NETL Research & Innovation Center's Advanced Alloy Development Research

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September 29, 2020

*retired

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Acknowledgement and Disclaimer

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Acknowledgement

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- **The Research was executed through the NETL Research and Innovation Center's Advanced Alloy Development Field Work Proposal.**

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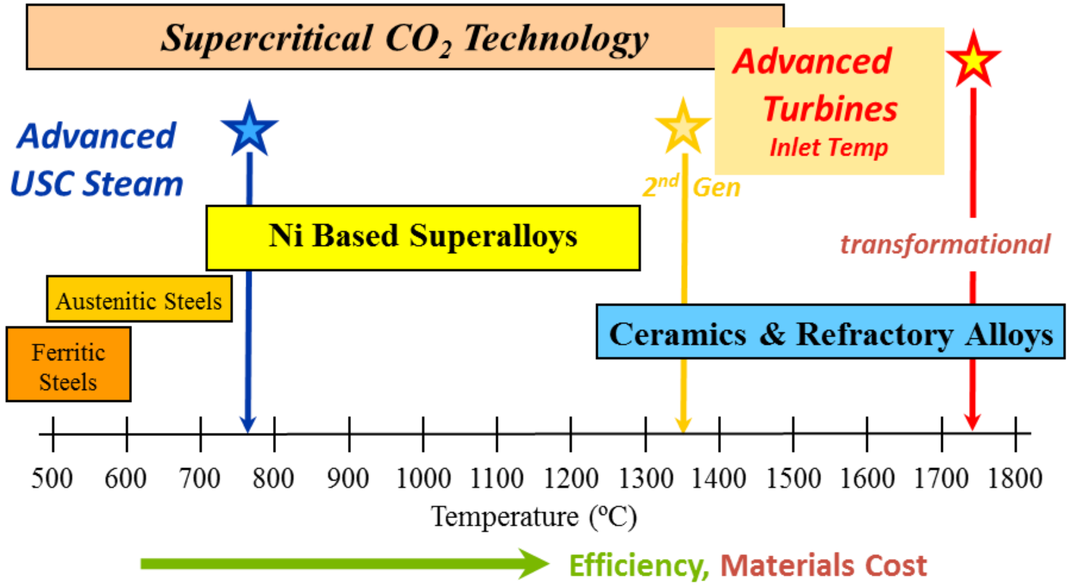
Advanced Energy Systems: Materials at Extremes

Structural Materials Development



POWER Engineering

Changing Mission Profiles

05/22/2017

By Mike Caravaggio and Norris Hirota, Electric Power Research Institute

Over the past decade, fossil and hydro generation plants have increasingly experienced significant changes in their operating strategies, or "mission profiles," compared to their original designs. These changes include new operating regimes with increased cycling, extended unit layups, and prolonged periods of low turndown.

The changes, in turn, are creating a multitude of challenges for the plants and their operating staff in areas ranging from component degradation to staffing levels, O&M budgets, and meeting environmental compliance under non-baseload conditions.

Materials Challenges:

- Higher Temperatures, Higher Pressures, Corrosion & Oxidation → Extreme Environments
- Large Components → Manufacturability
- Long Service Life Span >100,000 hrs → Durability
- Penetration of Renewable → Cycling Operational Conditions

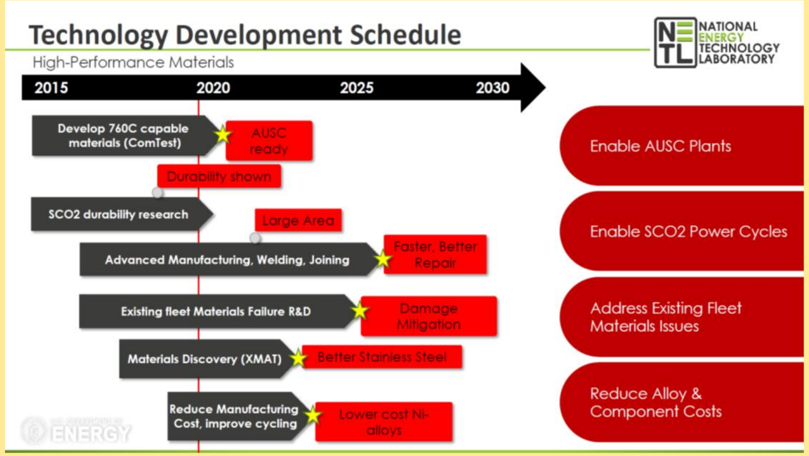
Technology Enabler: Affordable, Durable and Qualified Structural Materials for Harsh Service Life.

RIC Advanced Alloy Development FWP

Scope

The Advanced Alloy Development (AAD) Field Work Proposal (FWP) supports the mission, goals, and objectives of the DOE-FE/NETL High Performance Materials Program by **developing affordable, durable, cost effective, heat-resistant alloys and tools** necessary for **improving the existing fleet of Fossil Energy (FE) power plants, and enabling advanced FE systems,** such as advanced ultra-supercritical (A-USC) and supercritical carbon dioxide (sCO_2) power cycles.

Mission DOE-FE/NETL High Performance Materials Program: Characterize, produce, certify cost-effective alloys and high-performance materials suitable for extreme environments found in coal power **generation to support existing and new plants.**



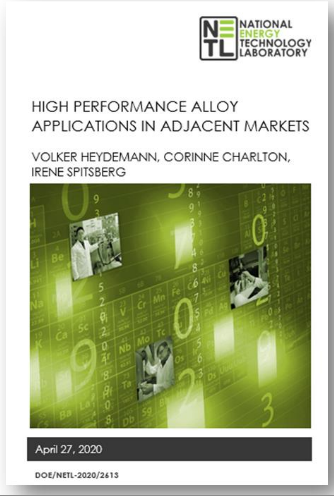
AAD-FWP Research

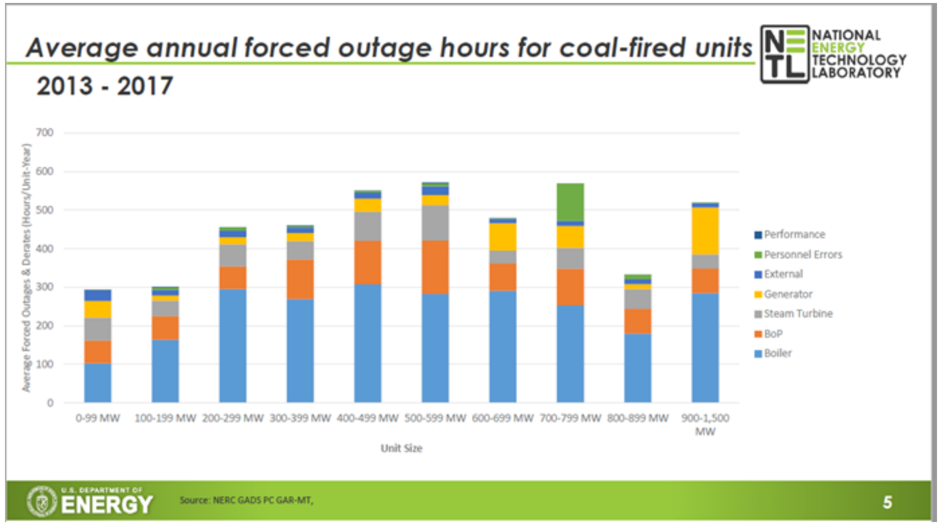
- ★ Identify supply chain issues and performance/cost benefits
- ★ Develop alternative cast and wrought alloys for A-USC and sCO_2 application
- ★ Increase temperature capabilities of steels, Ni alloys.
- ★ Improve melt processing of advanced alloys.
- ★ Assess, predict, and improve alloy cyclic & environmental performance.
- ★ Materials Performance under direct sCO_2 power cycles
- ★ Enable manufacture of compact heat-exchangers for sCO_2 power cycles.

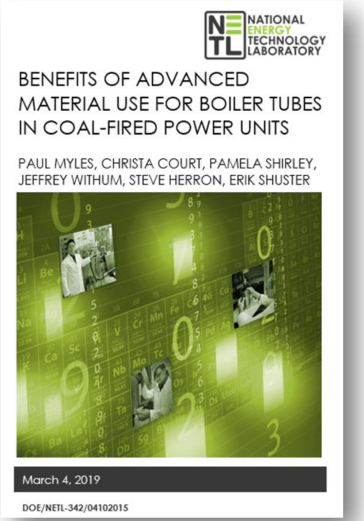
Techno-Economic & Market Assessments

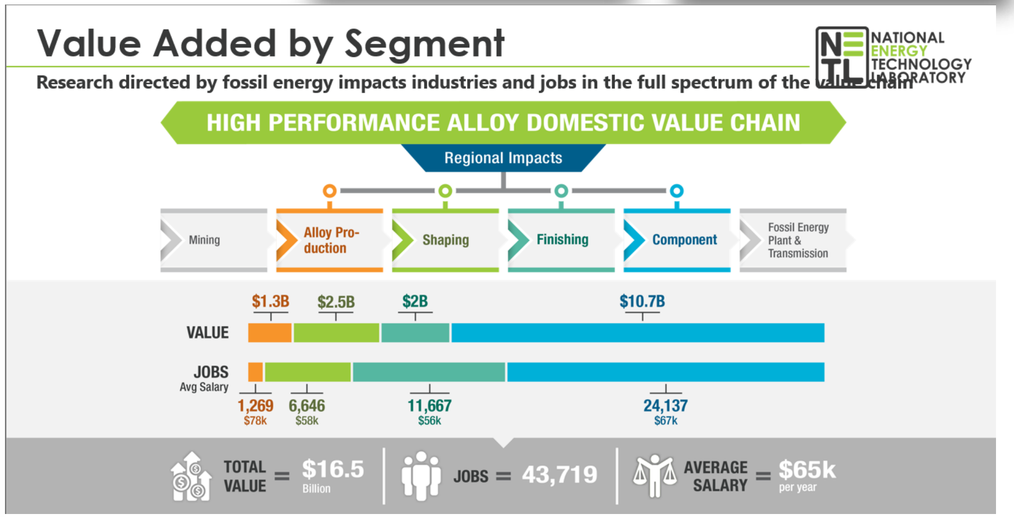
Research Guidance and Direction (Systems Engineering & Analysis)

- High Performance Alloy Applications In Adjacent Markets
- Understanding the Supply Chain of Advanced Alloys
- Benefits of Advanced Materials for Boiler Tubes
- Export Potential for High-Performance Materials Study
- GADS Failures subsets analysis for boiler tubes, turbine, and BOP









Fe-9Cr Alloy Development

NETL CPJ-7 and NETL JMP Steels

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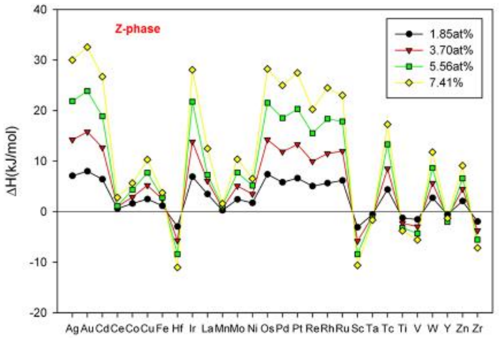
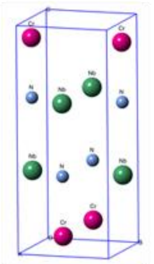
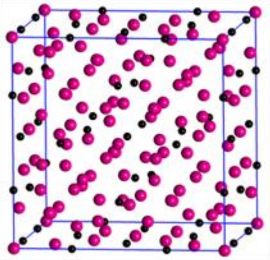
OPTIMIZE COMPOSITION



Z-phase (CrNNb)

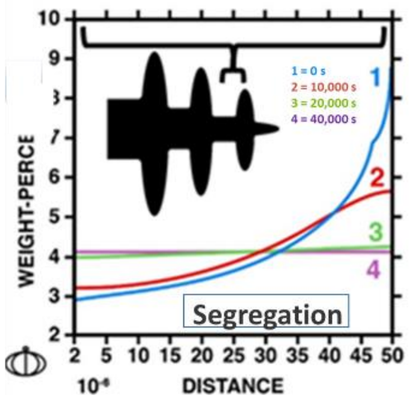


C_6Cr_{23} Carbide

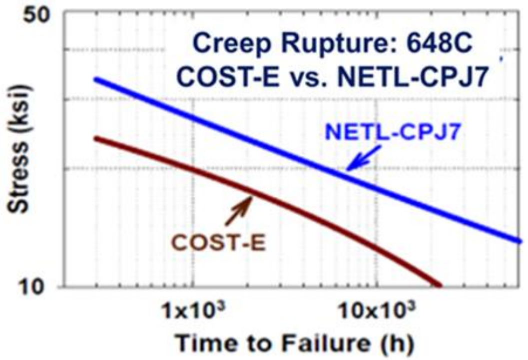


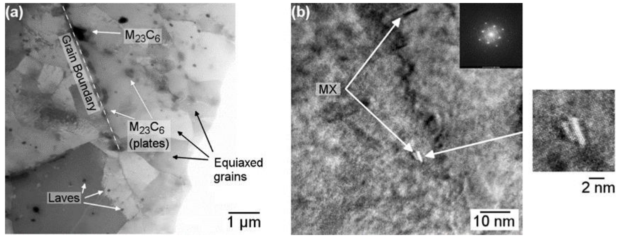
DFT and CALPHAD used to optimize alloy composition. Simulations used to determine the effect of alloying elements on the formation and stability of unwanted (Z-phase) and desired strengthening phases (Carbides).

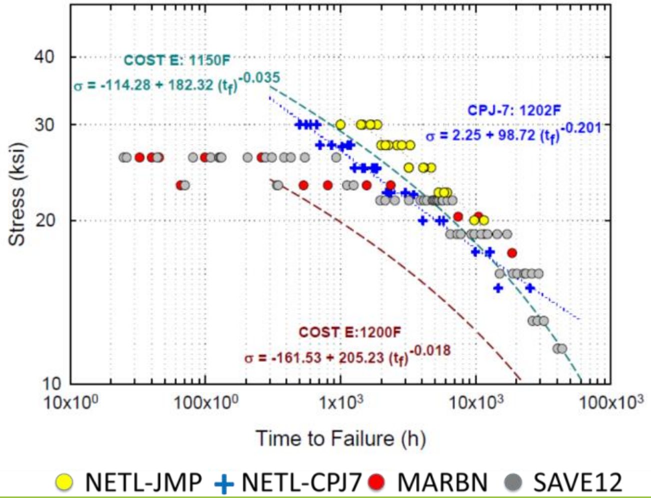
OPTIMIZE PROCESSING



NETL's R&D 100 award winning computational tool used to design heat-treating cycles to optimize the alloy's microstructure and properties.







- ★ Cast and wrought forms
- ★ 70 kg (150 lb) ingots produced (VIM, ESR)
  - Formulated ESR slag chemistry
- ★ Welding trials/studies
  - Conventional NETL
  - Friction Stir Welding PNNL
- ★ Material available for evaluation
  - EPRI (John Siefert, cast alloys, remnants of tested creep samples)

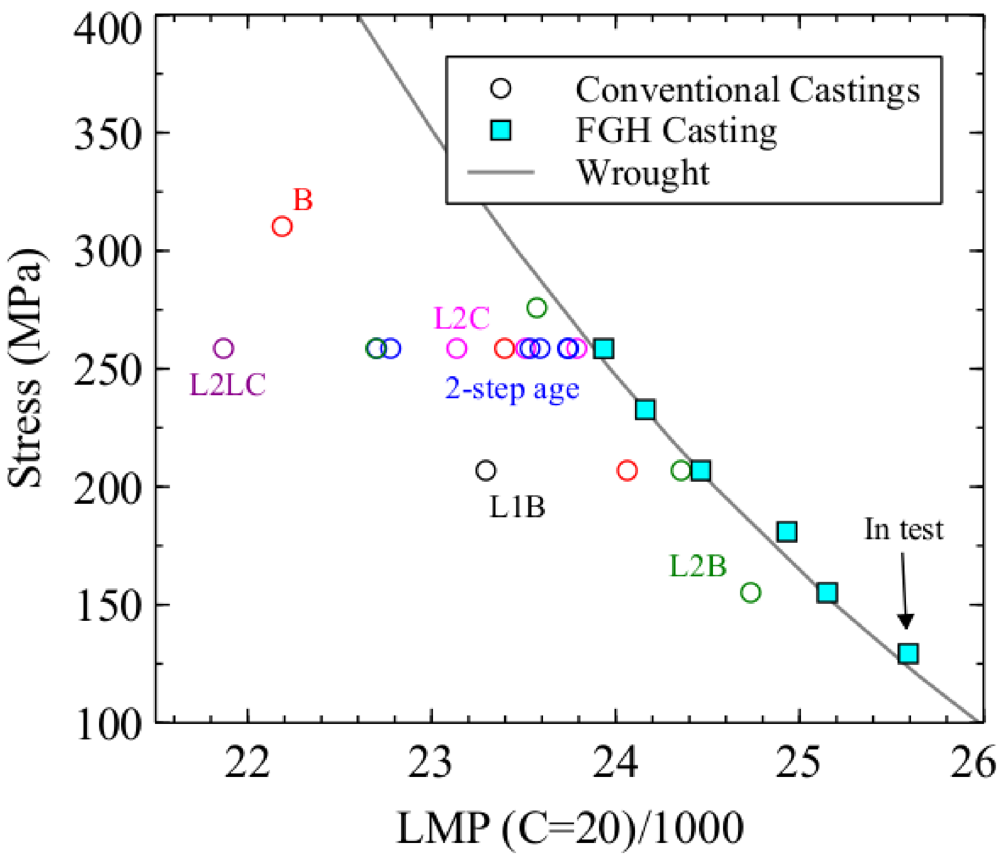
Outcome: **New Fe-9Cr Alloy with an Increase Temperature Capability** of ~50° F for this important class of power plant steel.

U.S. DEPARTMENT OF ENERGY

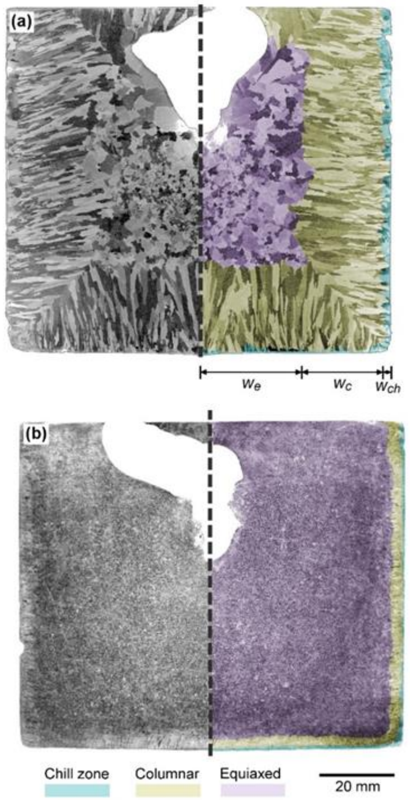
- U.S. Patent: Hawk, Jablonski & Cowen, Creep Resistant High Temperature Martensitic Steel, US 9,181,597 B1, November 10, 2015.
- U.S. Patent: Hawk, Jablonski & Cowen, Creep Resistant High Temperature Martensitic Steel, US 9,556,503, January 31, 2017.

Cast Version of Alloy 740H

Alloy (and supply chain) options for thick wall castings



Conventional casting
Non-Uniform Microstructure



NETL-modified casting
Uniform Microstructure

Modify the casting process for Inconel 740H to improve its mechanical properties in creep.

Conventional castings (open circles) showed poor and inconsistent creep lives.

*The NETL-process **(FGH)** to produced fine-grain casting o obtain a cast product matching the wrought alloy on the LMP plot.*

Outcome: **Creep resistant cast version of Alloy 740H.**

M.Detrois, K.A. Rozman, P.D. Jablonski, J.A. Hawk, "An Alternative Casting Technique to Improve the Creep Resistance of INCONEL Alloy 740H," Metall Mater Trans A 51, 3819–3831 (2020). https://doi.org/10.1007/s11661-020-05822-0

Superalloy Development

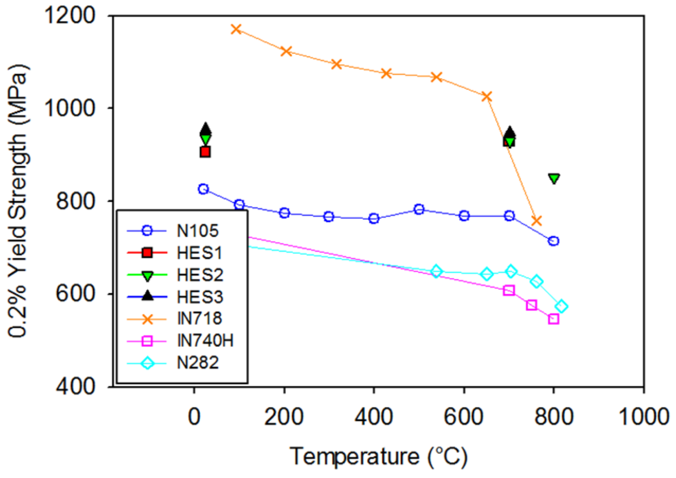
Increase temperature capability and strength of superalloys.

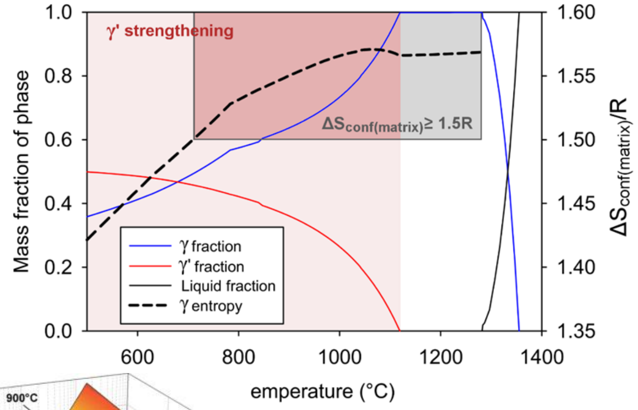
Enable increased operational temperature (efficiency) and/or reduce amount of alloy needed for manufacturing component (reduce cost).

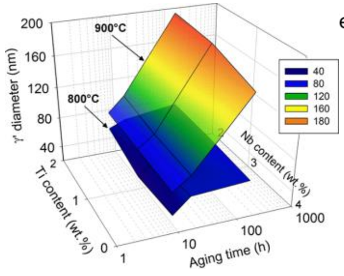
- ✓ *Increasing γ′ fraction/solvus in commercial Ni-based superalloys*
- ✓ Grain boundary re-design for Ni-based superalloys (Alloy 725)
- ✓ *High entropy matrix Ni-based superalloy*

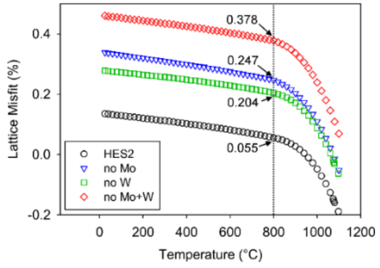
Re-design gamma matrix

High entropy matrix Ni-based superalloys



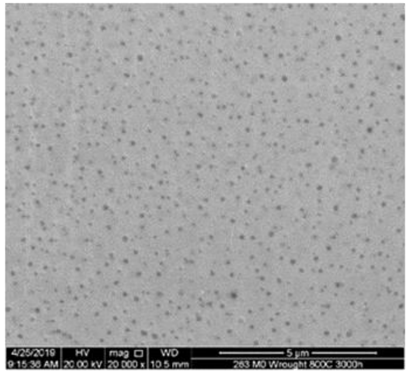


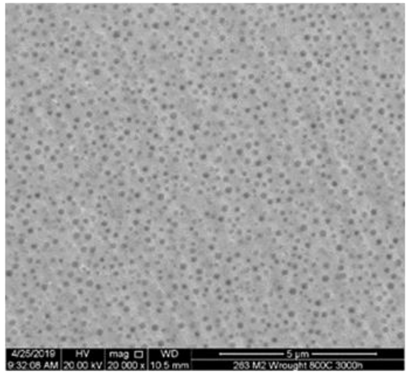




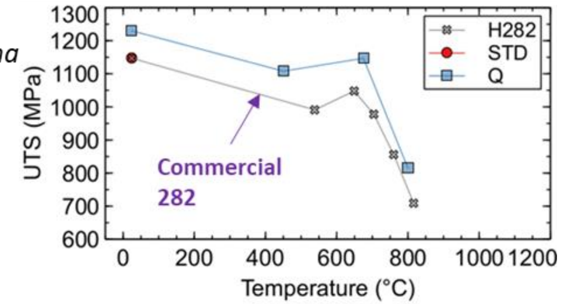
Outcome: **More stable gamma matrix** Increased strength compared to commercial superalloys.

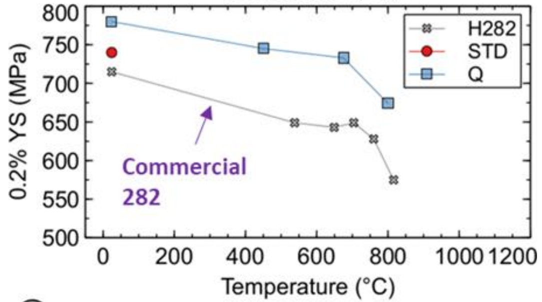
Alloy 282: Increase the gamma prime fraction/solvus to enhance >800C mechanical properties. Obtain a gamma prove fraction/solvus at 900C equal to tha of the commercial alloy at 800C. Also looking at Alloy 263 and Nimonic 105.

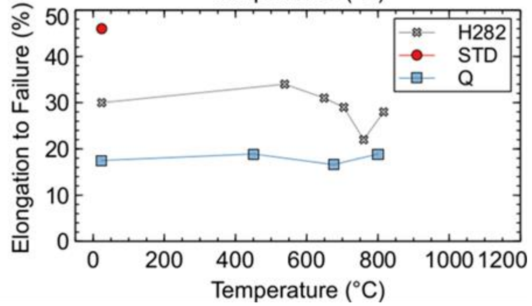




Increase Gamma Prime







Outcome: **Higher strength** version of H282 **with ductility.**

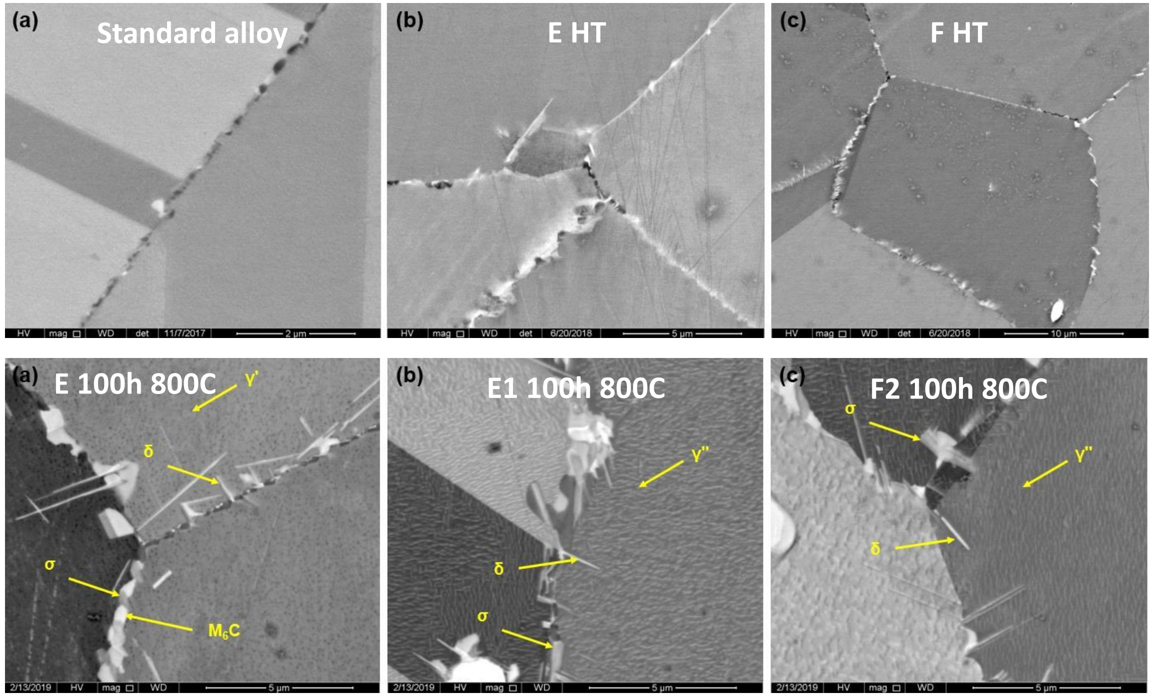
1. M. Detrois, P.D. Jablonski, S. Antonov, S. Li, Y. Ren, S. Tin, J.A. Hawk, “Design and thermomechanical properties of a γ′ precipitate-strengthened Ni-based superalloy with high entropy γ matrix” J. Alloys Compd. 792 (2019) 550–560. doi:10.1016/j.jallcom.2019.04.054.
2. M. Detrois, P.D. Jablonski, J.A. Hawk, “Precipiate Phase Stability and Mechanical Properties of Alloy 263,” in: S. Tin (Ed.), Proc. 14th Int. Symp. Superalloys (Superalloys 2020), Springer International Publishing, Seven Springs, PA, 2020. doi:10.1007/978-3-030-51834-9_17

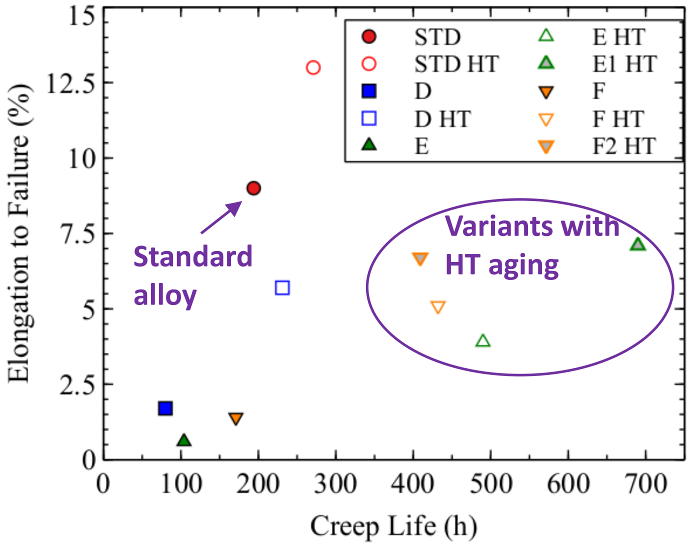
Superalloy Development

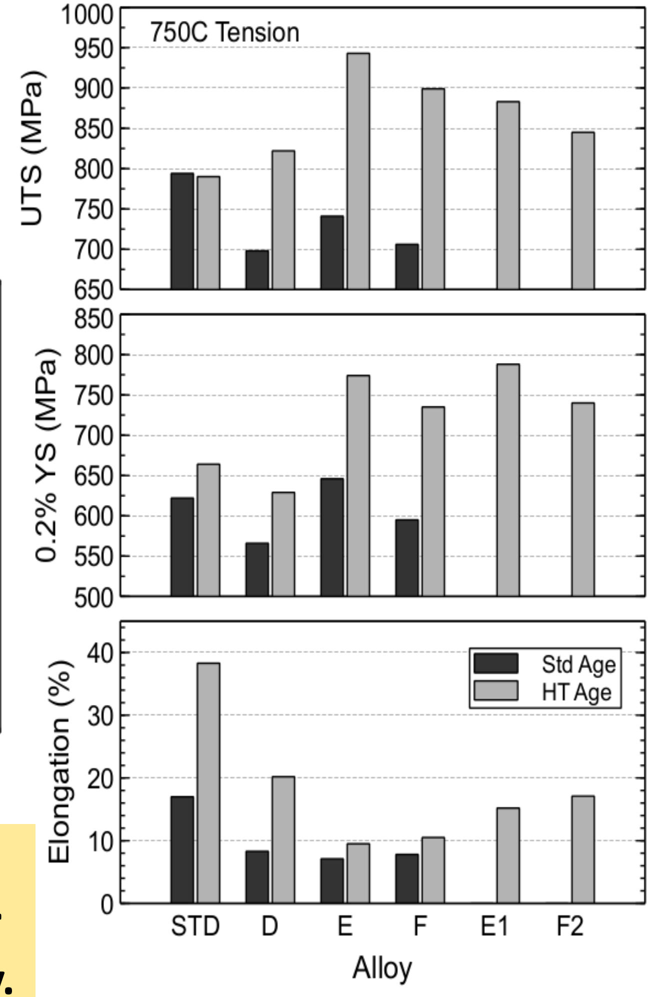
Grain boundary re-design of commercial alloys

Alloy 725:

*The alloy is subjected to (1) **NETL computationally optimized homogenization cycle** and (2) **high temperature (HT) post-TMP aging heat treatment** combined with **targeted elemental additions** that enables the intentional precipitation of secondary phases (i.e., δ and/or η) at the grain boundaries to increase their resistance to deformation and damage and γ′ and/or γ″ precipitates in the grain interior to facilitate high room and high temperature yield stress and tensile strength.*







Outcome: Improvement in creep life of >256% with similar ductility from the standard alloy.

High Entropy Alloy (HEA) Development

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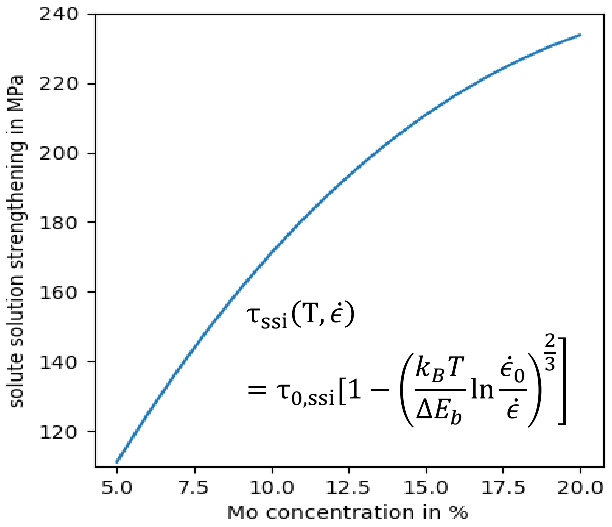
Design of Co-Cr-Fe-Ni-Mo HEAs

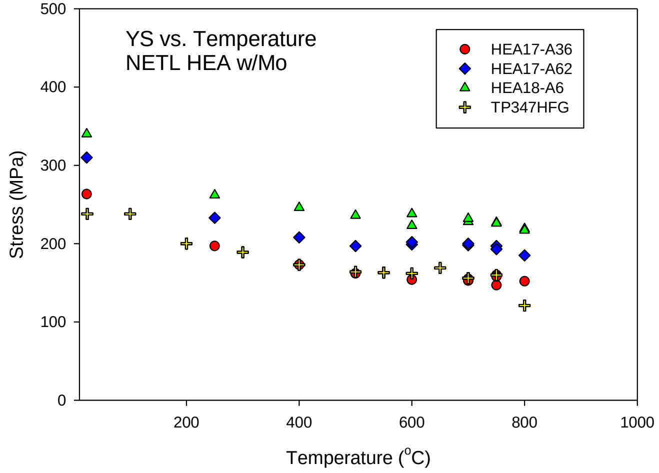


Stacking Fault Energy Co-Cr-Fe-Mn-Ni-Mo calculated using first-principles density functional theory.

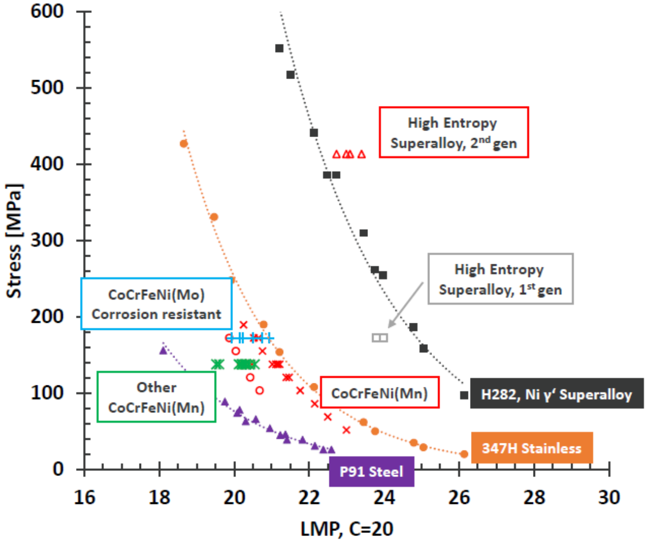
	A35	A36	A61	A62	A5	A6
NM	-0.019	-0.034	-0.023	-0.061	-0.003	-0.039
FM	-0.010	-0.008	-0.003	-0.023	-0.000	-0.031

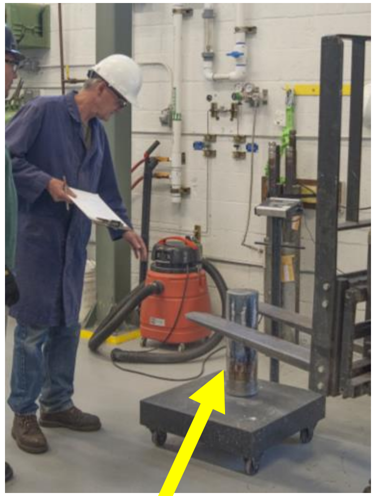
Properties of NETL HEAs

Yield Stress of Co-Cr-Fe-Ni-Mo HEAs compared to 347HFG



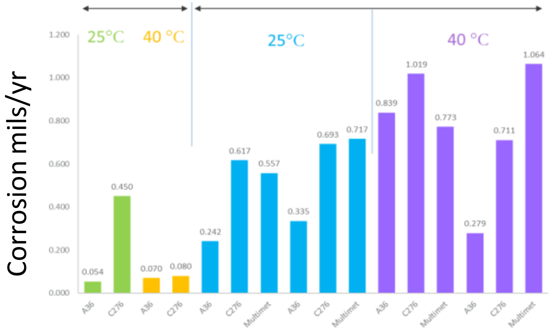
Creep behavior of HEAs and High Entropy Matrix Superalloys



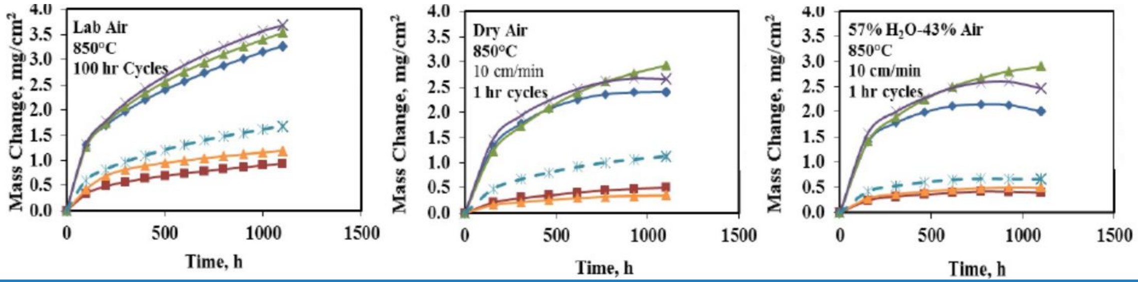


150-pound HEA alloy ingot produced at NETL

Corrosion of Co-Cr-Fe-Ni-Mo (A36) HEA compared to Hastelloy C276 and Multimet



Oxidation at 850C of NETL HEAs compared Alloy 2828. Similar behavior observed at 750C



J.A. Hawk, P.D. Jablonski, M. Ziomek-Moroz, J.H. Tylczak, M.C. Gao, and A.A. Rodriguez, “High Performance Corrosion-Resistant High-Entropy Alloys, US Patent Application Publication, Pub No. US 2020/0283874 A1, Sep. 10, 2020.

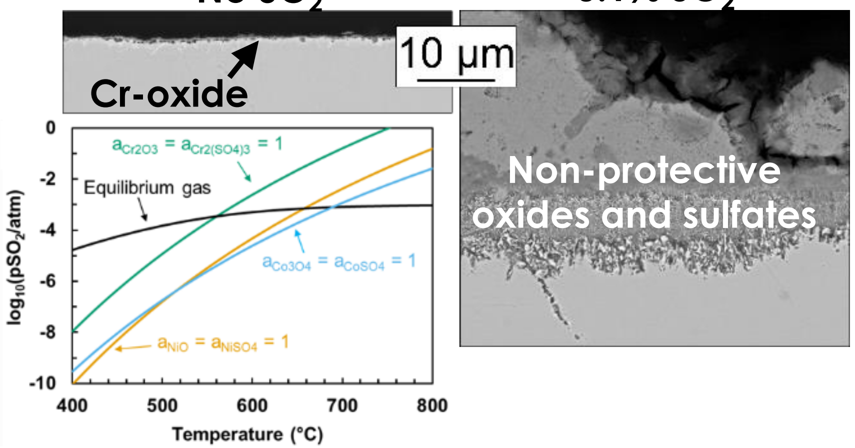
Z. Pei, J. Yin, J.A. Hawk, D.E. Alman and M.C. Gao, “Machine-learning Informed Prediction of High-entropy Solid Solution Formation: Beyond the Hume-Rothery Rules,” npj Comput. Mater., Vol. 6 (No. 50) (2020). (DOI: https://doi.org/10.1038/s41524-020-0308-7).

Materials Issues for Supercritical CO_2 Power Cycles

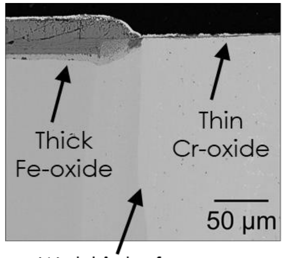
NATIONAL ENERGY TECHNOLOGY LABORATORY

HIGH-TEMPERATURE OXIDATION OF STEELS AND SUPERALLOYS

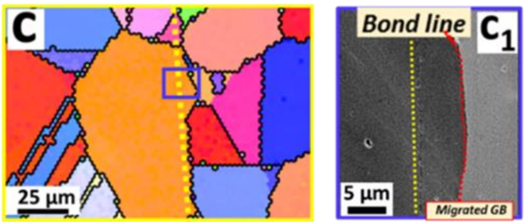
Effects of impurities and pressure



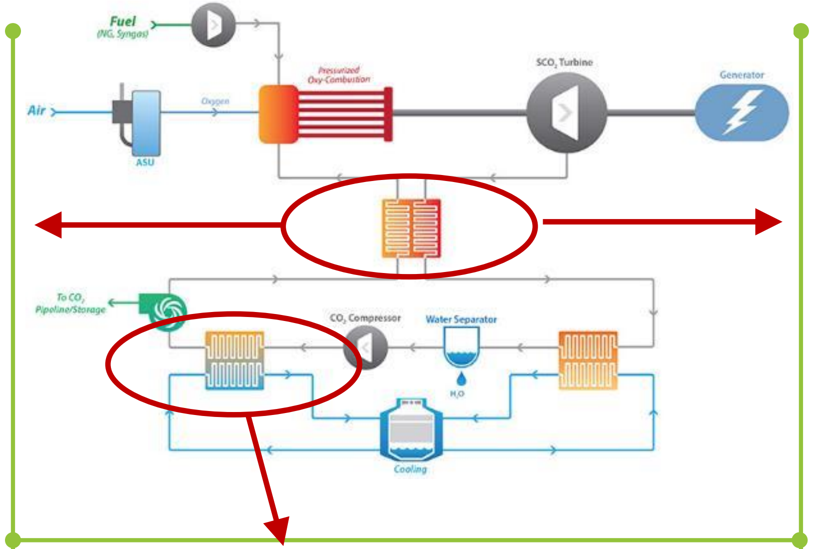
OXIDATION AND PERFORMANCE OF JOINED STRUCTURES AND MANUFACTURE OF COMPACT HEAT-EXCHANGERS



Weld interface

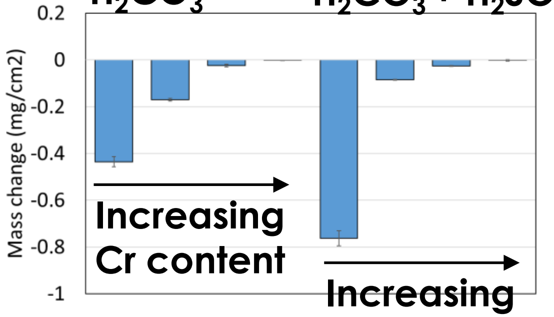


Diffusion bonding 740H

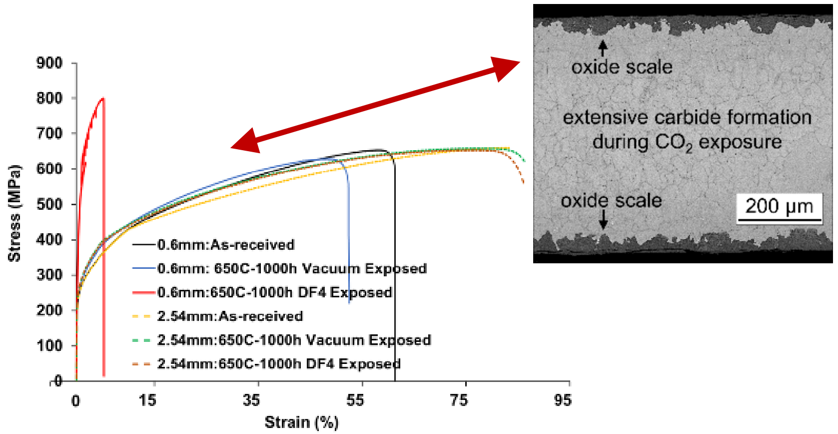


LOW-TEMPERATURE CORROSION

Identifying low-cost steels resistant to acidic condensates



LINKING OXIDATION BEHAVIOR AND MECHANICAL DEGRADATION



Select Recent Publications

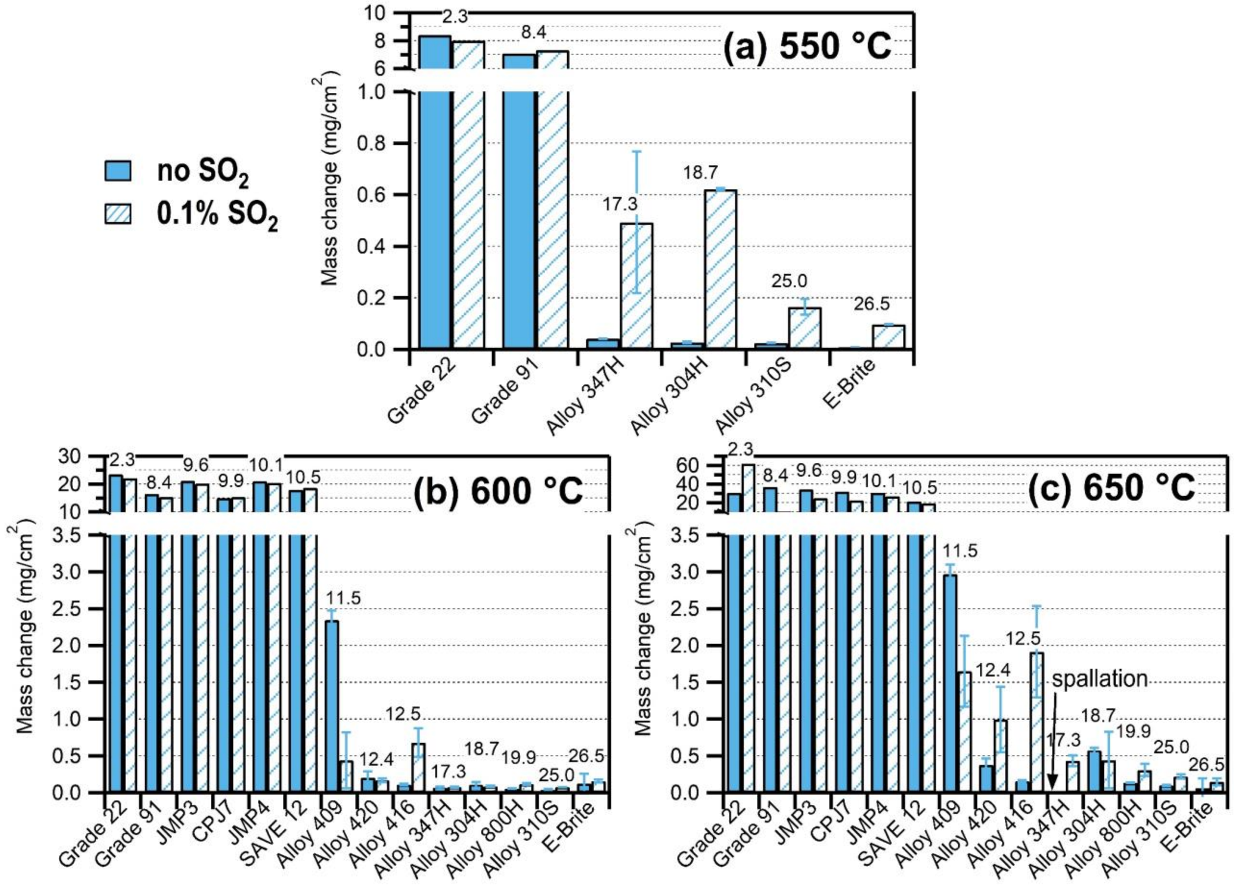
1. Temperature-Dependence of Corrosion of Ni-Based Superalloys in Hot CO2-Rich Gases Containing SO2 Impurities, R.P. Oleksak, J.H. Tylczak, G.R. Holcomb, Ö.N. Doğan, JOM (2020).
2. High temperature oxidation of steels in CO2 containing impurities, R.P. Oleksak, J.H. Tylczak, G.R. Holcomb, Ö.N. Doğan, Corrosion Science (2020).
3. Effect of surface finish during high temperature oxidation of steels in CO2, supercritical CO2 and air, R.P. Oleksak, G.R. Holcomb, C.S. Carney, L. Teeter, Ö.N. Doğan, Oxidation of Metals (2019) 92 525-540.
4. Effect of 730°C supercritical fluid exposure on the fatigue threshold of Ni-base superalloy Haynes 282, K.A. Rozman, G.R. Holcomb, C.S. Carney, Ö.N. Doğan, J.J. Kruzic, J.A. Hawk, Journal of Materials Engineering and Performance (2019) 28 (7) 4335-4347.
5. High-temperature oxidation of Ni alloys in CO2 containing impurities, R.P. Oleksak, J.H. Tylczak, G.R. Holcomb, Ö.N. Doğan, Corrosion Science (2019) 157 20-30.

Oxidation of Steels: Direct-Fired sCO_2 Environments

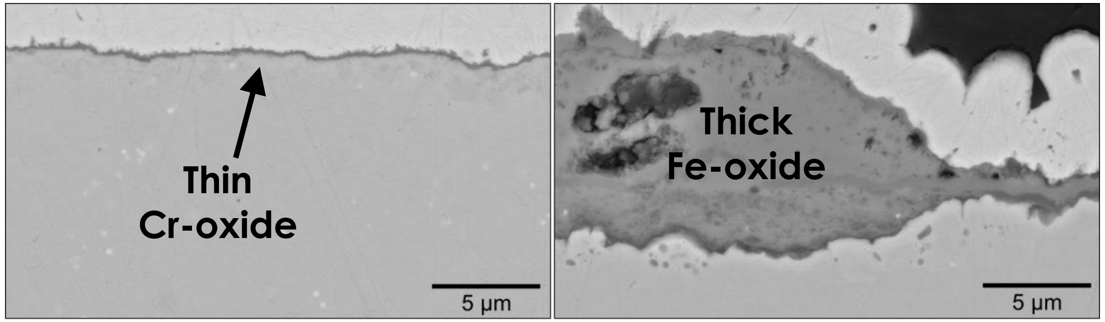
CO_2+4%$H_2$0+1%O_2+SO_2 Time: 2500 hrs

CO_2+4%H_2O+1%O_2 suggested by NETPower

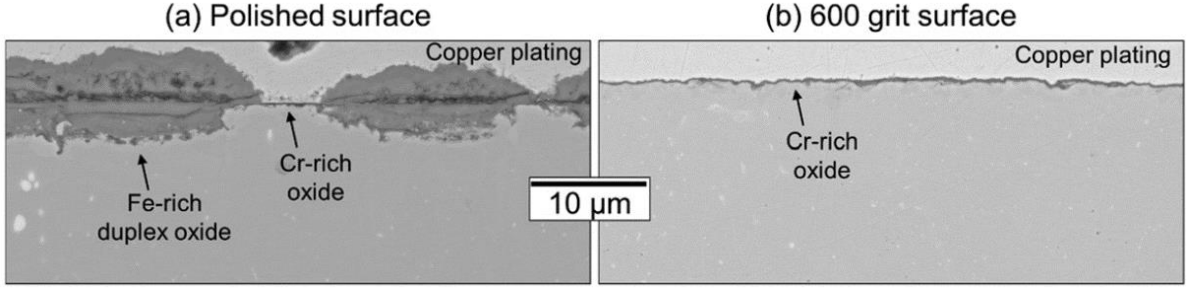
Determining critical Cr content required for protective scale formation



Effect of SO_2 impurities (347H)



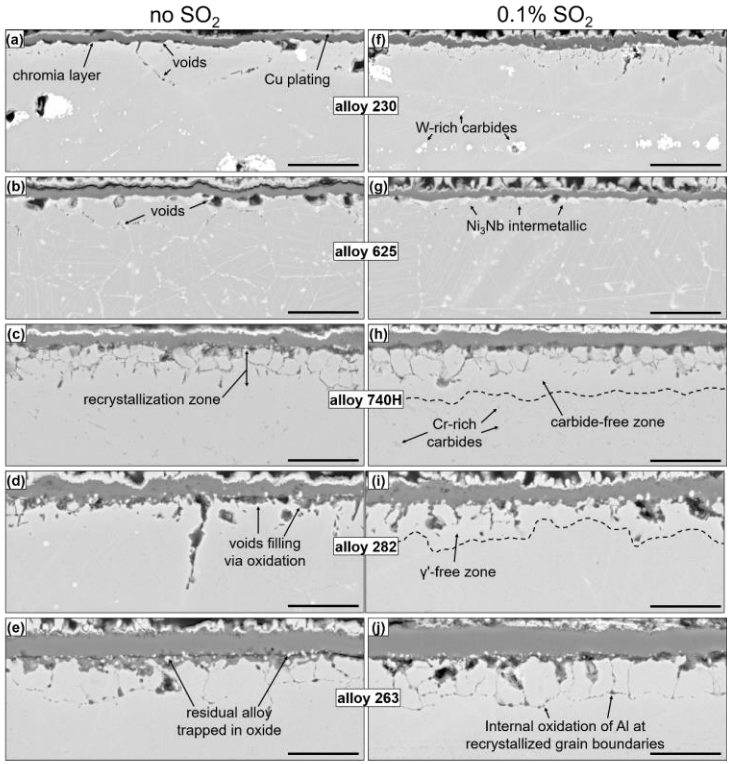
The role of surface finish (347H)

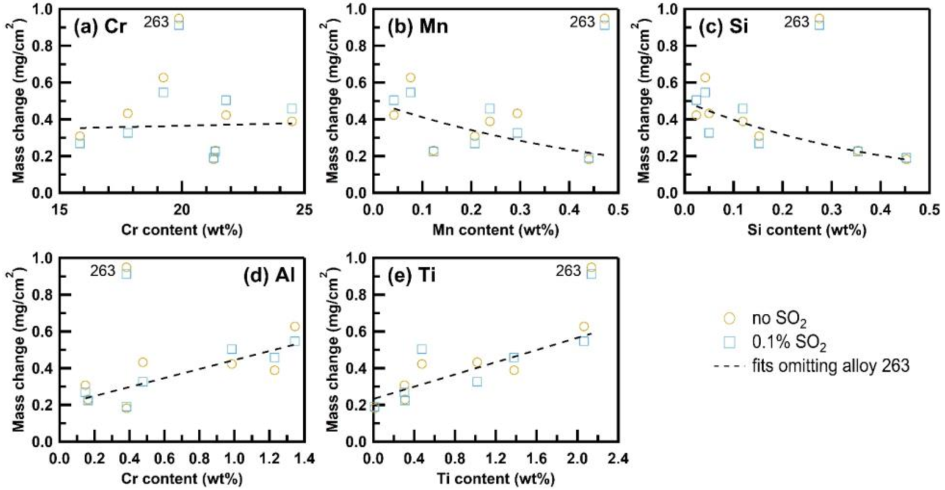


Pure CO_2 – repeating experiment under direct cycle environments

Oxidation of Ni Alloys: Direct-Fired sCO_2 Environments

The role of minor alloying elements in chromia-forming alloys





$CO_2+4\%H_20+1\%O_2+SO_2$

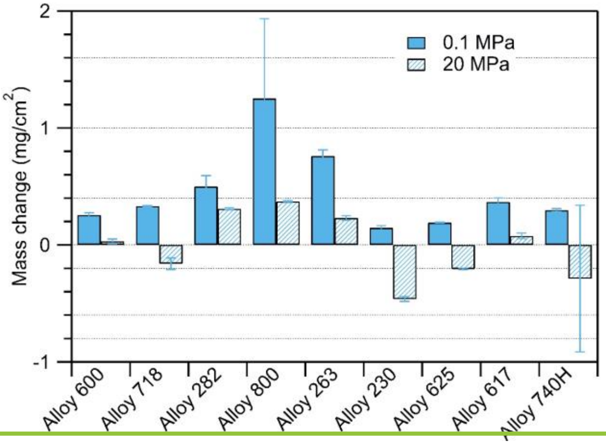
750°C-2500 hrs

$CO_2+4\%H_2O+1\%O_2$ suggested by NETPower

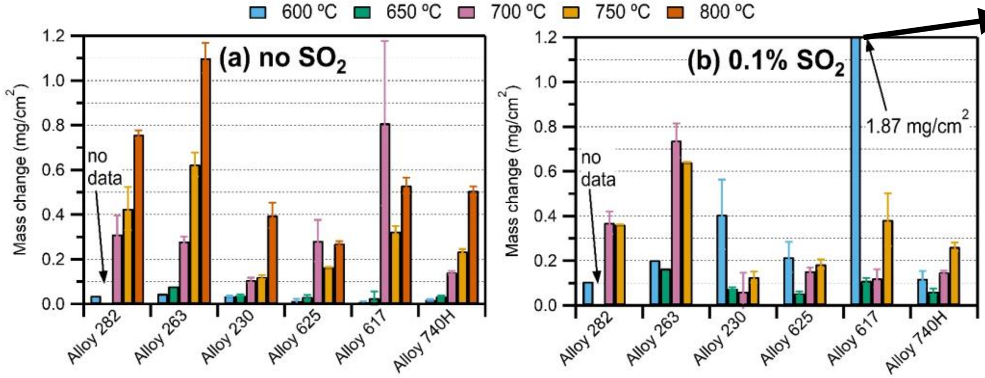
Effect of pressure

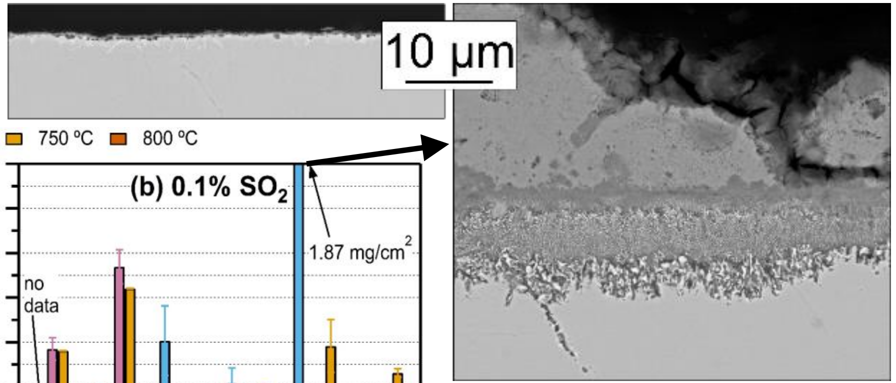
$CO_2+4\%H_20+1\%O_2$

750°C 1500 hrs (2500 hrs in progress)



Effect of SO_2 impurities





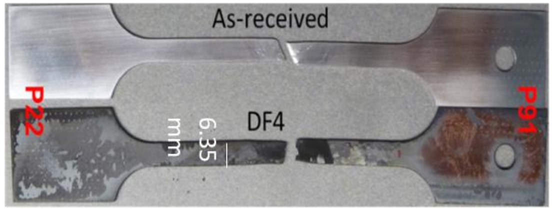
Impact of sCO_2 on Dissimilar Metal Welds

Dissimilar Welds

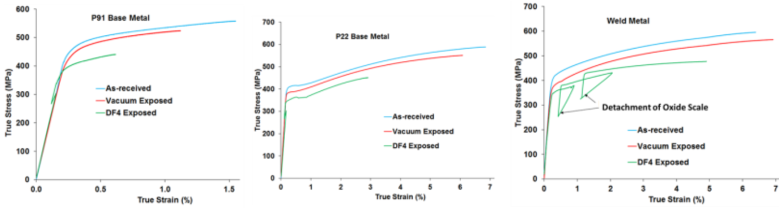
P22-P91
P91-347H
P22-Alloy 263
Alloy 625-Alloy 263
347H-Alloy 263

At Edison Welding Institute (EWI)
By Gas Tungsten Arc Welding (GTAW).
With Post Weld Heat Treatment.

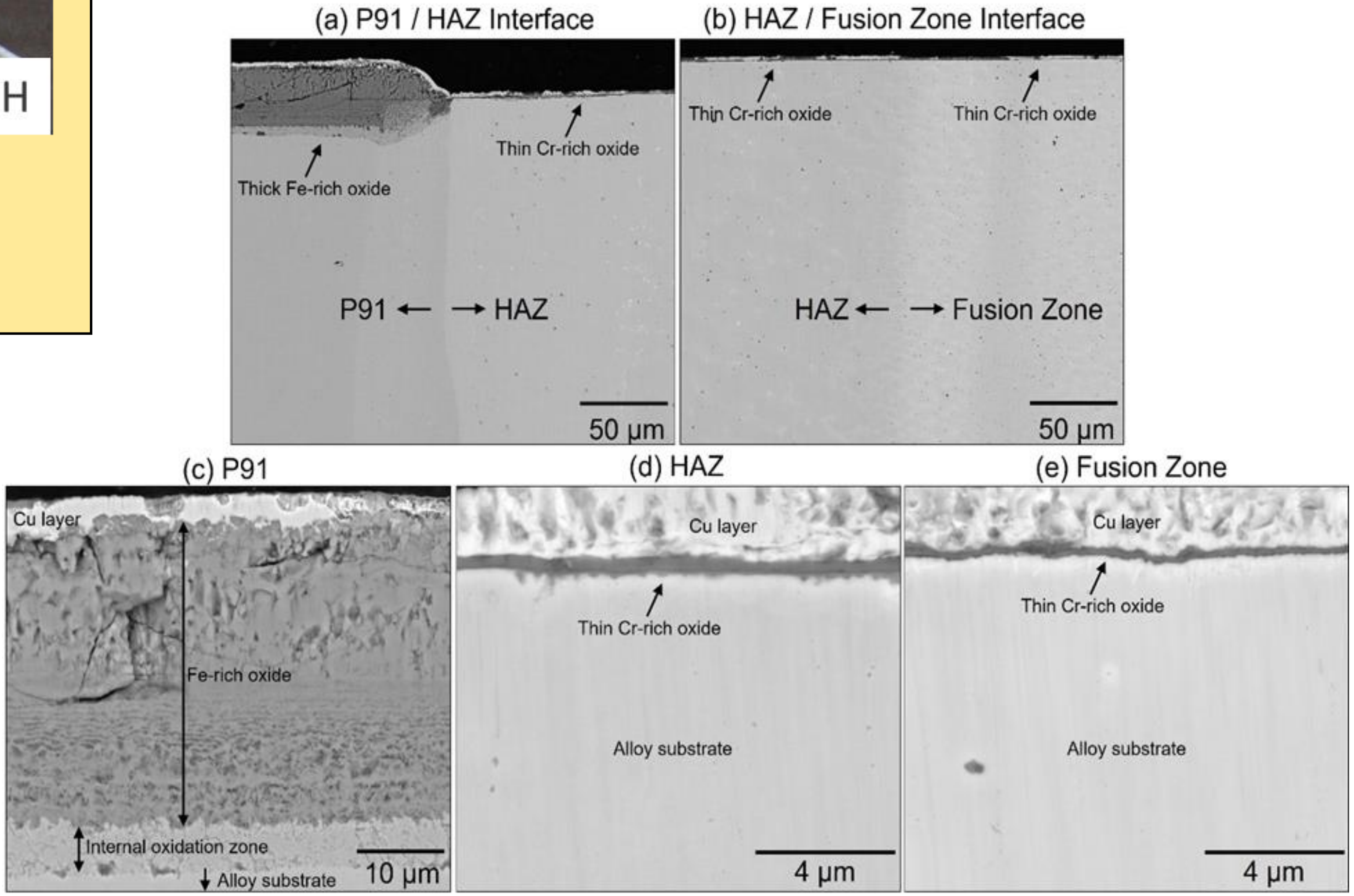
Oxidation and Deformation Behvaior of Dissimilar Metal Welds in Direct sCO_2 (CO_2+4%H_2O+1%O_2)



Exposure to CO_2+4%H_2O+1%O_2 (DF4) for 1000h



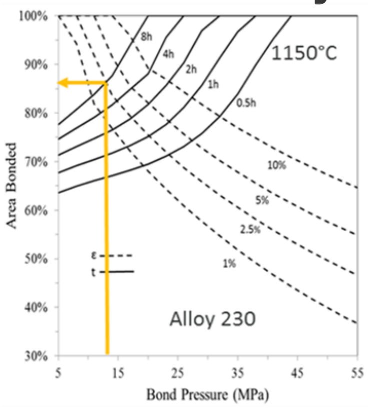
P91-347H weld exposed to sCO2: 550 °C and 200 bar for 1000 h.



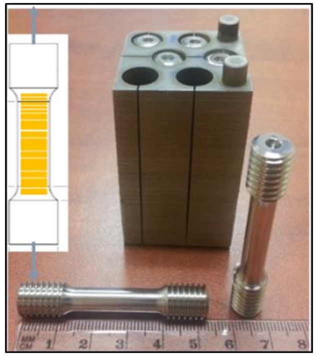
Compact Heat-Exchangers for sCO_2 Power Cycles

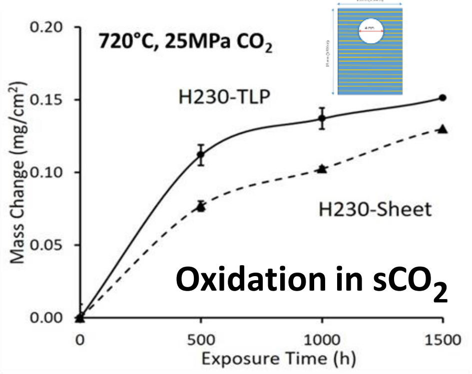
Micro-channel HX Via Diffusion Bonding **Ni-Superalloy** Sheets

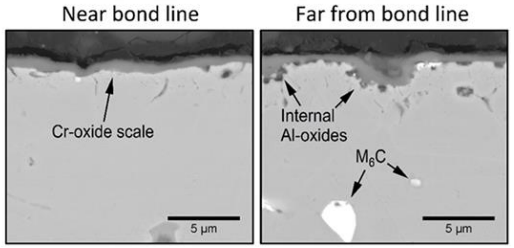
Transient-liquid-phase (TLP) bonding using Ni-P interlayers developed for Alloy 230.

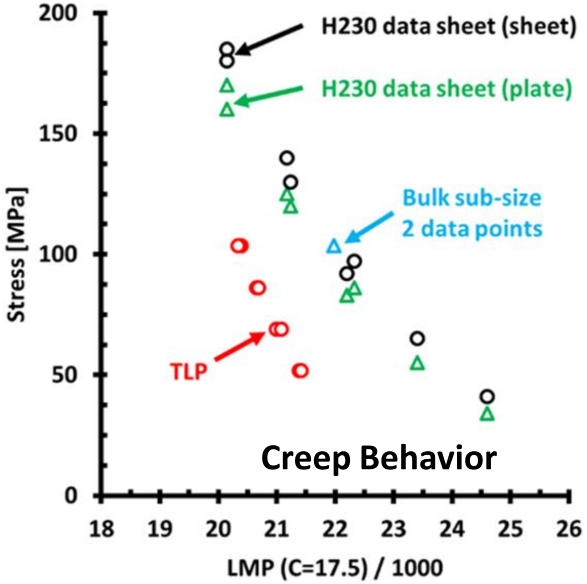


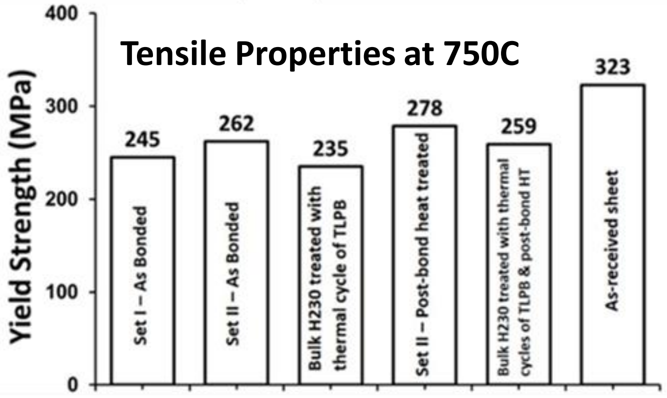
Strength of the bonded stacks was greater than 85% of base alloy 230 yield stress. Bonded stacks possessed acceptable low-cycle fatigue and creep properties. However, plastic strain localization in the bond region caused low tensile and creep elongation

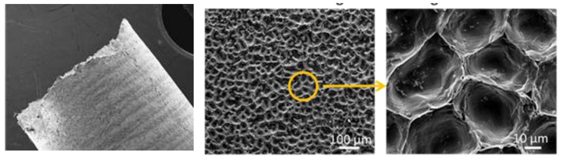












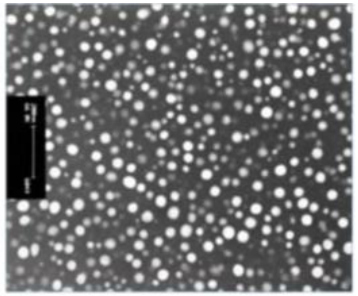
Diffusion Bonding IN-740H Sheets

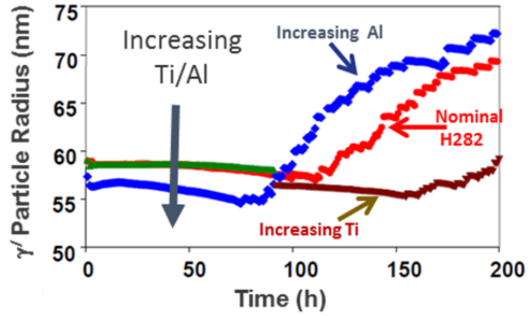
1. Creep Performance of Transient Liquid Phase Bonded Haynes 230 Alloy, K.A. Rozman, M.A. Carl, M. Kapoor, Ö.N. Doğan, J.A. Hawk, Materials Science and Engineering A, (2019) 768 138477.
2. Transient-Liquid-Phase bonding of H230 Ni-based alloy using Ni-P interlayer - Microstructure and Mechanical Properties, M. Kapoor, Ö.N. Doğan, C.S. Carney, R.V. Saranam, P. McNeff, B.K. Paul, Materials and Metallurgical Transactions A (2017) 48, 3343 - https://doi.org/10.1007/s11661-017-4127-5.

NETL Materials Performance Simulations

NATIONAL ENERGY TECHNOLOGY LABORATORY

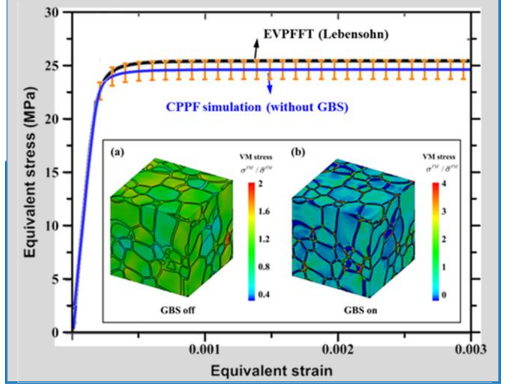
Gamma Prime Coarsening in H282



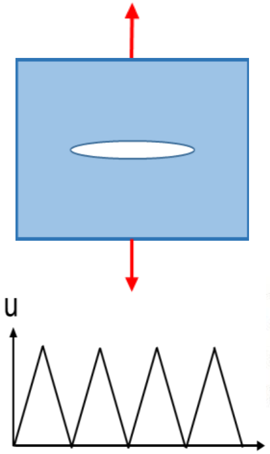


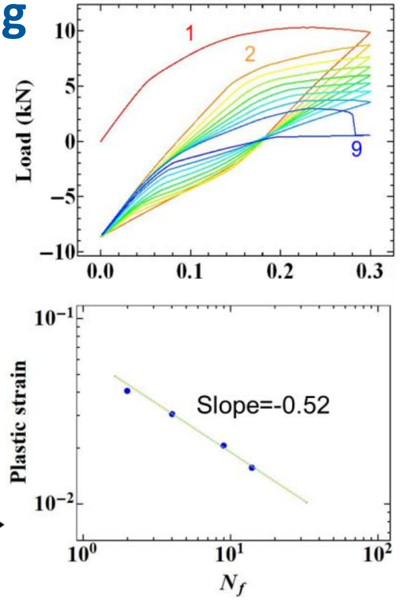
Alloy	Ni	Cr	Co	Mo	Ti	Al	Ti/Al
Nominal	Bal	18.5-20.5	9-11	8-9	1.9-2.3	1.38-1.65	
H282-B	Bal	19.22	9.86	8.49	2.22	1.27	1.75
H282-C	Bal	19.19	9.85	8.50	1.94	1.54	1.26

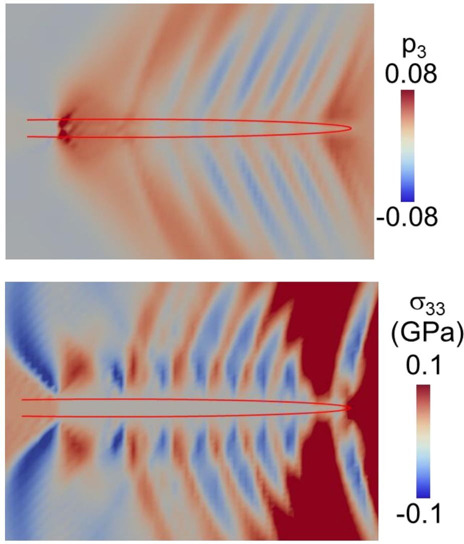
Creep modeling of polycrystalline with/without GBS



LCF modeling



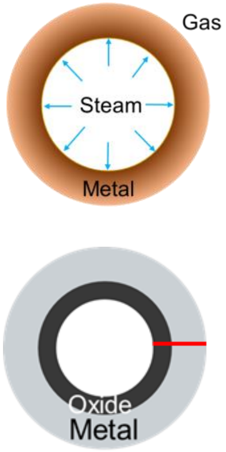


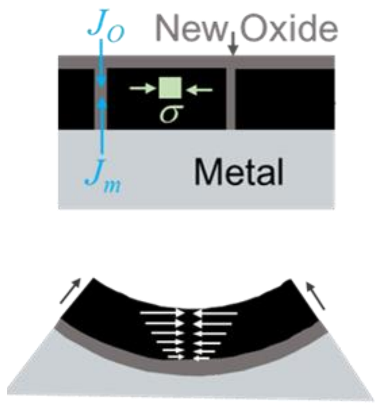


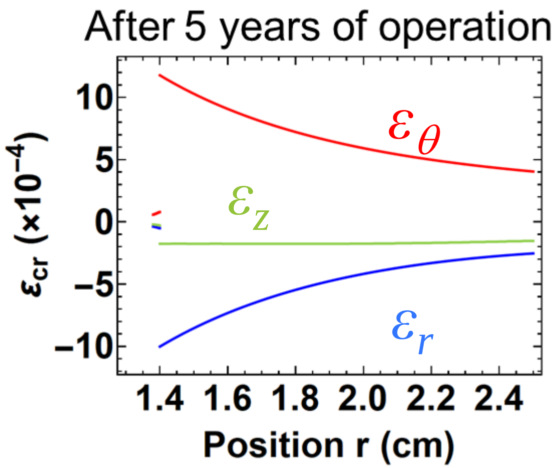
Oxide Scale Spallation

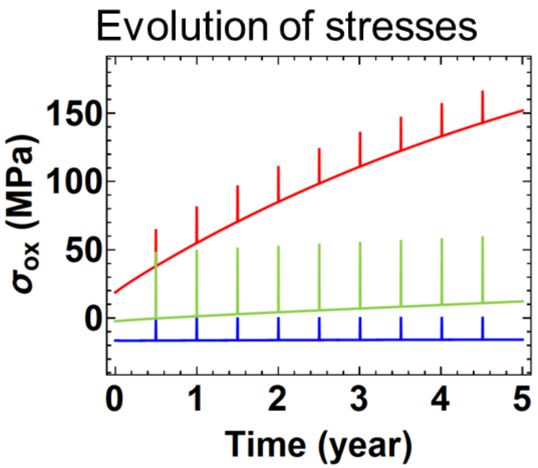
Spallation due to:

- Temperature (Different thermal expansion)
- Oxide growth strain with geometric constraint
- Different creep rate between oxide and metal







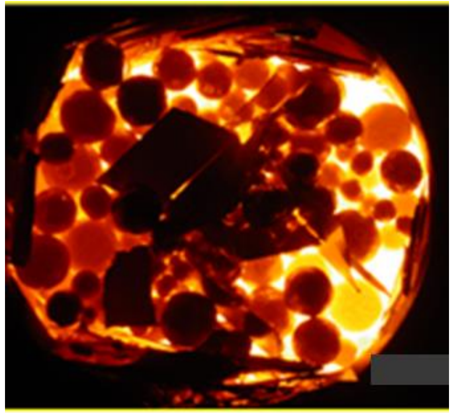


U.S. DEPARTMENT OF ENERGY

1. *Tianle Cheng et al.*, "Diffuse Interface Approach to Modeling Crystal Plasticity with Accommodation of Grain Boundary Sliding," *International Journal of Plasticity*, 114, p. 106-125, 2019
2. *Hu Chen et al.*, "A two-set order parameters phase-field modeling of crack deflection/penetration in a heterogeneous microstructure," *Computer Methods in Applied Mechanics and Engineering*, 347, p. 1085-1104, 2019
3. *Fei Xue et al.*, "Stress analysis of the steam-side oxide of boiler tubes: contributions from thermal strain, interface roughness, creep, and oxide growth," *Oxidation of Metals*, accepted for publication, 2020

Alloy Fabrication Capabilities

For Mission Critical Applications. Scales Translate to Industrial Practice.



Melt Processing Capabilities

- Air Induction Melting: up to 300 lbs
- VIM: 10, 50 and 500 lbs
- Vacuum Arc Remelt/Electro-Slag Remelt
  VAR/ESR: 3 to 8 inch diameter crucibles

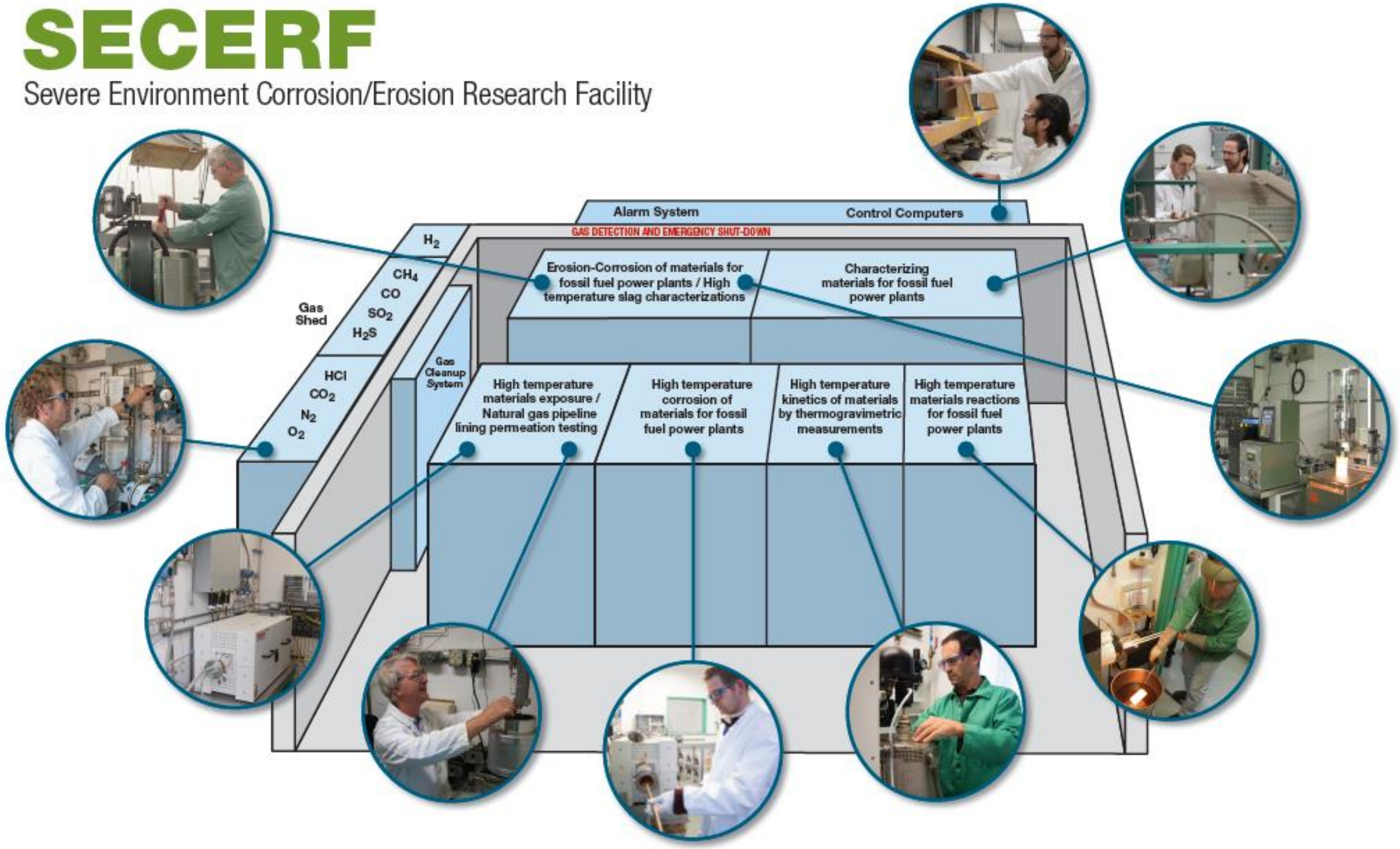
Thermo-Mechanical Processing Capabilities

- Heat-treatment furnaces:1650^{o}C, inert atmospheres and controlled cooling.
- Press Forge: 500 Ton
- Roll mills: 2 and 4 high configurations.

Materials Performance in Extreme Environments

SECERF

Severe Environment Corrosion/Erosion Research Facility



- Safety Integrated System to allow for safe 24/7 unattended operations.
- Gas environment tailored by mixing with programmable mass flow controllers.
- Available gases: CO, CO_2, CH_4, H_2, H_2S, SO_2, HCl, O_2, N_2, He, air, H_2O vapor.
- Gas flow rates: 5-1600 ml/min (depending on gas).
- Maximum temperature: furnaces: 1600C; erosion rig: 750C

Corrosion & Oxidation Laboratories

- Ultra-super-critical (USC) Steam Autoclave: Dual rated: 310 bar at 760C and 345 bar at 746C. System to control steam chemistry (dissolved oxygen). Computer controlled for 24/7 unattended operations.
- Supercritical CO_2 Autoclave: rated at 800C and 275bar
- Autoclaves (5000psi-250C), Flow Through Autoclaves (5000psi-500C), Rocking Autoclave (7250psi-400C). CO_2 O_2, SO_2, H_2S. *Autoclave for performing electrochemical experiments under pressure and temperature.*
- Potentiostats, Galvanostats , Electrochemical Impedance Spectroscopy.
- Static and cyclical oxidation furnaces for 24/7 exposures to O_2, H_2O vapor, CO_2
- Rotary kiln furnace for evaluating refractory materials performance in flowing slag environments under thermal gradients in combustion atmospheres

Fracture Mechanics and Creep Laboratories

- Screw driven & servo-hydraulic frames for strength and fatigue (max. load 1000 kn, 1600C, air). Constant stress & strain load frames for creep testing (1000C, air, CO_2)

NETL Computational Resources

Accelerating Technology Development – accessed at ALL NETL research sites

NATIONAL ENERGY TECHNOLOGY LABORATORY

Center for Computational Science and Engineering

JOULE 2.0

- At **3.6 petaflops** JOULE is the **10th fastest** supercomputer within DOE National Laboratories.
- This provides NETL and partners with high-performance computational power to solve challenges in energy.

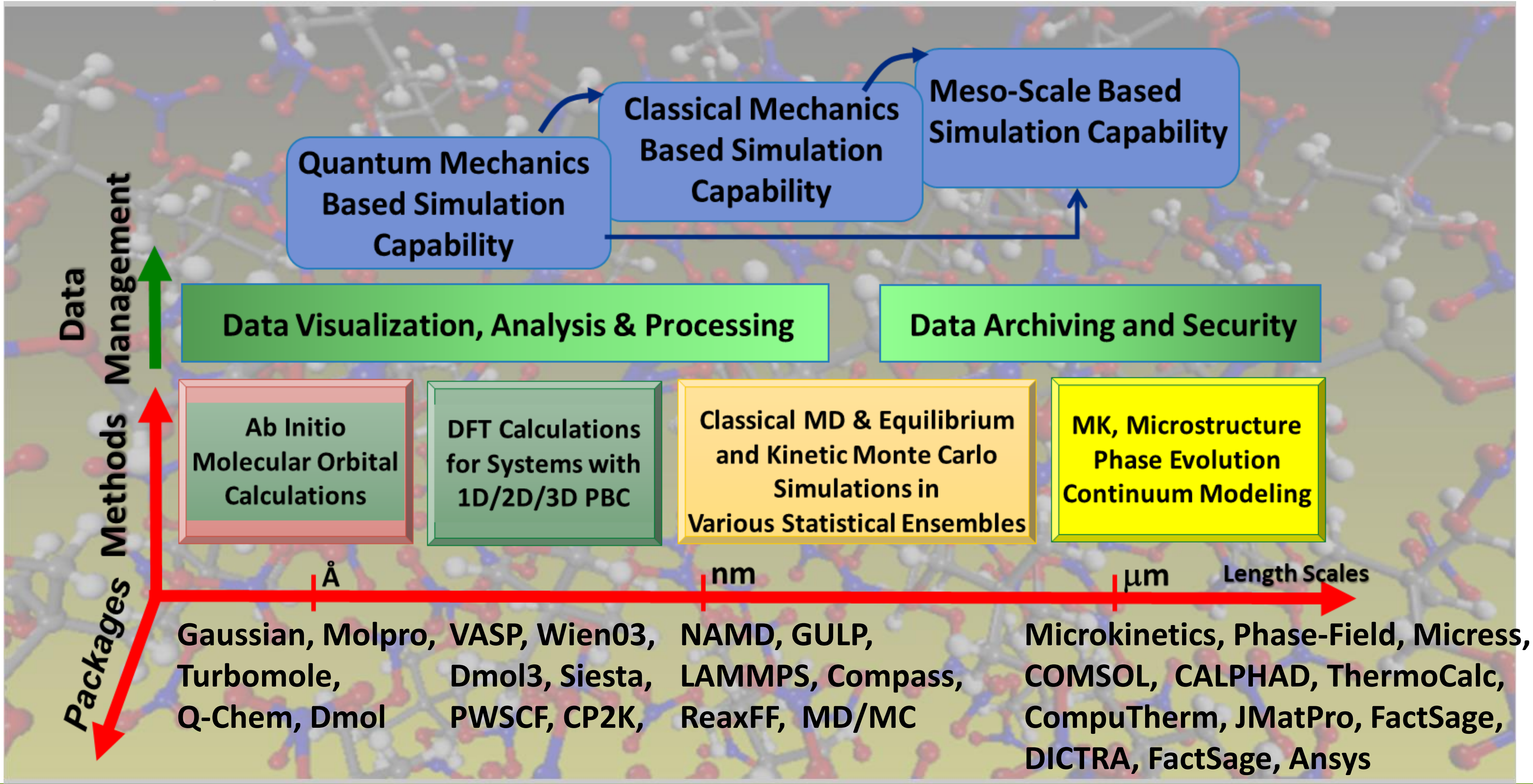
Center for Artificial Intelligence and Machine Learning

WATT

- Links **104 GPUs** with **16 petabytes** of storage to provide unparalleled opportunities for the use of AI/ML to enable scientific discovery and R&D acceleration.

Computational Materials Capabilities

Multiscale Modelling

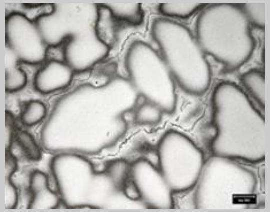


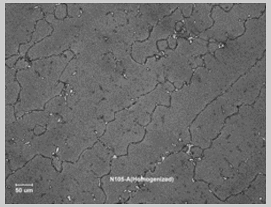
U.S. DEPARTMENT OF ENERGY

Impact & Innovation: Structural Materials Team

Enabling Advanced Energy Systems and Advancing the Fossil Energy Mission

NETL's Computational Tool to Specify Alloy Homogenization



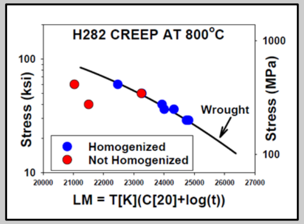


Enabling technology for **Advanced Ultra-Super Critical Steam** (A-USC) Turbines.

Specified heat-treatments:

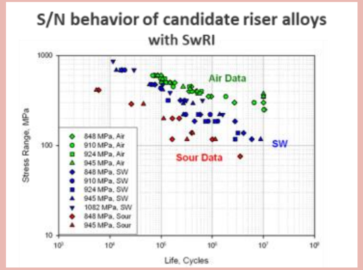
2016

- **Special Metals:** ESR/VAR **10,000 lb** superalloy ingot.
- **GE:** ½ actual size **cast valve body** for an A-USC turbine **18,500 lb** superalloy casting.

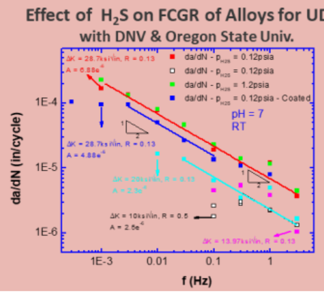


High-Performance Materials (Cross-Cutting Research)

Materials Performance Assessment for Reliability



Off-Shore



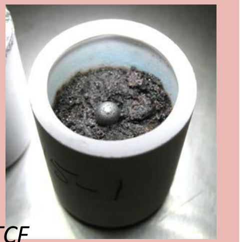
NETL Developed Refractory Brick

- Licensed to Harbison-Walker
- Commercially produced as **Aurex 95P**.
- Used in nearly **every slagging gasifier** world-wide.
- NETL technology **doubled refractory** service life.

High-Performance Materials (Cross-Cutting Research) & Gasification

Materials Recovery & Recycling

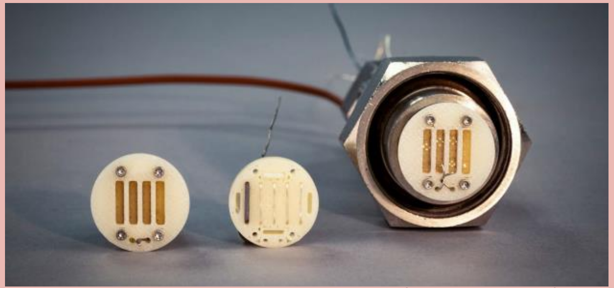
- ***Rare Earth Element Extraction from Coal and Gasification Slags*** *Through Additive Fusion Technology, US Patent: 10,358,649 B2*
- *Carbothermal Reduction of Gasification Slags to Recover Nickel and Vanadium, US Patent: 10,323,298 B2*



Rare Earth Elements, Gasification, & TCF

Advanced Membrane-Based Electrochemical Sensors

- **Increase** in pipeline **efficiency & safety**.
- **Real time simultaneous monitoring** of natural gas **environment** and pipeline **corrosion.**



Natural Gas Infrastructure (Midstream)

QUESTIONS?

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