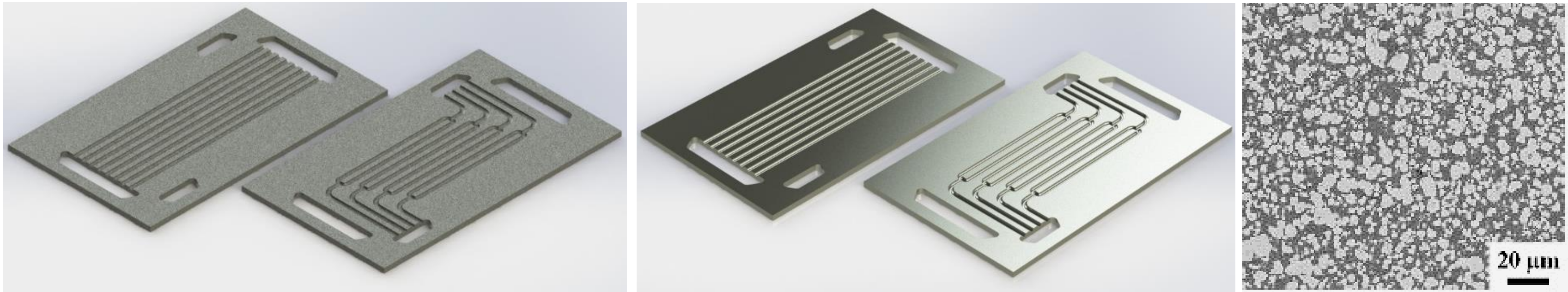
Robust High-Temperature Heat Exchangers
(Topic 2A Gen 3 CSP Project; DE-EE0008369)



Illustrations of: (left) porous WC preform plates, (middle) dense-wall ZrC/W plates with horizontal channels and vertical vias. (Right) Backscattered electron image of the dense microstructure of a ZrC/W cermet.

Team: Ken H. Sandhage[1] (PI), Kevin P. Trumble[1] (Co-PI), Asegun Henry[2] (Co-PI), Aaron Wildberger[3] (Co-PI)

[1]School of Materials Engineering, Purdue University, W. Lafayette, IN
[2]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA
[3]Vacuum Process Engineering, Inc., Sacramento, CA

Massachusetts Institute of Technology

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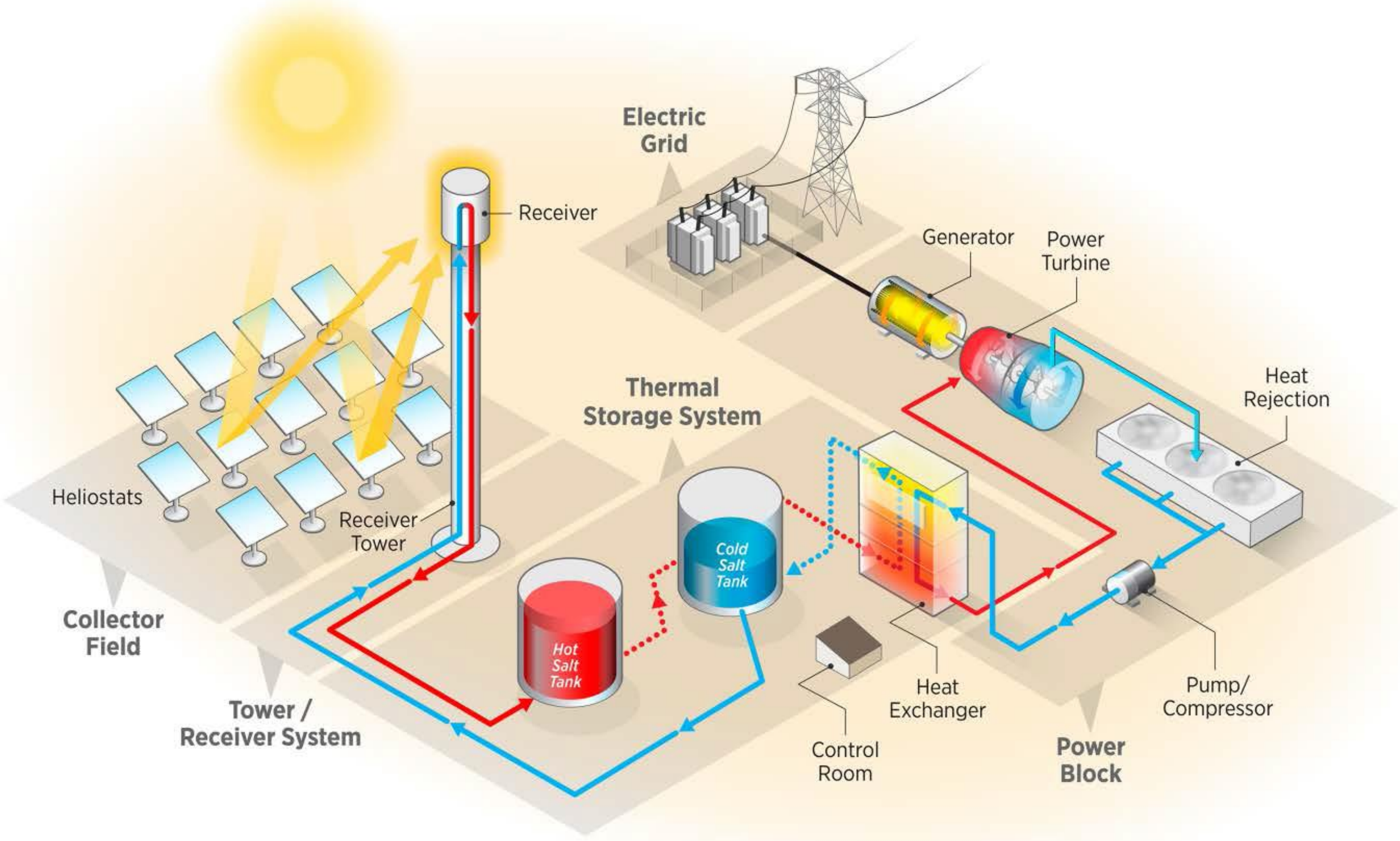
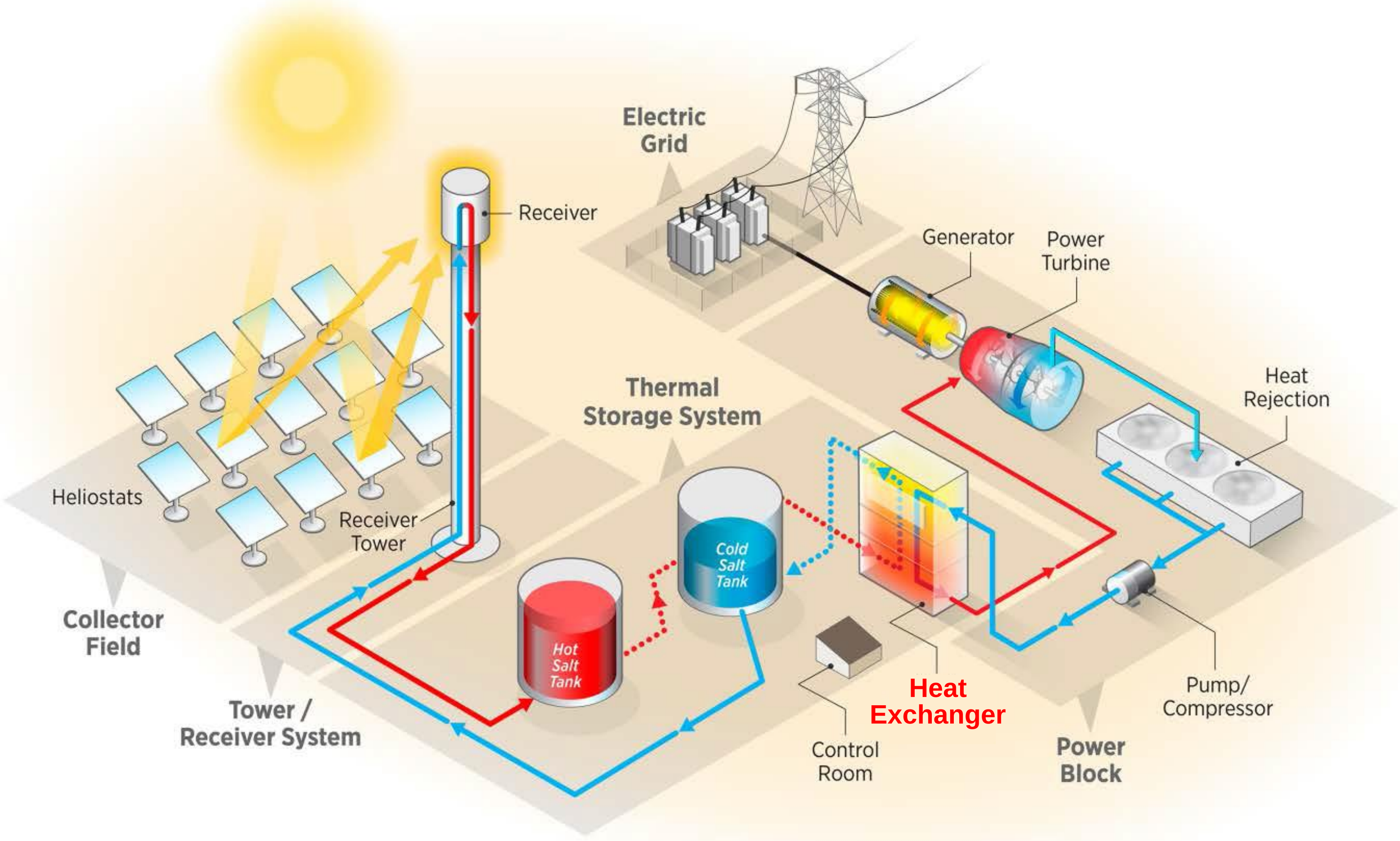
Concentrated Solar Power Tower



“Concentrating Solar Power Gen3 Demonstration Roadmap,” M. Mehos, C. Turchi, J. Vidal, M. Wagner, Z. Ma, C. Ho, W. Kolb, C. Andraka, A. Kruizenga, Technical Report NREL/TP-5500-67464, National Renewable Energy Laboratory, 2017

Concentrated Solar Power Tower



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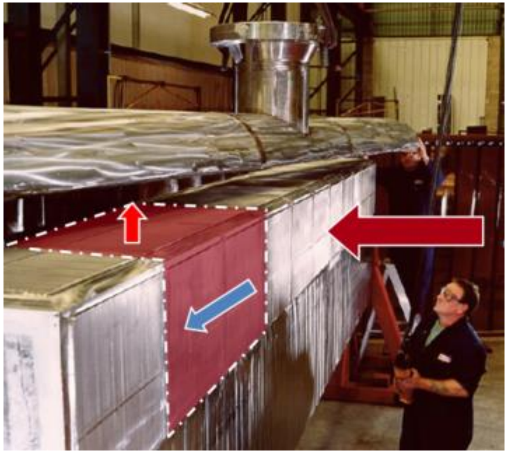
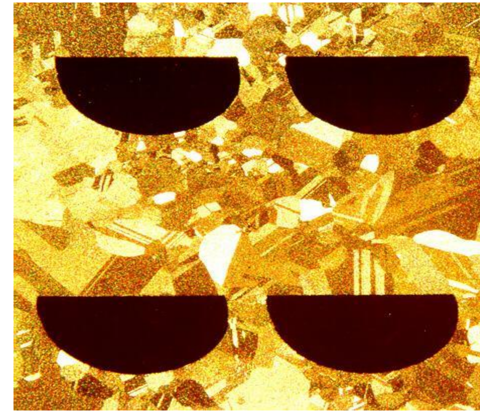
State of the Art: Metal Alloy Printed Circuit HEXs





Current Technology:

- **Printed Circuit HEXs: patterned etching of metallic alloy plates, then diffusion bonding**
- **Metal alloy mechanical properties degrade significantly above 600°C**

D. Southall, S.J. Dewson, *Proc. ICAPP '10*, San Diego, CA, 2010; R. Le Pierres, et al., *Proc. SCO_2 Power Cycle Symposium 2011*, Boulder, CO, 2011; D. Southall, et al., *Proc. ICAPP '08*, Anaheim, CA, 2008.

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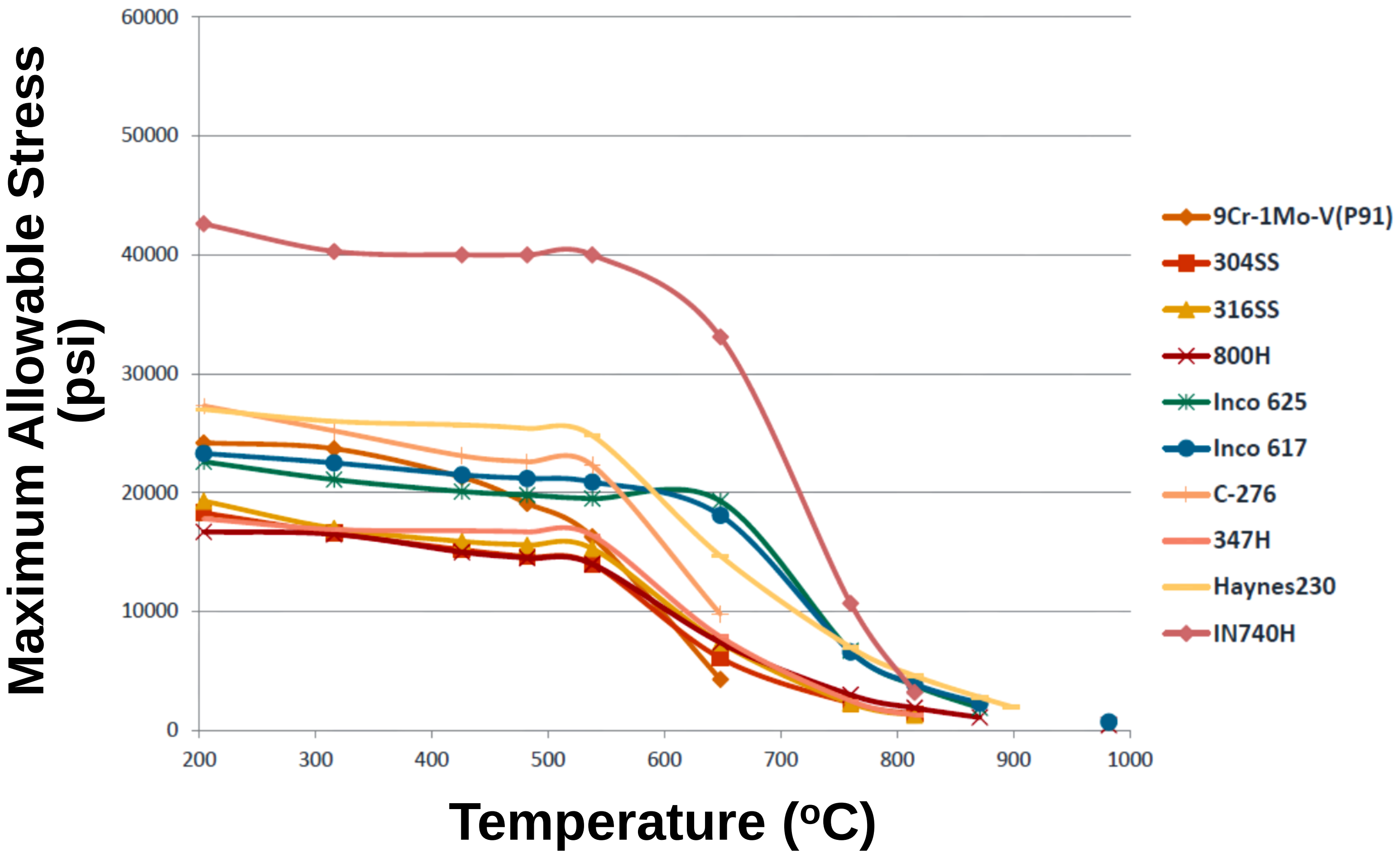
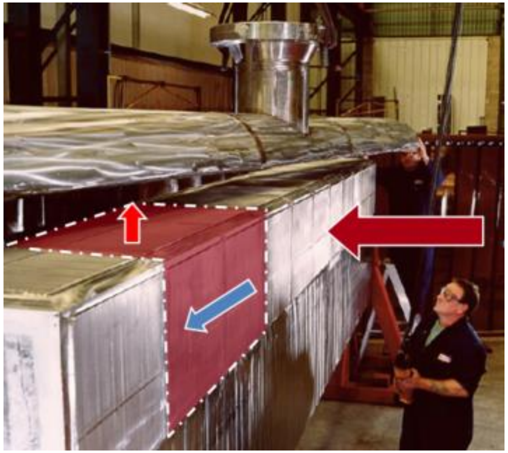
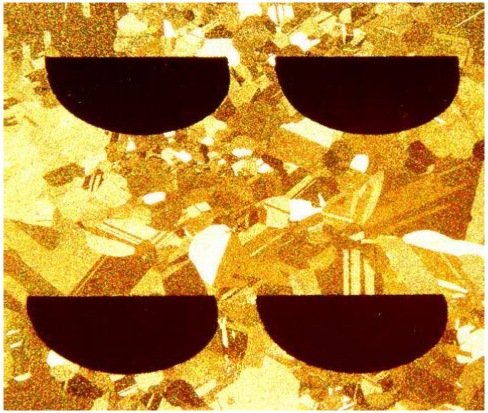


2010 ASME Boiler Pressure Vessel Code, Sec. II, from Tables 1A and 1B, July 1, 2010, New York, NY (compiled by Mark Anderson)

An Attractive Alternative: Compact Cermet HEXs





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Current Technology:

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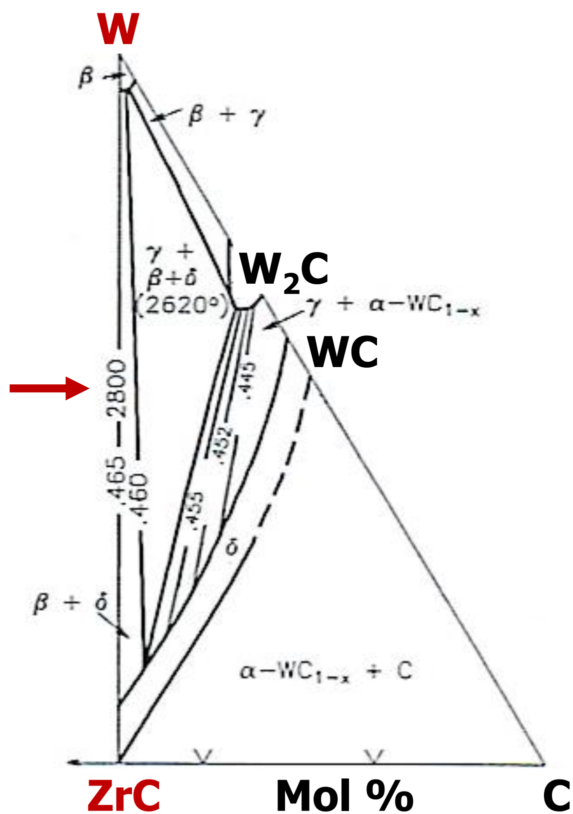
New Technology*:

- **ZrC/W HEXs: mechanical forming of channeled porous WC plates, conversion into dense net-size ZrC/W plates, then diffusion bonding**
- **Higher stiffness, strength, and thermal conductivity at ≥ 720°C**

***A. Henry, K. H. Sandhage, PCT/U.S. Patent Application**

Attributes of Co-Continuous ZrC/W Composites

- **High melting point and chemical compatibility** ($T_{Solidus}$ = 2,800°C, well above superalloys; tie line between ZrC and W)



- V. N. Eremenko, et al., *Phase Diagrams for Ceramists*, Vol. X, C-W-Zr System (Fig. 9034), Ed. A. E. McHale, The American Ceramic Society, 1994

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- Y.-W. Zhao, et al., "Microstructure and Properties of ZrC-W Composite Fabricated by Reactive Infiltration of Zr_2Cu into WC/W Preform," *Mater. Chem. Phys.*, 153, 17-22 (2015)
- S. Zhang, et al., "Microstructure and Properties of W-ZrC Composites Prepared by the Displacive Compensation of Porosity (DCP) Method," *J. Alloys Compounds*, 509, 8327-8332 (2011)
- Y.-W. Zhao, et al., "Microstructure and Mechanical Properties of ZrC-W Matrix Composites Prepared by Reactive Infiltration at 1300^{o}C," *Int. J. Refr. Metals Hard Metals*, 37, 40-44 (2013)
- W. D. Callister, *Materials Science and Engineering - An Introduction*, 6th Edn., John Wiley & Sons, 2003
- http://www.refractories.saint-gobain.com/hexoloy/hexoloy-grades

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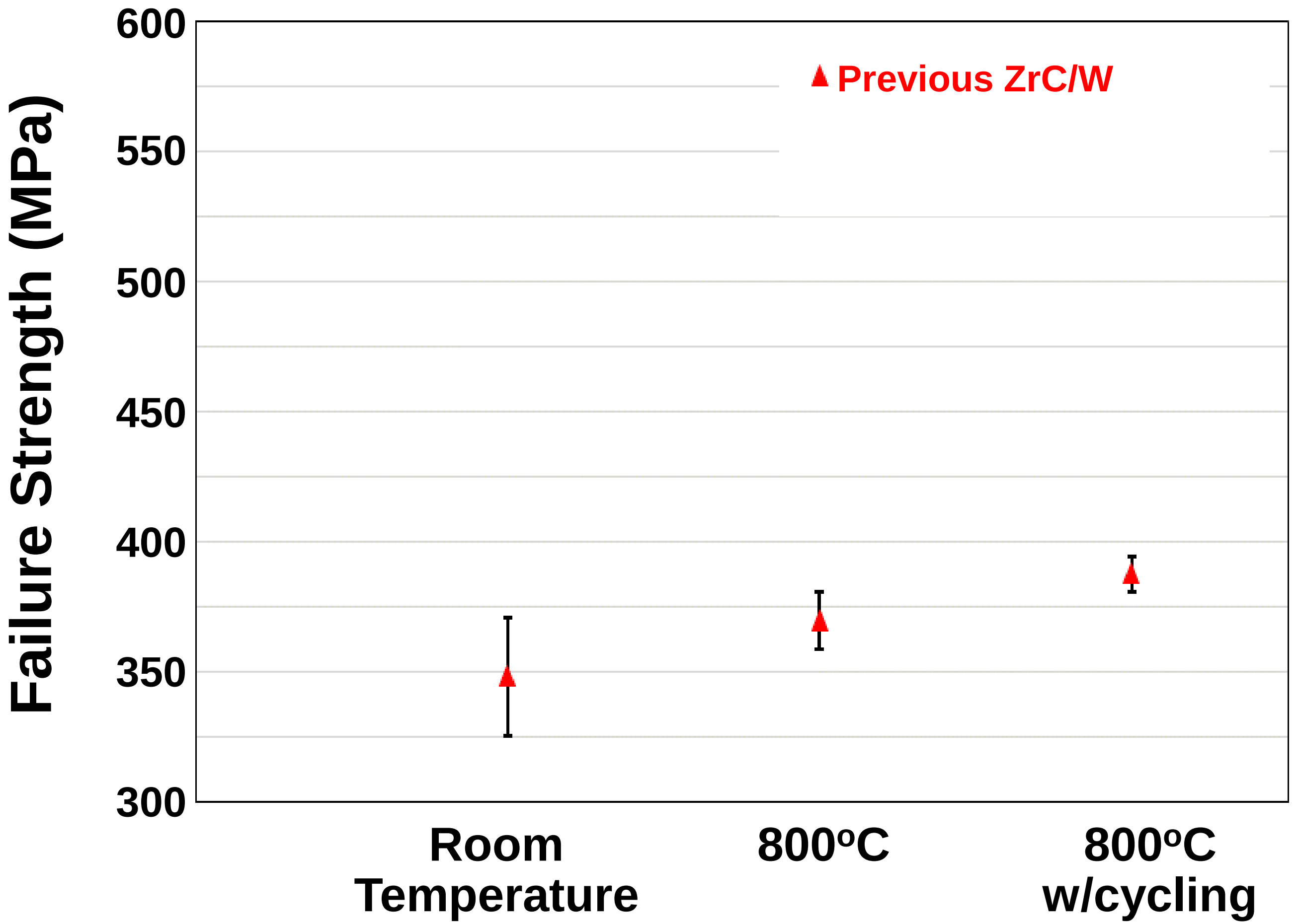
Failure Strength of Current Optimized ZrC/W



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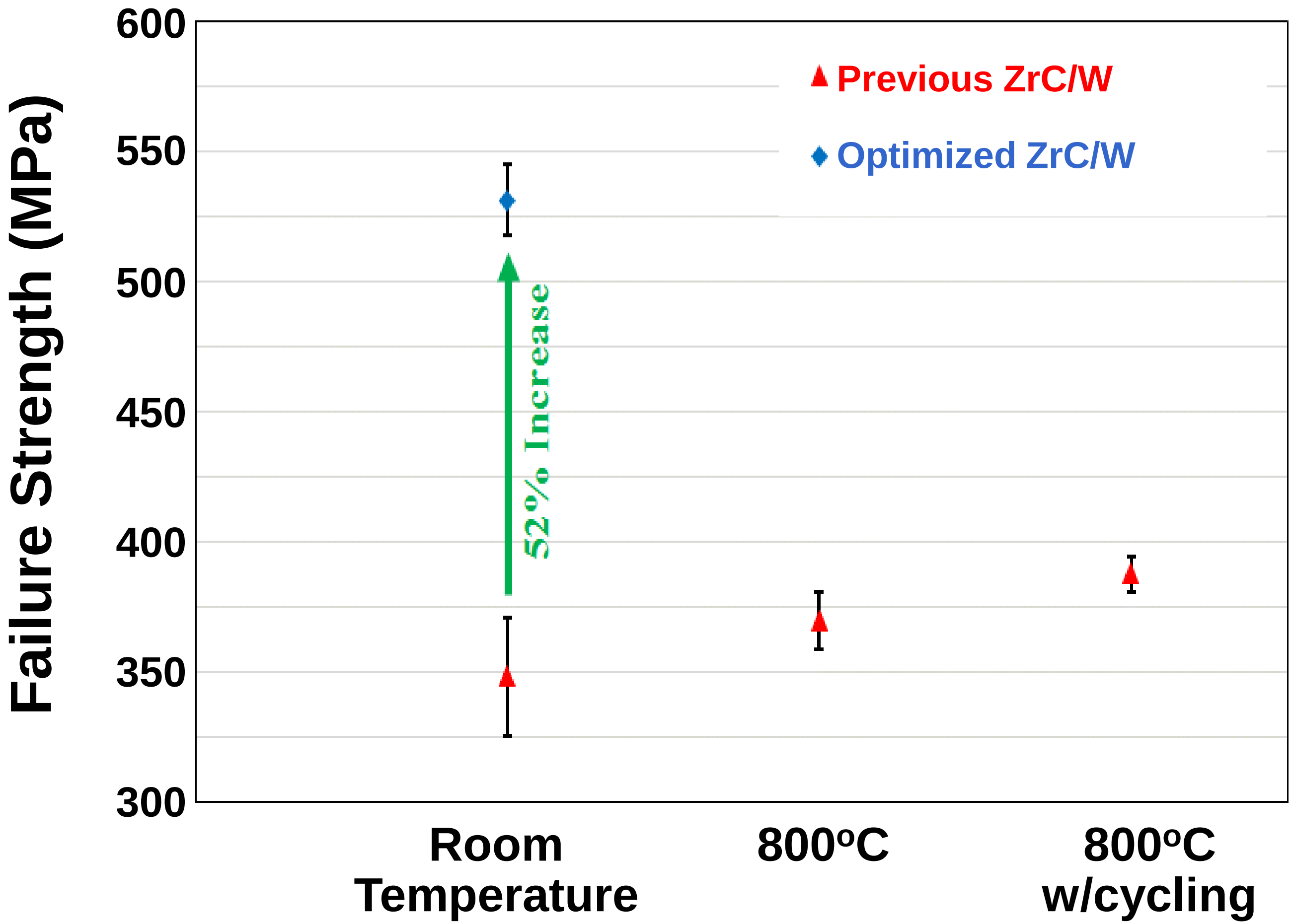

Average RT Failure Strength:
531 ± 14 MPa; 77.0 ± 2 ksi

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- Y. S. Touloukian, R. K. Kirby, R. E. Taylor, P. D. Desai, *Thermal Expansion: Metallic Elements and Alloys*, *Thermophysical Properties of Matter*. Vol. 12. Plenum Press, New York, NY, 1975
- Y. S. Touloukian, R. K. Kirby, R. E. Taylor, PT. Y. R. Lee, *Thermal Expansion: Nonmetallic Solids, Thermophysical Properties of Matter*. Vol. 13. Plenum Press, New York, NY, 1977

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- **High thermal conductivity** (κ = 66.0 W/m-K at 800°C vs. 22.1 W/m-K for IN740H, 24.4 W/m-K for H230)

- http://www.specialmetals.com/files/PCC%20EG%20740H%20White%20Paper.pdf
- http://www.hightempmetals.com/techdata/hitempHaynes230data.php
- A. Sommers, et al., "Ceramics and Ceramic Matrix Composites for Heat Exchangers in Advanced Thermal Systems – A Review," *Appl. Thermal Eng.*, 30, 1277-1291 (2010)
- D.-M. Liu, B.-W. Lin, "Thermal Conductivity in Hot-Pressed Silicon Carbide," *Ceram. Int.*, 22, 407-414 (1996)
- K. Watari, et al., "Effect of Grain Boundaries on Thermal Conductivity of Silicon Carbide Ceramic at 5 to 1300 K," *J. Am. Ceram. Soc.*, 86 (10) 1812-1814 (2003)

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Attributes of Co-Continuous ZrC/W Composites

- **Thermal shock resistance and thermal cyclability**

  (ZrC/W nozzles have survived >10^3 ^oC/sec heatup to 2500^oC in a Pi-K rocket test; thermal cycling at 10^oC/min from RT to 800^oC has not resulted in a decrease in fracture strength at 800^oC)

- M. B. Dickerson, P. J. Wurm, J. R. Schorr, W. P. Hoffman, E. Hunt, K. H. Sandhage, "Near Net-Shaped, Ultra-High Melting, Recession-Resistant Rocket Nozzles Liners via the Displacive Compensation of Porosity (DCP) Method," *J. Mater. Sci.*, 39 (19) 6005-6015 (2004)

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- **Corrosion resistance**

  (Purification of the molten $MgCl_2$-KCl salt, and the addition of 50 ppm CO to the sCO_2 with a Cu layer on the ZrC/W surface, have rendered ZrC/W composites resistant to corrosion at 750^oC; PCT/U.S. patent application)

- **K. H. Sandhage, "Method for Enhancing Corrosion Resistance of Oxidizable Materials and Components Made Therefrom," *PCT/U.S. Patent Application*, 2017; *U.S. Provisional Patent Application*, 2016.**

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- **Cost-effective fabrication of ZrC/W-based HEX plates**

  (Scalable, low-cost forming and shape/size-preserving DCP reaction processing of ZrC/W-based plates with tailorable channels and headers for HEXs; PCT/U.S. patent application[4])

- K. H. Sandhage, et al., *U.S. Patents No. 6,833,337, No. 6,598,656, No. 6,407,022.*
- A. Henry, K. H. Sandhage, "Methods for Manufacturing Ceramic and Ceramic Composite Components and Components Made Thereby," *PCT/U.S. Patent Application*, 2017; *U.S. Provisional Patent Application*, 2016.

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Project Objectives

- **To design a robust ZrC/W-based heat exchanger with effectiveness and pressure drop values acceptable for the NREL test facility**

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Project Objectives

- To design a robust ZrC/W-based heat exchanger with effectiveness and pressure drop values acceptable for the NREL test facility
- To demonstrate scalable methods for:
  - fabricating thin ($\leq$3 mm) channeled ZrC/W-based HEX plates with integral headers
  - bonding such plates into HEX stack assemblies connected to Ni alloy tubes

Massachusetts Institute of Technology

Vacuum Process Engineering

Purdue University

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  - **bonding such plates into HEX stack assemblies connected to Ni alloy tubes**
- **To develop a manufacturing pathway for, and determine the cost of, a 2 MW_{th} ZrC/W-based heat exchanger for Phase 3 of the Gen 3 CSP program**

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VPE Vacuum Process Engineering

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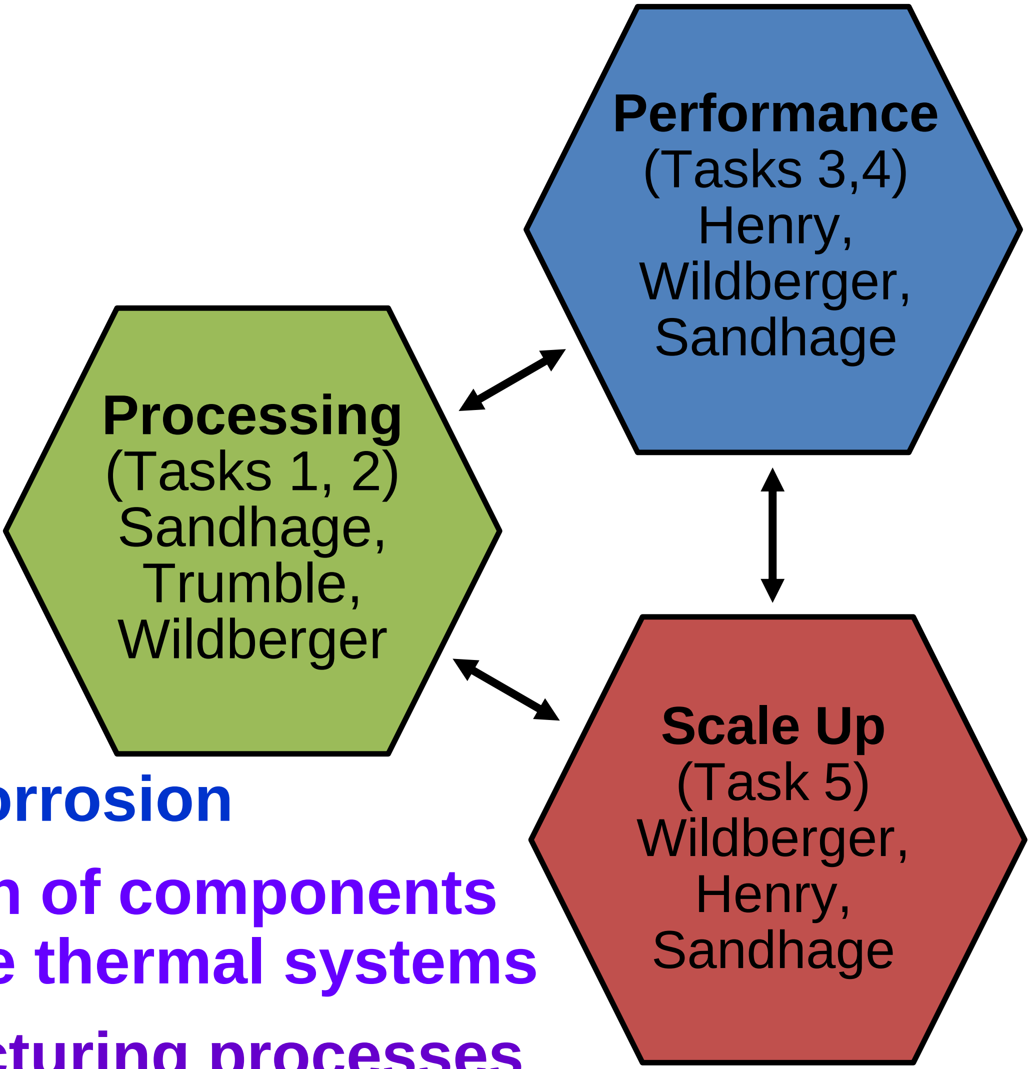
Thrusts and Expertise

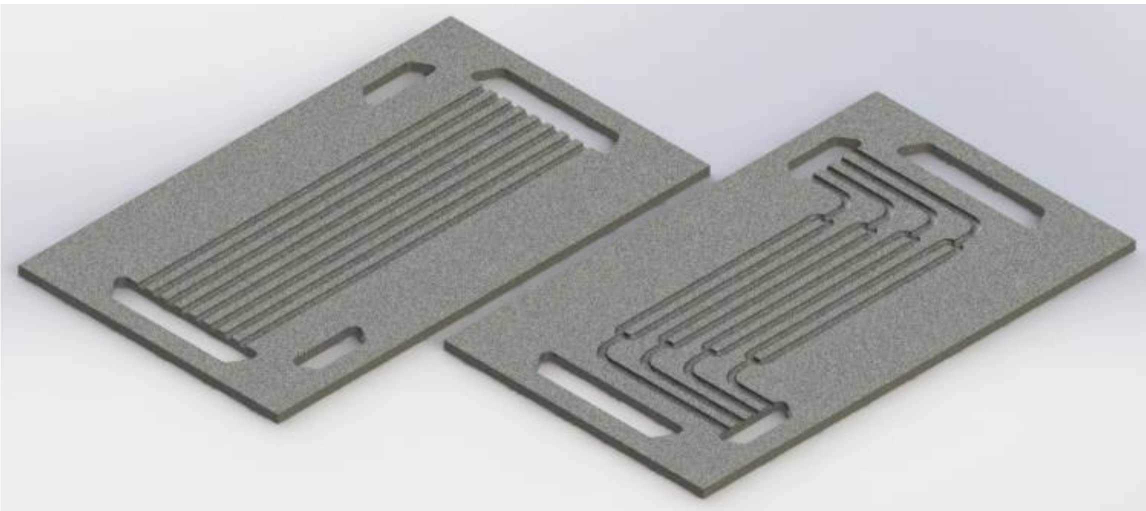
Areas of Expertise:

- **Ceramic forming**
- **Thermal processing of ceramics**
- **Reactive melt infiltration**
- ***Near net-shape* processing**
- **Joining**
- **High-temperature corrosion**
- **Modeling and design of components for high-temperature thermal systems**
- **Scale up of manufacturing processes**

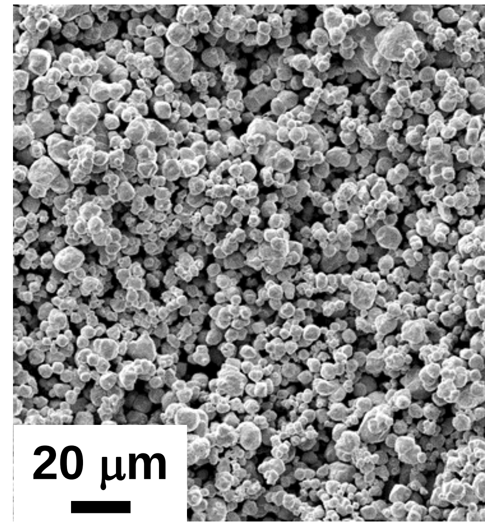


Manufacturing of ZrC/W HEX Plates

Fabricate porous WC preform plates



Schematic illustrations of porous WC preform plates



Secondary electron image of a fractured cross-section

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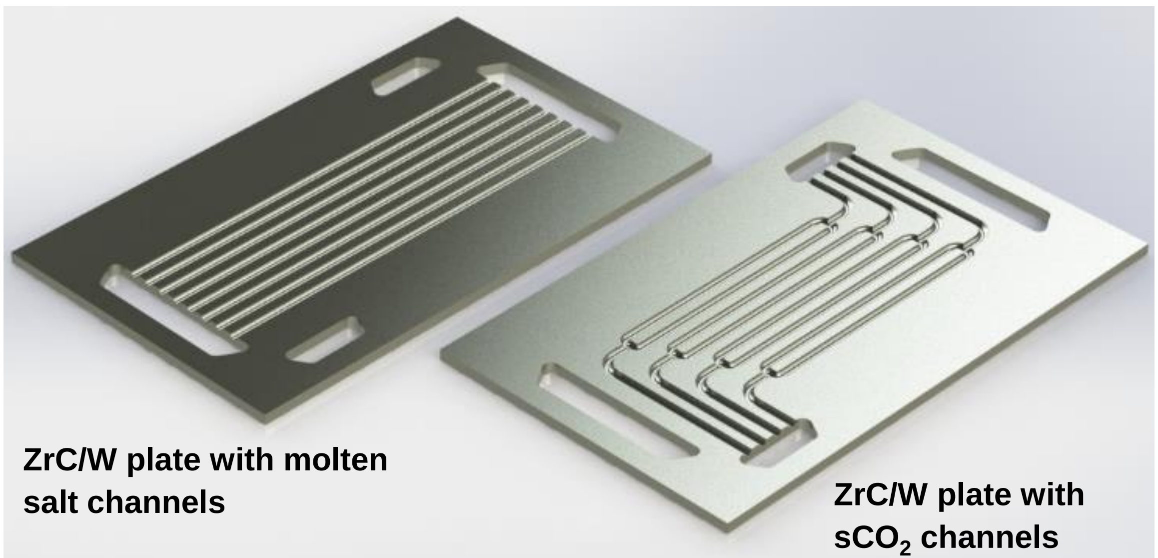
Manufacturing of ZrC/W HEX Plates

Fabricate porous WC preform plates

Generate net-size dense ZrC/W plates via DCP process



Schematic illustrations of dense-wall ZrC/W HEX plates

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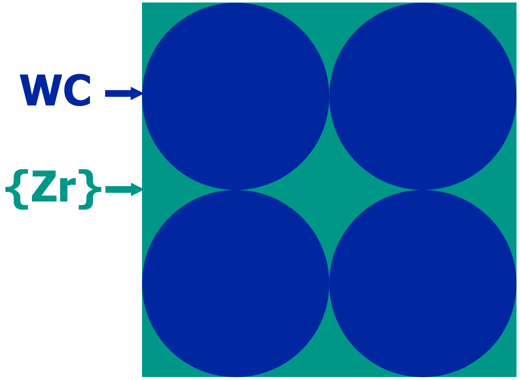
Displacive Compensation of Porosity

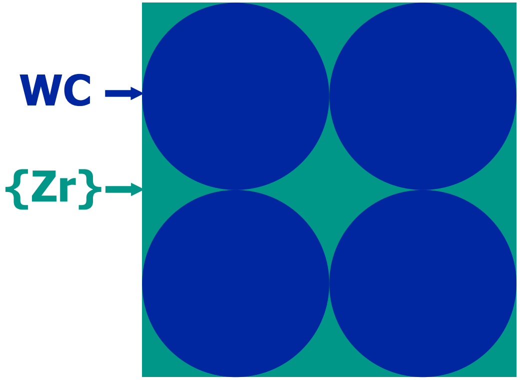
$WC(s) + \{Zr\}$



Infiltrated

Displacive Compensation of Porosity

$$WC(s) + \{Zr\} \Rightarrow ZrC(s) + W(s)$$



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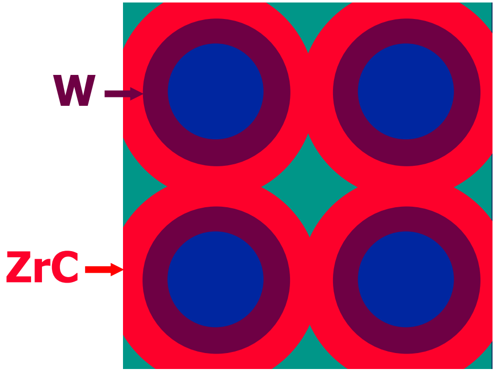

Partial Rxn

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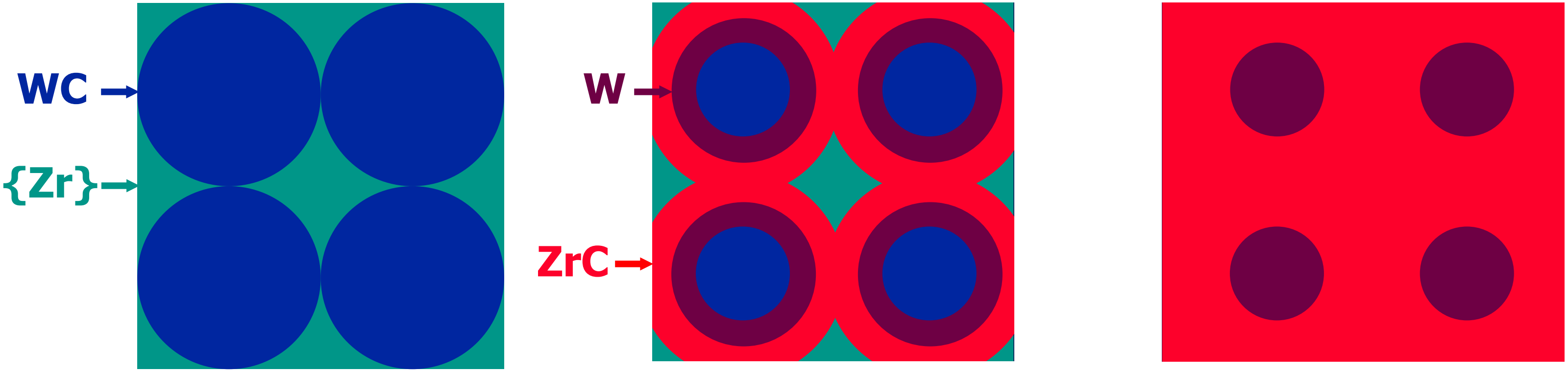
Displacive Compensation of Porosity

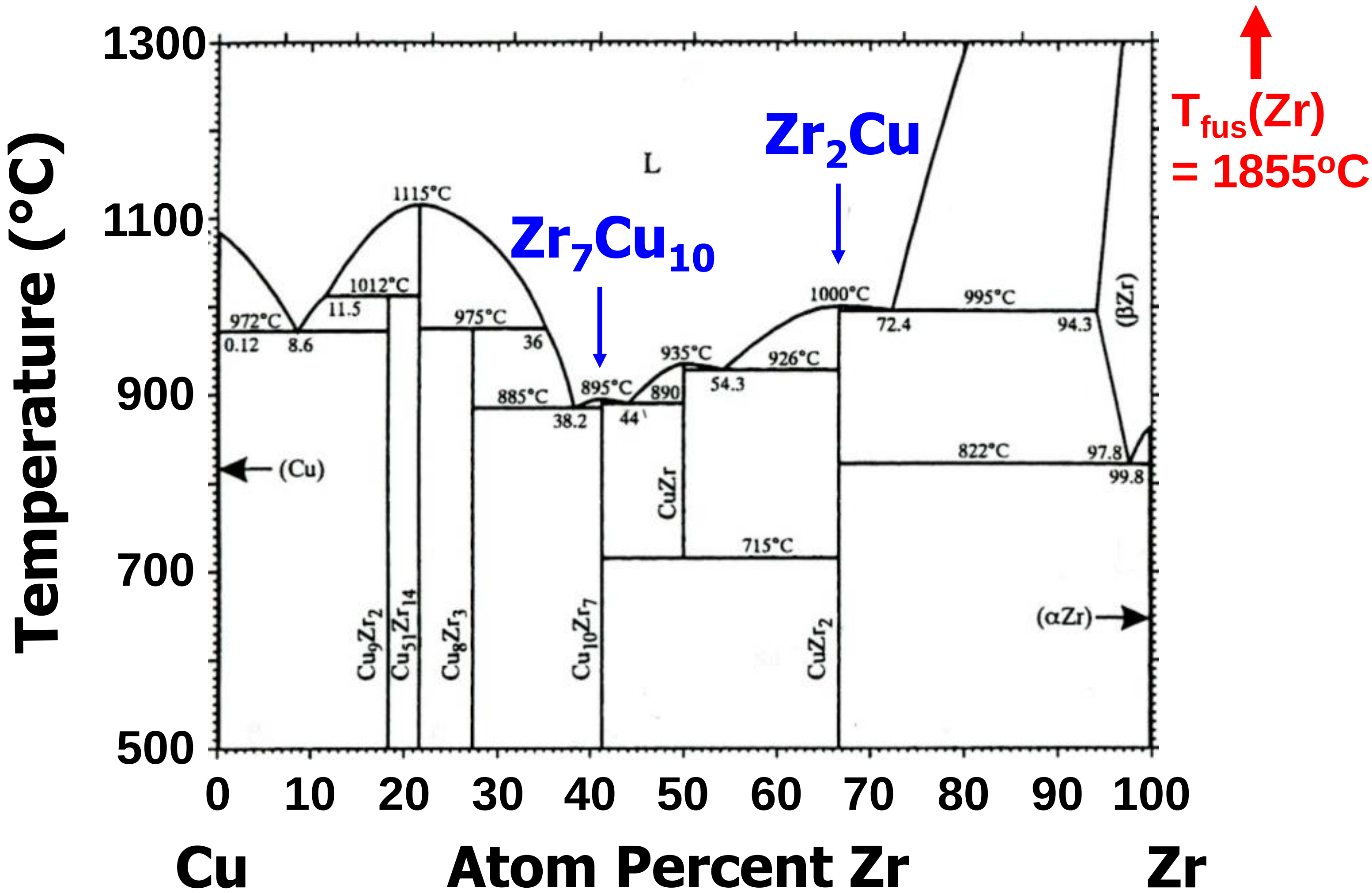
$$WC(s) + \{Zr\} \Rightarrow ZrC(s) + W(s)$$

where $V_m[ZrC + W] = 2.01V_m[WC]$



Infiltrated **Partial Rxn** **Complete Rxn**

Cu-Zr Phase Diagram



D. Arias, J. P. Abriata, *Bull. Alloy Phase Diagrams*, 11 (5) 452 (1990).

Melt Preparation and Infiltration Equipment

Cold-wall, Induction-heated Melt Infiltration System

A. Intermediate oil-based HEX for cooling of the Cu induction coils (coupled to a closed chilled water loop)
B. Oil and water collector systems
C. Antechamber
D. Actively-cooled universal ram
E. Melt box (with induction coils for heating WC preforms and the Zr-Cu melt)
F. Pressure release valve
G. Pipe for venting of melt box

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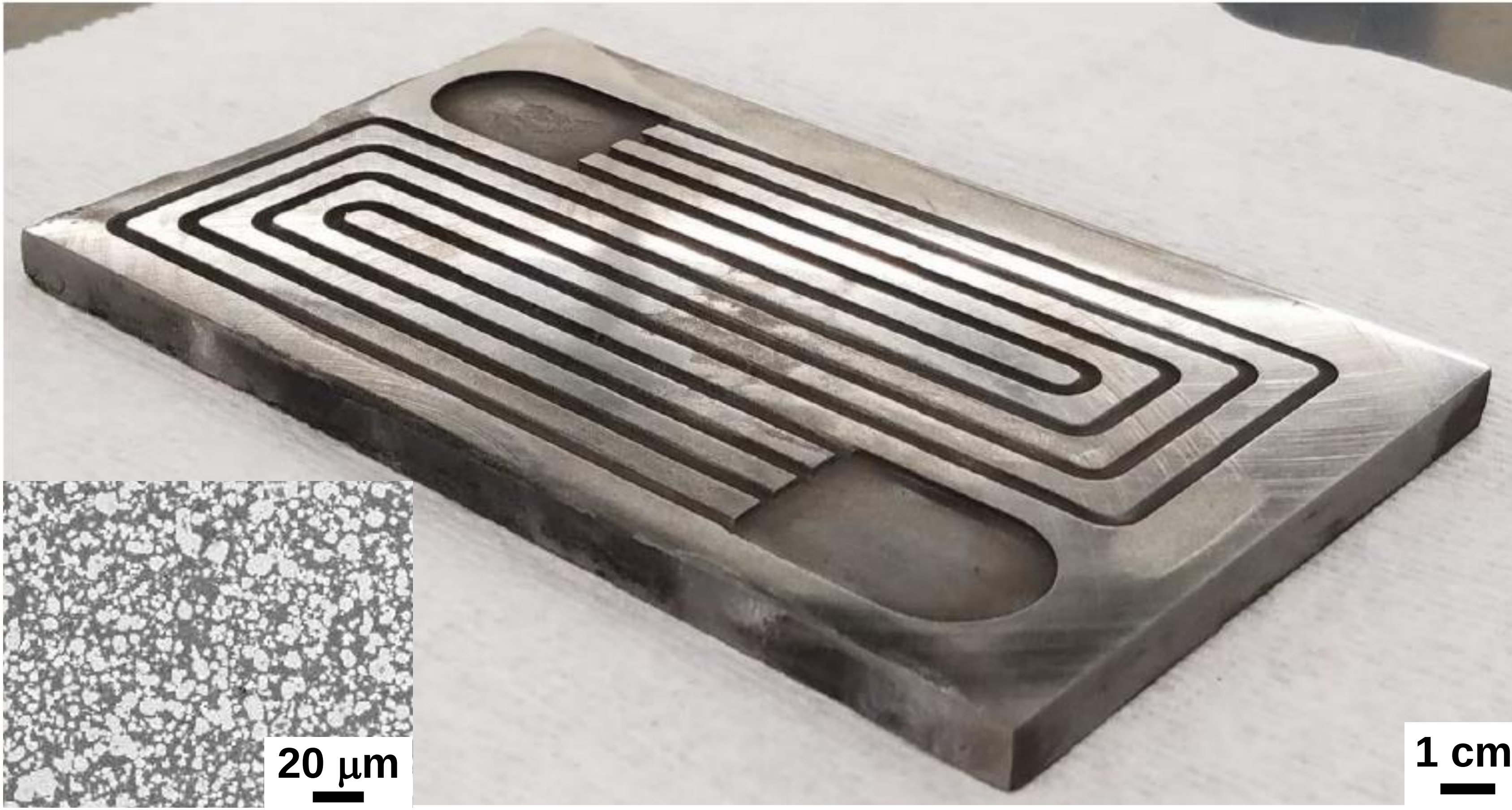
Current ZrC/W-based HEX Plates

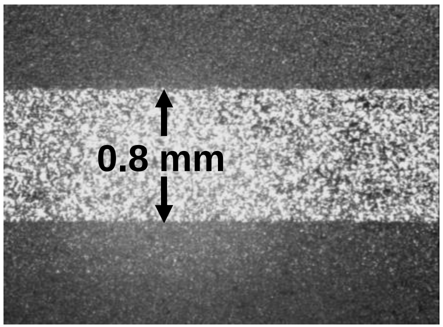


Dense channeled ZrC/W plate generated by shape/size-preserving reactive melt infiltration (DCP process) of a machined porous WC plate

Thinner ZrC/W-based HEX Plates

◆ **The fabrication of thinner (< 3 mm) ZrC/W plates will be examined by:**

- **tape casting**



Optical micrograph of a cross-section of a multilayer $B_4C/B_4C\text{-}TiO_2$ composite produced by tape casting of layers of B_4C and $B_4C\text{-}TiO_2$, drying, stacking of alternating layers, and then thermal treatment (Trumble, et al.)

- **uniaxial pressing**

Photograph of a thin (1.7 mm) rigid porous WC plate produced by uniaxial pressing of a WC/binder mixture and then thermal treatment (Sandhage, et al.)

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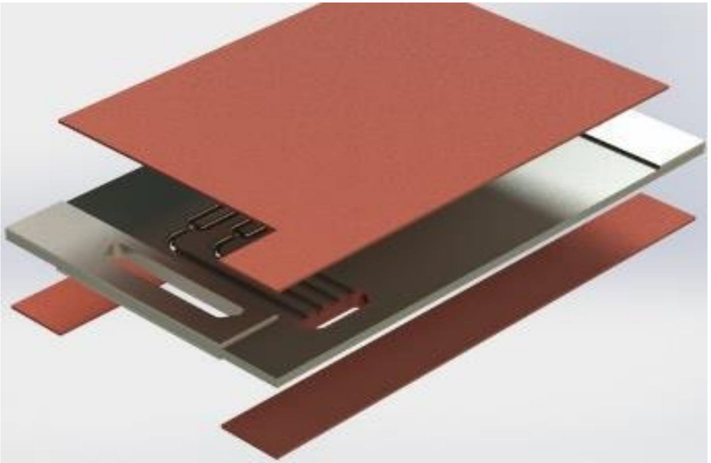
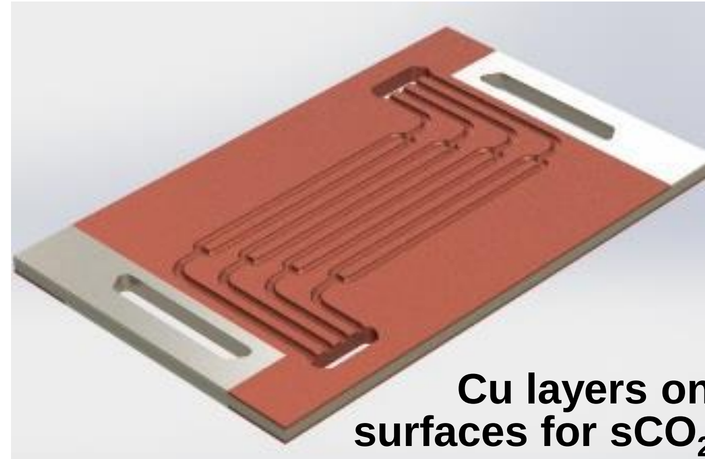
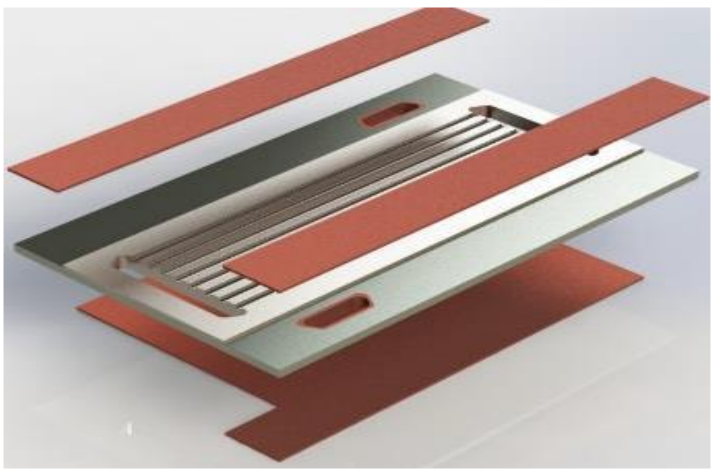
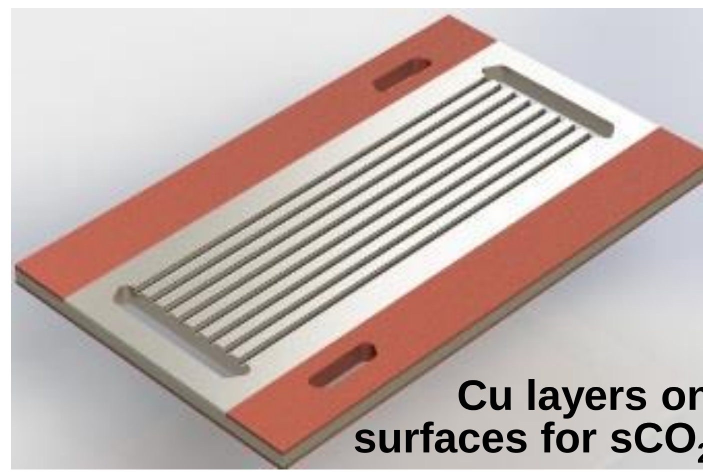
Diffusion Bonding of Cu Layers









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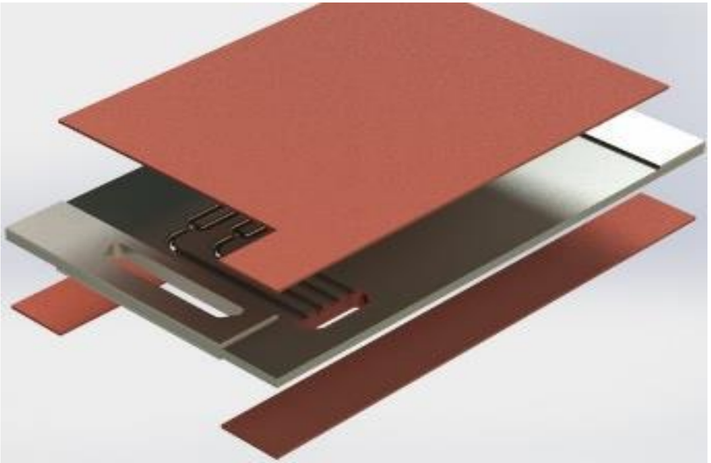
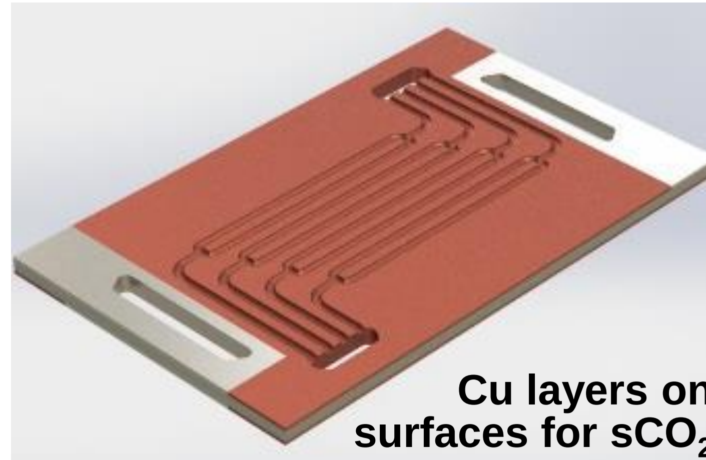
Diffusion Bonding of Cu Layers





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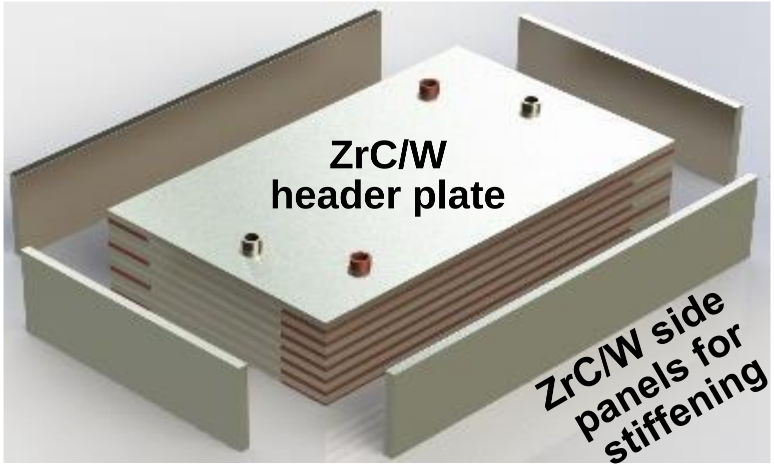
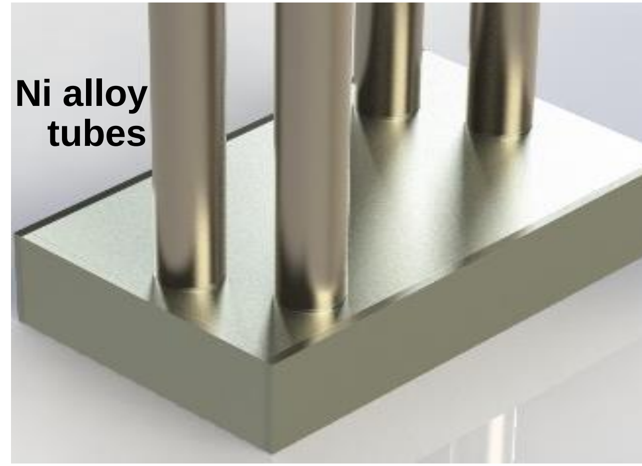
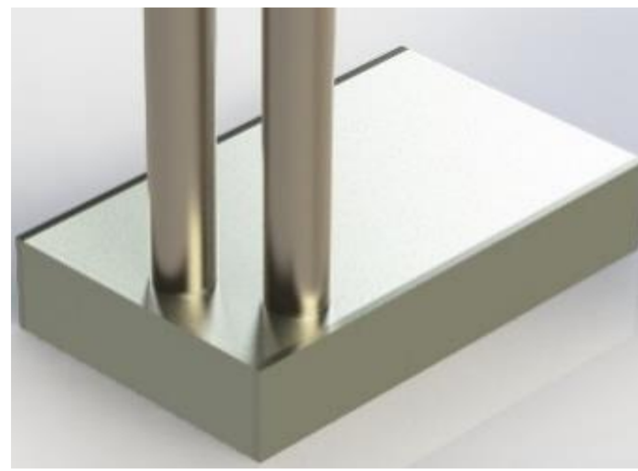
Diffusion Bonding of HEX Assembly





Gas pressure test assembly (inlet tubes only)



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HEX Design and Performance Modeling

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- **The geometries and dimensions of the HEX channels and vias will be tailored to simultaneously optimize the effectiveness, pressure drops, and thermo-mechanical reliability**

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Scale Up of Manufacturing

- **Work will be conducted to evaluate scalable:**
  - **WC preform plate forming (casting, compaction, stamping) and heat treatments (drying, sintering)**
  - **ZrC/W plate production (melt infiltration)**
  - **Diffusion bonding (metal layers, plate stacks)**
  - **Joining of Ni alloy tubes to header plates**
- **VPE capabilities and expertise (thermal treatments, bonding) fit well with much of this scale-up work**
- **Additional required equipment, facilities, and partners or vendors will be identified**

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VPE Vacuum Process Engineering

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Summary

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Summary

- ZrC/W cermets provide an attractive combination of high-temperature properties relative to state-of-the-art metal alloys
- Low-cost ceramic forming methods, coupled with a shape/size-preserving reactive melt infiltration (DCP) process, can be used to fabricate dense ZrC/W HEX plates with tailorable channel patterns
- Scalable strategies for manufacturing robust ZrC/W-based HEX assemblies have been identified

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- Low-cost ceramic forming methods, coupled with a shape/size-preserving reactive melt infiltration (DCP) process, can be used to fabricate dense ZrC/W HEX plates with tailorable channel patterns
- Scalable strategies for manufacturing robust ZrC/W-based HEX assemblies have been identified
- Work with VPE and other (TBD) partners/vendors will be conducted to develop a manufacturing pathway to a 2 MW_{th} ZrC/W HEX for Phase 3 of the Gen3 CSP program

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Questions?

Suggestions?

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