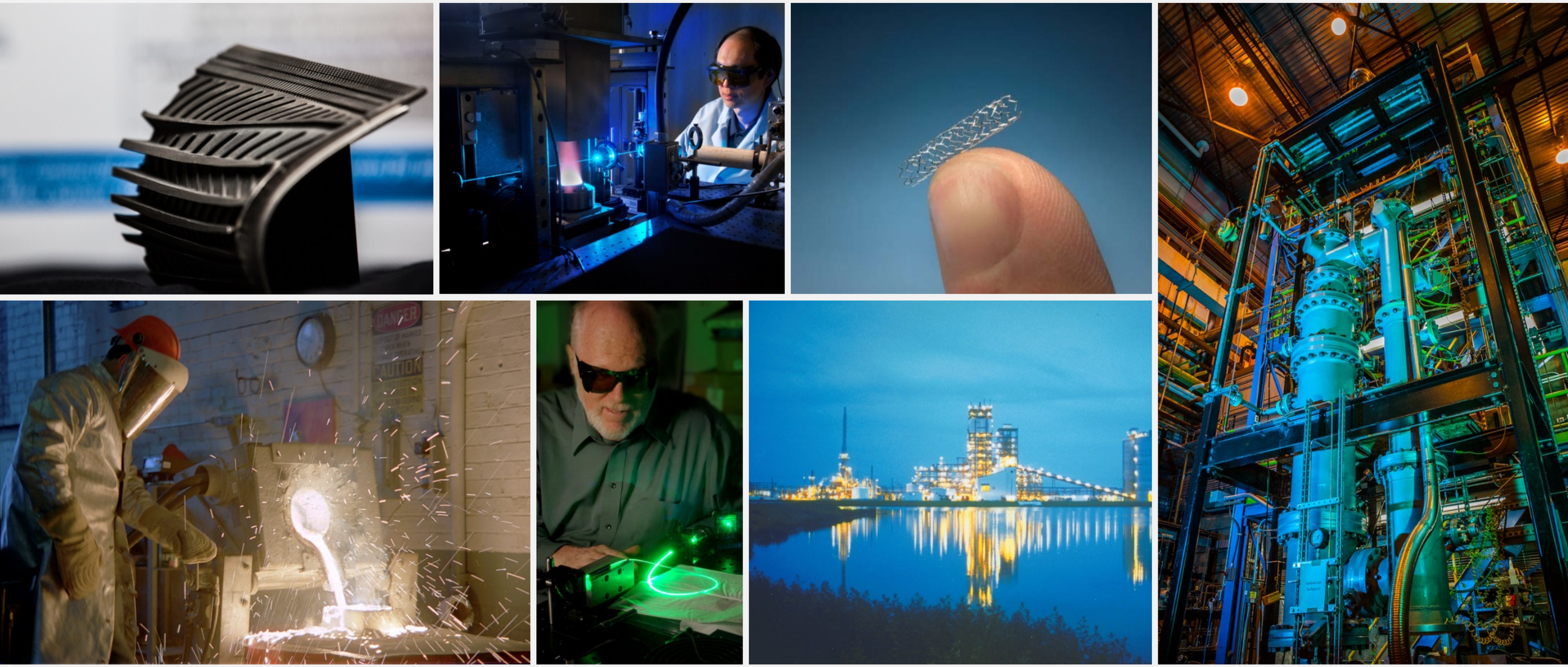
Driving Innovation ♦ Delivering Results



US-UK Collaboration on Fossil Energy Advanced Materials: Task 1—Steam Oxidation (NETL-US)

Gordon R Holcomb
Joseph Tylczak
Casey Carney

US-UK Collaboration on Fossil Energy R&D: Advanced Materials Workshop
Pittsburgh, PA, April 19, 2017

U.S. Department of Energy
National Energy Technology Laboratory

Acknowledgements

Funding and Support

This work was funded by the Cross-Cutting Technologies Program at the National Energy Technology Laboratory (NETL) – Strategic Center for Coal, managed by Robert Romanosky (Technology Manager) and Charles Miller (Technology Monitor). The Research was executed through NETL's Office of Research and Development's Innovative Process Technologies (IPT) Field Work Proposal.

Disclaimer

"This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

Outline

- **Deliverables**
- **Products**
- **Transition from Phase 2 to Phase 3**

US-Led or Co-Led Deliverables

- **Phase I Paper**
  - A. T. Fry, I. G Wright, N. J Simms, B. McGhee, and G. R. Holcomb, "Steam Oxidation of Fossil Power Plant Materials: Collaborative Research to Enable Advanced Steam Power Cycles," Materials at High Temperatures, 30, 4(2013): pp. 261-270.
- **Report on the inter-comparison exercise (leads are Tony Fry and Gordon Holcomb)**
  - NETL conducted tests of 300 and 1000 hours, sent report to Tony Fry
  - G. R. Holcomb, "Steam Oxidation Laboratory Comparison Exercise," US-UK Energy RTD Collaboration 2009-2013: Advanced Materials, DOE/NETL-2014/1652, April 15, 2014.
- **Verification of Cr evaporation model with respect to gas velocity**
  - G.R. Holcomb, J. Tylczak, and R. Hu, "Materials Performance in USC Steam," Proceedings of the 25th Annual Conference on Fossil Energy Materials, Portland, OR, April 26-28, 2011.
- **Experiments on hydrogen permeation through pure Fe and Ni specimens**
  - Separate rates of hydrogen emission into the gas and into the specimen were measured during oxidation of Fe and Ni in an Ar-3%H_2O atmosphere.

Phase II Products (US), 2011-present

- **Peer Reviewed Journals**
  - N. Mu, K. Y. Jung, N. M. Yanar, F. S. Pettit, G. R. Holcomb , B. H. Howard, G. H. Meier, "The Effects of Water Vapor and Hydrogen on the High-Temperature Oxidation of Alloys," Oxidation of Metals, 79, 5-6 (2013): pp. 461-472.
  - G. R. Holcomb, "High Pressure Steam Oxidation of Alloys for Advanced Ultra-supercritical Conditions," Oxidation of Metals 82, 3-4(2014): pp. 271-295.
  - N. M. Yanar, B. S. Lutz, L. Garcia-Fresnillo, M.P. Brady and G.H. Meier, "The Effects of Water Vapor on the Oxidation Behavior of Alumina Forming Austenitic Stainless Steels", Oxidation of Metals, 84, 5-6(2015): pp. 541-561.
  - G. R. Holcomb, Ö. N. Doğan, C. Carney, "Oxidation of Alloys for Energy Applications in Supercritical CO_2 and H_2O," Corrosion Science (2016). **[Transitional to Phase III]**
- **Proceedings and Book Chapters**
  - G.R. Holcomb, J. Tylczak, and R. Hu, "Materials Performance in USC Steam," Proceedings of the 25th Annual Conference on Fossil Energy Materials, Portland, OR, April 26-28, 2011.
  - G. R. Holcomb, "Environmental Degradation—Steam Oxidation," Chapter 11 in <u>Power Plant Life Management and Performance Improvement</u>, Ed. J. E. Oakey, Woodhead Publishing, Cambridge, UK, September, 2011, ISBN: 978-1-84569-726-6.
  - G. R. Holcomb, "Chromia Evaporation in Advanced Ultra-Supercritical Steam Boilers and Turbines," Chapter 9 in <u>Thermodynamics - Kinetics of Dynamic Systems</u>, Ed. J. C. Moreno-Piraján, InTech, Rijeka, Croatia, September, 2011, ISBN: 978-953-307-318-7.
  - G. R. Holcomb, J. Tylczak, G. H. Meier, B. S. Lutz, N. M. Yanar, F. S. Pettit, J. Zhu, A. Wise, D. E. Laughlin, and S. Sridhar, "Oxy-Combustion Environment Characterization: Fire- and Steam-Side Corrosion in Advanced Combustion," Proceedings of the 26th Annual Conference on Fossil Energy Materials, Pittsburgh, PA, April 17-19, 2012.
  - G. R. Holcomb, "High Pressure Steam Oxidation of Ni-base Superalloys in Advanced Ultra-Supercritical Steam Boilers and Turbines," in the Proceedings of the 8th International Symposium on Superalloy 718 and Derivatives, Edited by: E. Ott, A. Banik, X. Liu, I. Dempster, K. Heck, J. Andersson, J. Groh, T. Gabb, R. Helmink, and A. Wusatowska-Sarnek, TMS, 2014.
  - G. R. Holcomb, Ö. N. Doğan, C. Carney, K. Rozman, J. A. Hawk, and M. H. Anderson, "Materials Performance in Supercritical CO2 in Comparison with Atmospheric Pressure CO_2 and Supercritical Steam," proceedings of the 5th International Supercritical CO2 Power Cycles Symposium, San Antonio, TX, March 29-31, 2016. **[Transitional to Phase III]**

Phase II Products (US), 2011-present

- **Selected Presentations**
  - G. R. Holcomb, "Oxidation Mechanisms of Alloys for Advanced Ultra-Super Critical Steam Applications," invited presentation at the 227th ECS Meeting, Chicago, IL, May 24-28, 2015.
  - G. R. Holcomb, "High Pressure Steam Oxidation of Boiler Alloys," invited presentation at the Gordon Research Conference on High Temperature Corrosion, New London, NH, July 26-31, 2015.
  - G. R. Holcomb, M. Lukaszewicz, N. J. Simms, B. H. Howard, N. M. Yanar, G. H. Meier, "Hydrogen Transport during Steam Oxidation of Iron and Nickel Alloys," presented at MS&T 2015, Columbus, OH, Oct. 4-8, 2015.
  - G. R. Holcomb, Ö. N. Doğan, C. Carney, K. Rozman, J. A. Hawk, and M. H. Anderson, "Materials Performance in Supercritical CO2 in Comparison with Supercritical Steam and Atmospheric Pressure CO_2," invited presentation at the EPRI International Conference on Corrosion in Power Plants, San Diego, CA, October 12-15, 2015. **[Transitional to Phase III]**
  - G. R. Holcomb, J. Tylczak, and C. Carney, "High Pressure Steam Oxidation of Boiler and Turbine Alloys," invited presentation at TMS 2016, Nashville, TN, February 14-18, 2016.

Phase III Products (US)

- **Proceedings**
  - Ö. N. Doğan, C. Carney, G. R. Holcomb, L. Teeter, and J. D. Tucker, “High-Temperature Corrosion of Diffusion Bonded Ni-based Superalloys in Supercritical CO_2 Cycle Conditions,” proceedings of the 5th International Supercritical CO_2 Power Cycles Symposium, San Antonio, TX, March 29-31, 2016.
- **Selected Presentations**
  - Ö. N. Doğan, C. Carney, R. Oleksak, C. Disenhof, and G. R. Holcomb, “High-Temperature Corrosion of Diffusion Bonded Haynes 230 in Supercritical CO_2 Cycle Conditions,” presentation at TMS 2016, Nashville, TN, February 14-18, 2016.

Phase III Plan

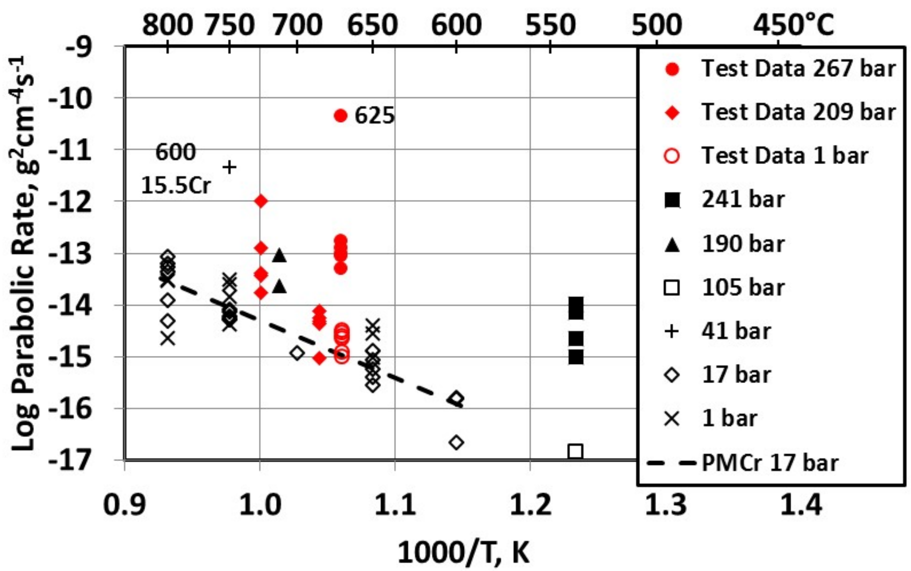
- **Continue oxidation testing in high pressure steam**
  - More emphasis on water quality
  - Longer duration tests
  - Use of Ni-xCr model alloys to examine changes in critical Cr content with pressure
    - x = 12, 14, 16, 18, 20, 22, 24
  - Use of Ni-5Cr and Ni-2.3Al-4.6Cr model alloys to examine changes in internal oxidation morphology with pressure
- **Participate in NETL's Advanced Combustion program for sCO_2 power cycles**
  - High temperature/pressure oxidation in pure CO_2 [indirect cycles]
  - High temperature/pressure oxidation in CO_2 + H_2O [related to direct cycles]
    - More complex atmospheres (some containing SO_2 are discussed in Task 2
  - Oxidation effects on mechanical properties
  - Use model alloys to determine the effect of Si on carburization
    - Ni-22Cr-xSi, Fe-22Cr-xSi, Fe-22Ni-22Cr-xSi, where x ranges from 0 to 1.5 wt%
  - Compact heat exchanger materials
    - Diffusion bonded materials
    - Thickness effects

sCO_2 compared with sH_2O

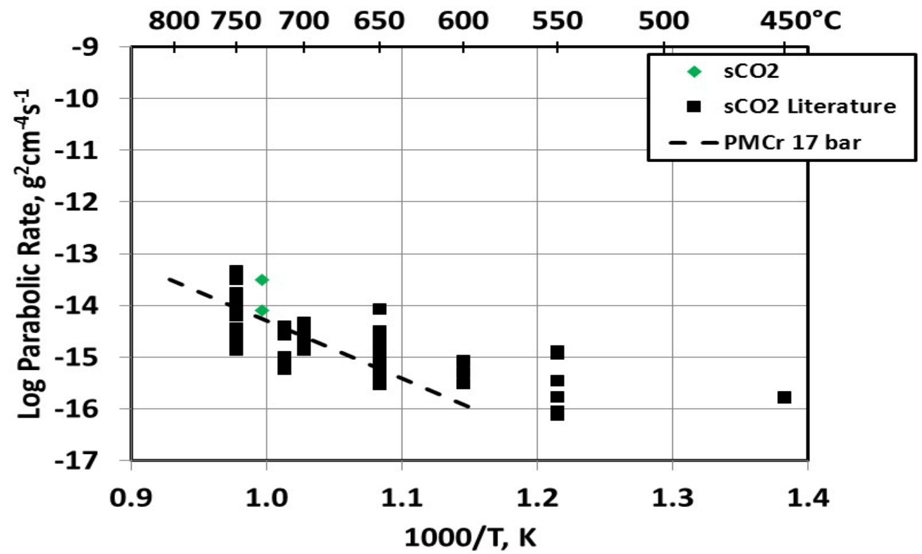
- **Currently in the commissioning process for sCO_2 autoclave**
  - Up to 800°C/277 bar
  - Up to 25% H_2O along with CO_2
- **Complements existing sH_2O autoclave**
  - Effective range of up to 670°C/344 bar or 725°C/227 bar
- **Preliminarily Results Indicate:**
  - Nickel-base alloys
    - Unlike in sH_2O, there is no evidence of significant increased oxidation rates at high pressure in sCO_2
  - Fine-grain austenitic steels
    - Similar increase in oxidation with pressure in both sH_2O and sCO_2
    - More Fe-rich oxide nodule formation with pressure
    - Variability in results associated with nodule formation/lateral growth
  - Coarse-grain austenitic steels
    - No measurable increase in oxidation with pressure in sH_2O
    - Not examined in sCO_2

Ni-base Alloys

H_2O



sCO_2, 200-207 bar, 99.99+%

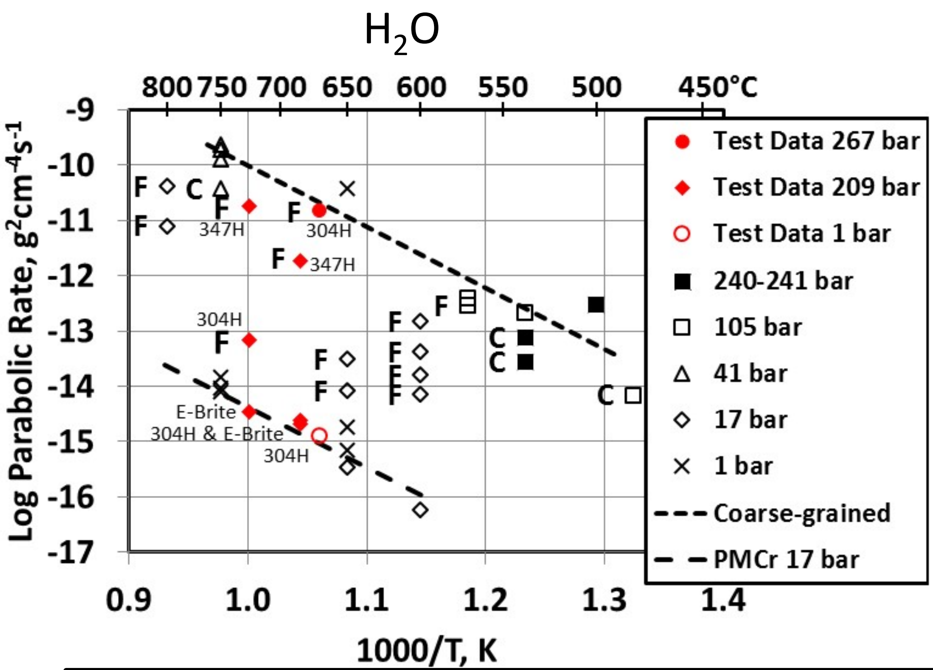


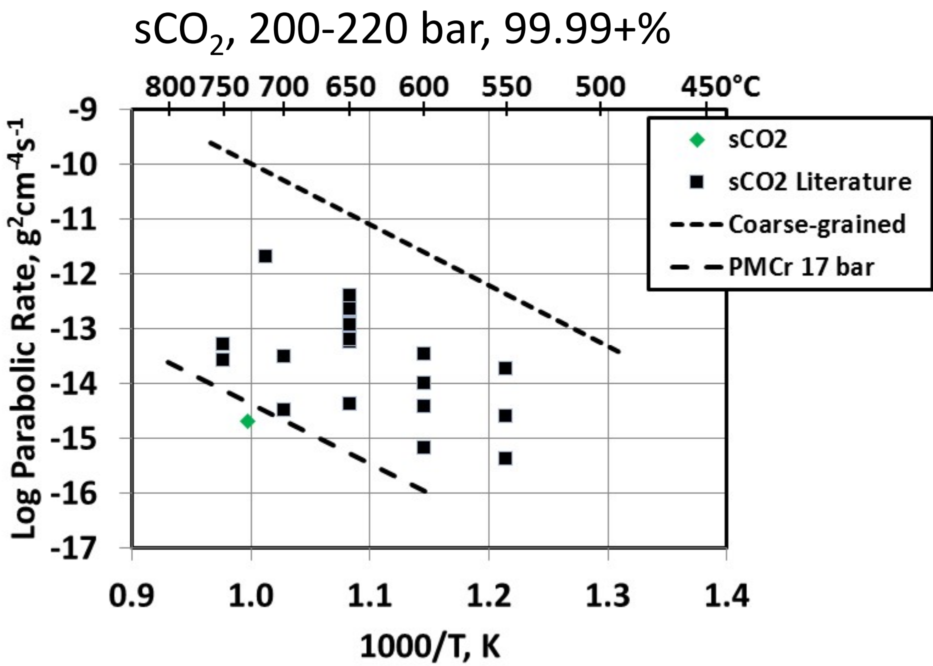
- **The highest pressures in sH_2O show an increased oxidation rate**
- **No evidence of increased oxidation rates at high pressure in sCO_2 (at temperatures of interest)**
- **625 has ~8000 h in a steam superheater at ~713°C/190 bar with good performance Knödler (2014)**

H_2O adapted from the compilation of Wright & Dooley (2010), plus Knödler (2014), Holcomb (2014) and Holcomb (2016)
sCO_2 adapted from Pint (2014), Dunlevy (2007), Lee (2014, 2015), Firouzdor (2013), Dheeradhada (2015), and Mahaffey (2015)

Note: PMCr forms pure chromia scale

300 Series (18Cr-8Ni)/E-Brite





- **Similar behavior in both sH_2O and sCO_2 (but note the gap in sCO_2)**
- **A variable increase in oxidation of fine-grain alloys with pressure**
- **Variability arises from Fe-rich nodule formation and lateral growth to disrupt protective chromia scale**

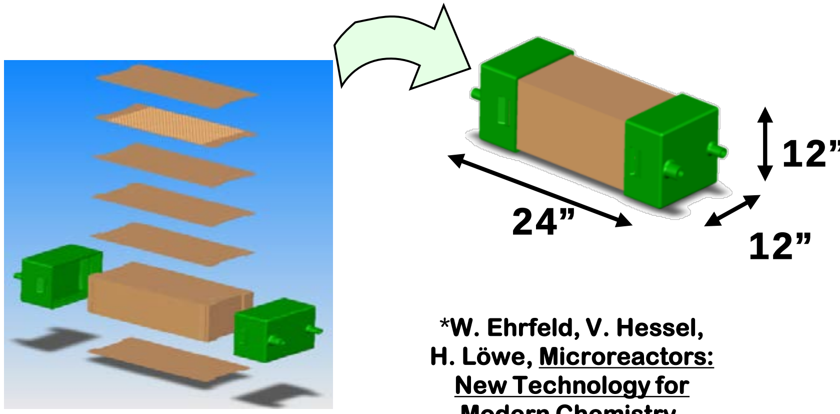
H_2O adapted from the compilation of Wright & Dooley (2010), plus Holcomb (2014) and Holcomb (2016)
sCO_2 adapted from Furukawa (2011), Cao (2012), Pint (2014), Lim (2008), Olivares (2015), Dunlevy (2007), and Lee (2015)

Note: PMCr forms pure chromia scale

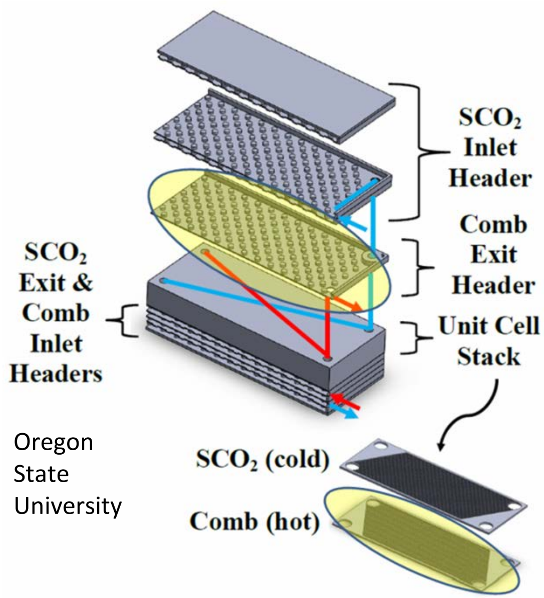
Typical Microchannel HX Fabrication Process

Microlamination-

1. **Pattern microscale flow paths into laminae using a variety of methods (etching, micromachining, laser cutting, EDM, others)**
2. **Bond these laminae using a variety of methods (diffusion bonding, laser welding, brazing, others). For sCO_2, diffusion bonding seems to be the most robust approach**

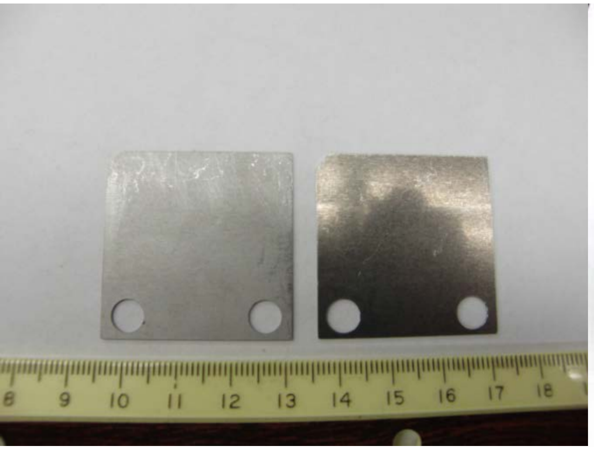


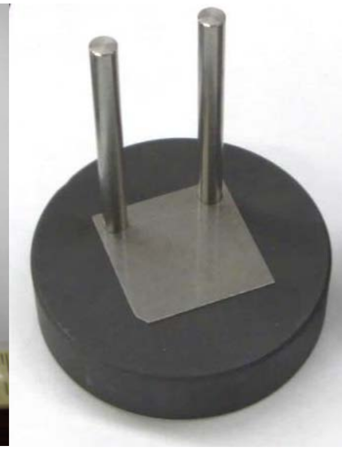
*W. Ehrfeld, V. Hessel, H. Löwe, Microreactors: New Technology for Modern Chemistry, Wiley-VCH, 2000.

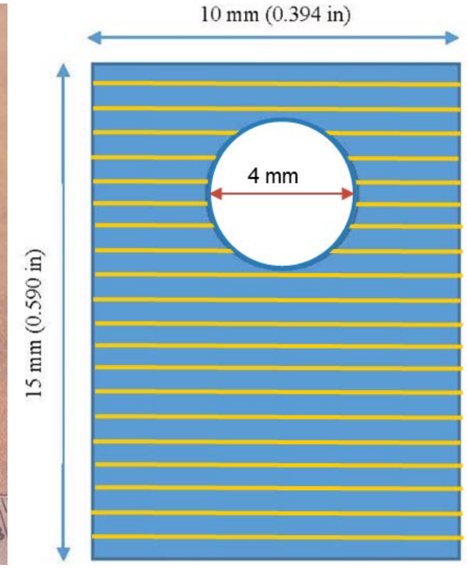


Oregon State University

Diffusion Bonded Ni-base Superalloys







Mass changes as a result of the CO_2 exposure at 700°C for 500 h. Averages and standard deviations are from three coupons for each condition.		
	Average mass change (mg/cm²)	Standard deviation (mg/cm²)
H230	0.077	0.012
H230-DB	0.115	0.013
H230-DB-Ni	0.112	0.005
H282	0.038	0.022
H282-DB-Ni	0.236	0.008

H230: Minor mass change increase

H282: More significant mass change increase