hood + SO_2 detector

LCF results: Similar cycles to failure for bare and coated CM247LC in air. Next step is to evaluate LCF in air+0.1%SO_2

Salt sprayed at the specimen surface inside the LCF chamber using the extensometer port

~18 h at 750°C



Equipment & then staffing issues for past 10 months have limited further progress

Summary and status: the project is nearing completion

- Task 1. Lifetime modeling
  - wrapping up: writing more papers
    - M. Romedenne, R. Pillai, S. Dryepondt, B. A. Pint, "Effect of water vapor on lifetime of 625 and 120 foils during oxidation between 650 and 800 °C," *Oxidation of Metals* 96 (2021) 589-612.
    - R. Pillai and B. A. Pint, "The Role of Oxidation Resistance in High Temperature Alloy Selection for a Future with Green Hydrogen," JOM 73 (2021) 3988-3997.
    - M. Romedenne, R. Pillai, S. Dryepondt, B. A. Pint, "Oxidation lifetime modeling of 625 and 120 foils after long-term exposure in flowing air + 10% H_2O at 700 and 800°C, submitted to *Oxidation of Metals*, February 2022
- Task 2. >100°C material investigation
  - 850°C oxidation and creep testing of AFA steels: complete
    - M. Romedenne, R. Pillai, S. Dryepondt, M. Lance and B. A. Pint, "High temperature oxidation behavior of alloy foils in water vapor at 850°C," NACE Paper C2021-16594, Houston, TX, presented virtually NACE Corrosion 2021
  - Mechanical testing of patented alloy larger heat: in progress
- Task 3. Combined fatigue/corrosion testing of coatings
  - Test rig operational: no-cost extension to complete testing
- Task 4. Advanced characterization (D. Singh, ANL)
  - complete

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  - Capstone Green Energy, D. Ayers

- ORNL team
  - Oxidation experiments: Mike Stephens, John Wade, George Garner
  - Characterization: Tracie Lowe, Victoria Cox
  - Mechanical properties: Shane Hawkins
  - TEM: Yi-Feng Su

What's next? ORNL provides broad expertise and unique facilities for evaluating H_2 material compatibility issues

- **Production**
  - Experience characterizing and modeling component lifetimes in industrial processes: electrolysis, gasification, photosynthesis, etc.
- **Transportation & Storage**
  - Experience evaluating coatings (possible solution for H_2 pipelines)
- **Pre-combustion**
  - 25 years experience H_2 loading alloys in high temperature H_2
  - Expertise in measuring mechanical properties in extreme environments
  - Intense industry concern about high temperature H_2 material compatibility needs to be addressed immediately
    - Need to de-risk the use of conventional and new alloys handling H_2 at ≤600°C
- **Combustion**
  - 15 years experience studying H_2 combustion; steels, superalloys, ceramics
  - Developed framework for lifetime modeling in H_2 combustion (high H_2O)

H_2 loading in vanadium

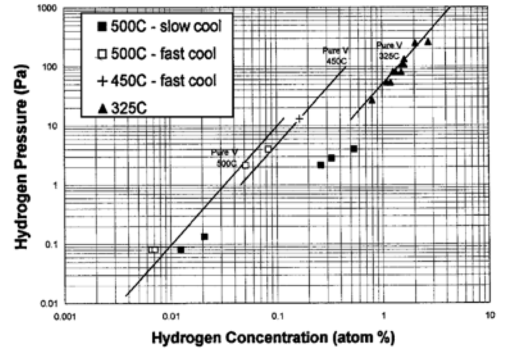

Fig. 1. Hydrogen concentrations in V–5Cr–5Ti and unalloyed vanadium [7,8] after exposure to low-pressure hydrogen at 500°C.

Simulated high H_2O rig at ≤1500°C

ORNL team: B. Pint, S. Dryepondt, R. Pillai