U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

SOLAR ENERGY TECHNOLOGIES OFFICE

SETO CSP Program Summit 2019

Robust High-Temperature Heat Exchangers

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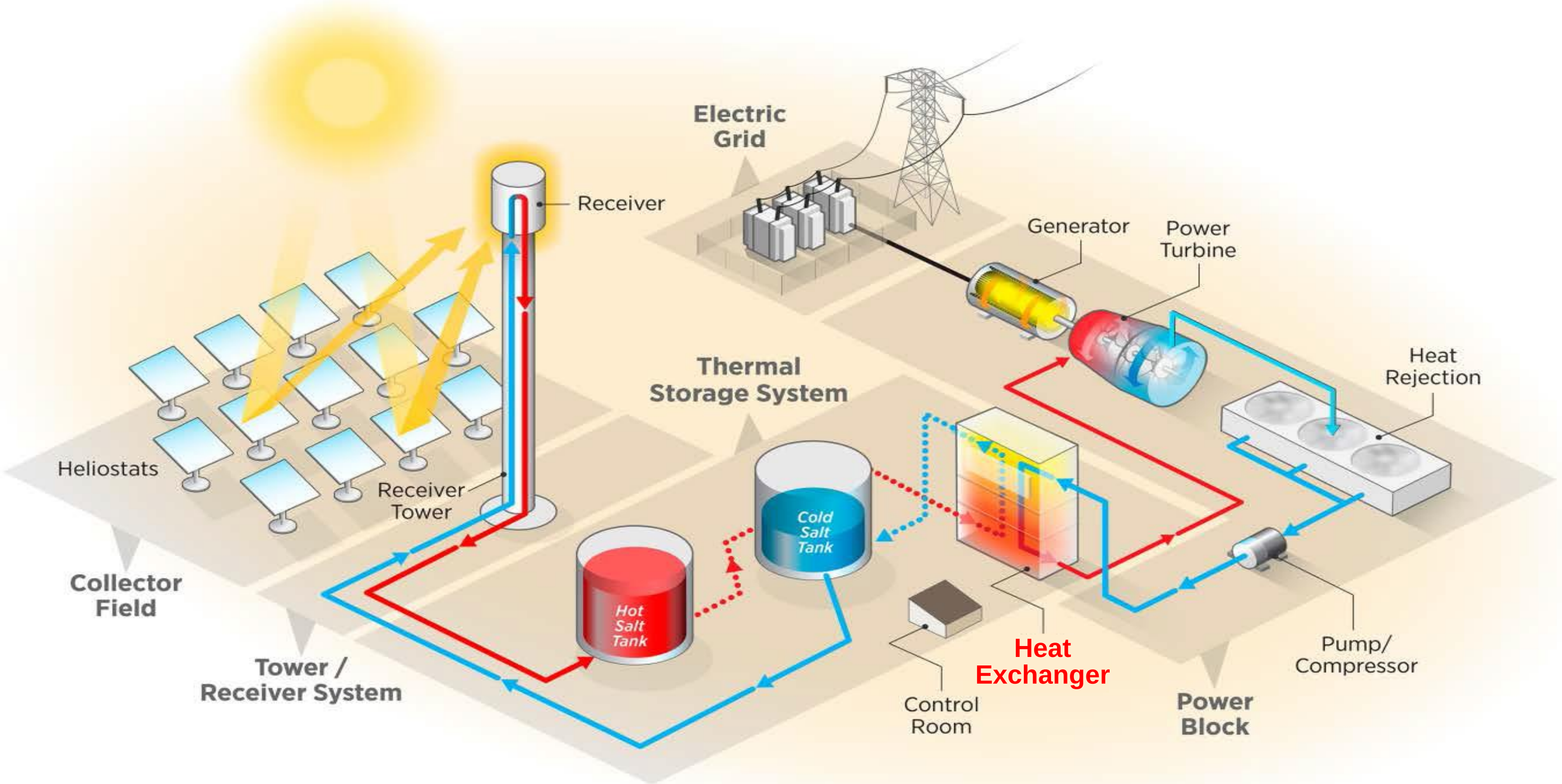
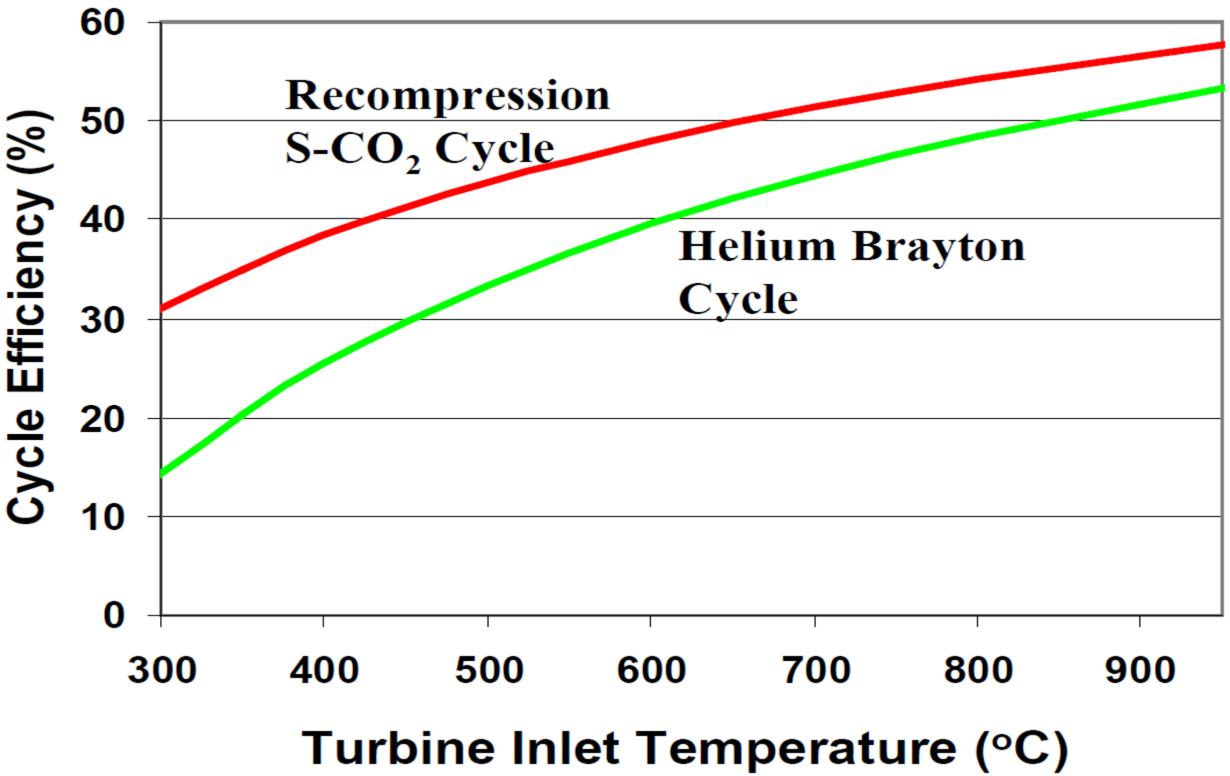
VACUUM PROCESS ENGINEERING

Concentrated Solar Power Tower



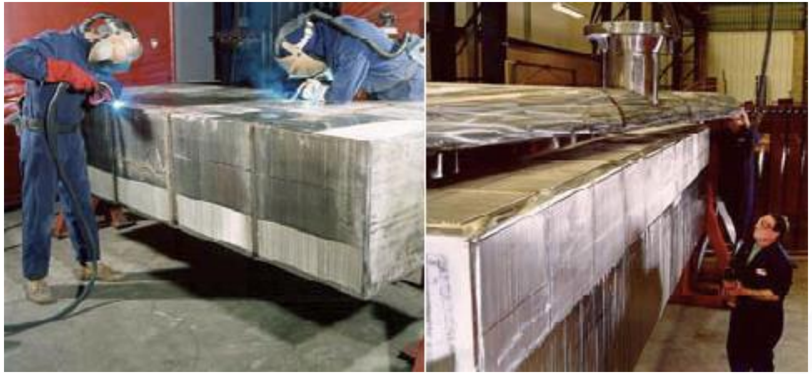
"Concentrating Solar Power Gen3 Demonstration Road-map," M. Mehos, C. Turchi, J. Vidal, M. Wagner, Z. Ma, C. Ho, W. Kolb, C. Andraka, A. Kruizenga, *Technical Report NREL/TP-5500-67464*, NREL, 2017

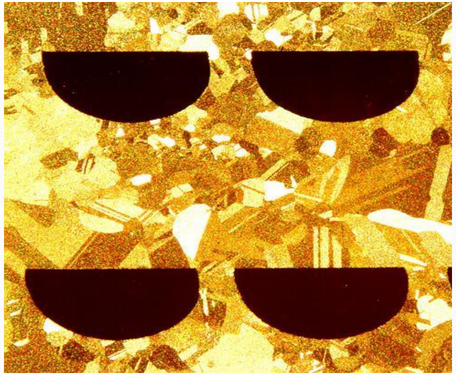
Desire for Higher Turbine Inlet Temperatures



V. Dostal, M. J. Driscoll, P. Hejzlar, N. E. Todreas, *Proc. 10th Intl. Conf. Nuclear Engineering*, ICONE 10, Arlington, VA, 2002; V. Dostal, P. Hejzlar, M. J. Driscoll, *Nuclear Technol.*, 154, 283-301 (2006).

Current Technology: Printed Circuit Alloy HEXs





Current Technology:

- *Alloy PCHEXs*: Patterned etching of plates, then diffusion bonding
- 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 Symp. 2011*, Boulder, CO, 2011; D. Southall, et al., *Proc. ICAPP '08*, Anaheim, CA, 2008.

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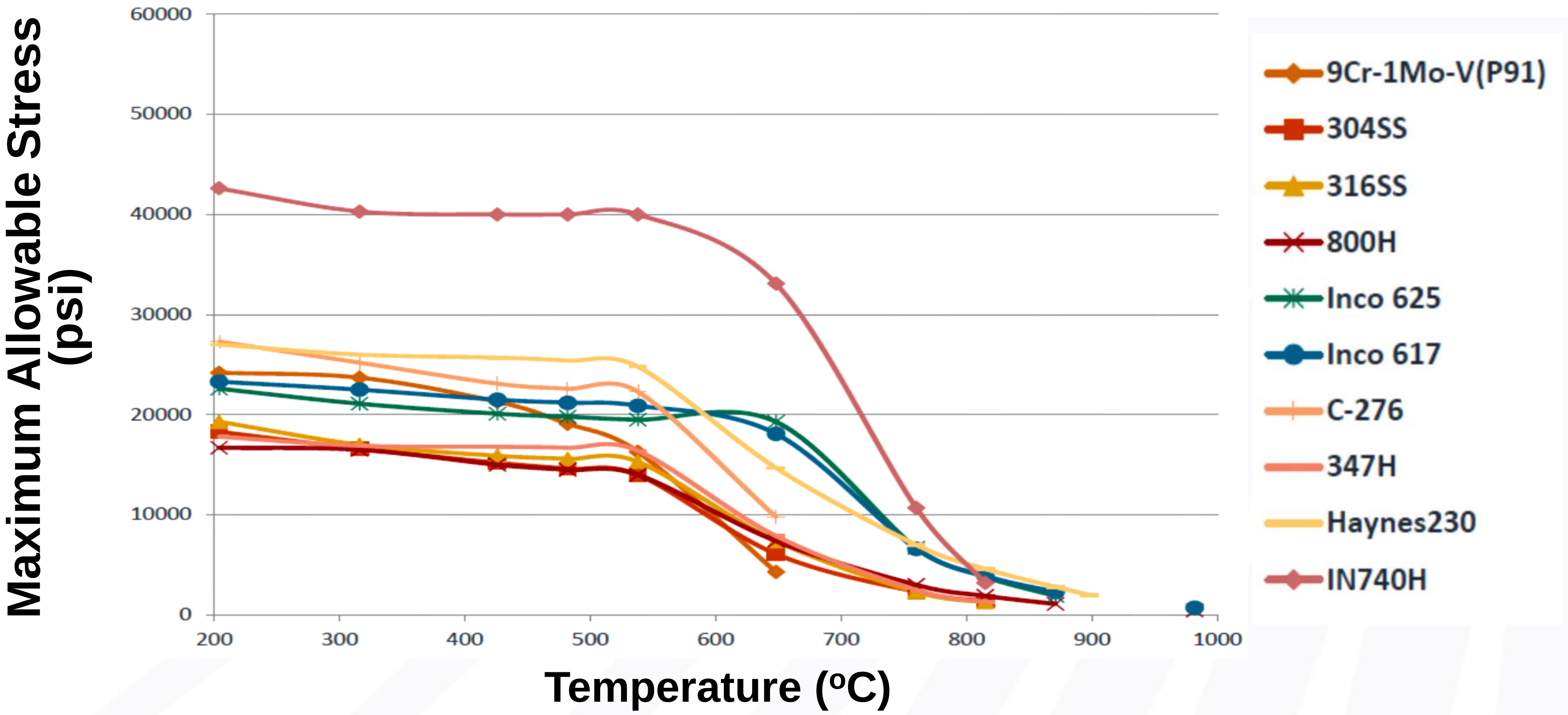
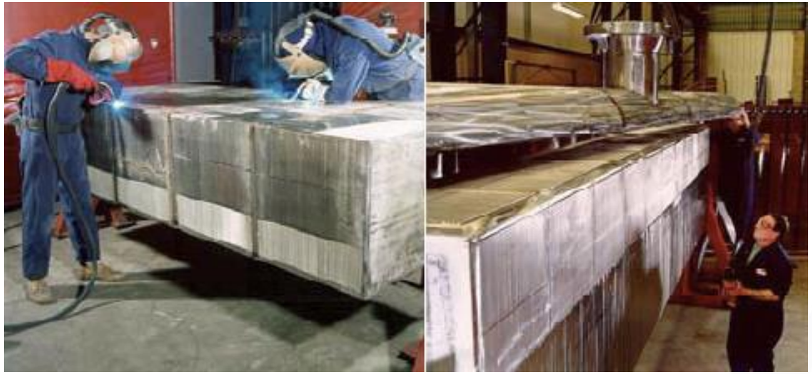
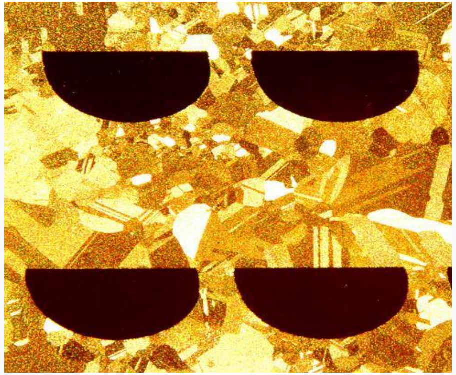


2010 ASME Boiler Pressure Vessel Code, Sec. II, from Tables 1A and 1B, July 1, 2010, New York, NY (compiled by Mark Anderson)

New Technology: Compact Ceramic/Metal HEXs





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

Current Technology:

- ***Alloy PCHEXs*: Patterned etching of plates, then diffusion bonding**
- **Alloy mechanical properties degrade significantly above 600^{o}C**

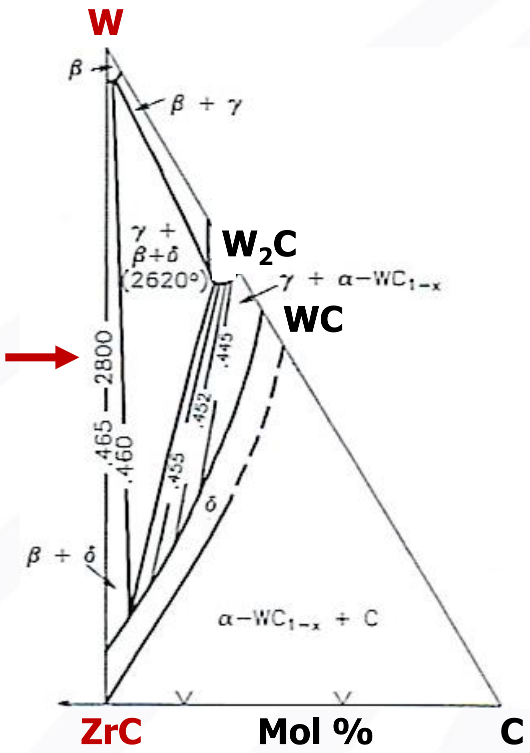
New Technology*:

- ***ZrC/W HEXs*: Mechanical forming of porous WC plates; conversion of porous plates into dense-wall, net-size ZrC/W plates; then bonding**
- **Higher stiffness, failure strength, and thermal conductivity at ≥ 750^{o}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; ZrC and W are connected by a tie line)



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

Attributes of Co-Continuous ZrC/W Composites

- **High melting point and chemical compatibility**
  ($T_{Solidus}$ = 2,800^{o}C; ZrC and W are connected by a tie line)
- **Retention of stiffness and strength at 800^{o}C**
  (E $\geq$ 28x10^{6} psi/193 GPa; $\sigma_F \geq$ 50x10^{3} psi/350 MPa at RT and at 800^{o}C)
- **Enhanced toughness w.r.t. conventional monolithic ceramics**
  (K_{1C} = 9.4 MPa·$m^{1/2}$ vs. $\leq$ 0.8 MPa·$m^{1/2}$ for Pyrex, $\leq$ 1.4 MPa·$m^{1/2}$ for concrete, $\leq$ 4.8 MPa·$m^{1/2}$ for Hexoloy SiC)

- M. Caccia, et al., *Nature*, 562 (7727) 406-409 (2018)
- Y.-W. Zhao, et al., *Mater. Chem. Phys.*, 153, 17-22 (2015)
- S. Zhang, et al., *J. Alloys Compounds*, 509, 8327-8332 (2011)
- Y.-W. Zhao, et al., *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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- **Similar coefficients of thermal expansion (unusual for cermets)**
  (W: 4.5x10^{-6}/°C - 9.2x10^{-6}/°C for RT - 2700°C;
  ZrC: 4.0x10^{-6}/°C - 10.2x10^{-6}/°C for RT - 2700°C)

- 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 at 800°C**
  (κ = 66.0 W/m-K 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

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^{o}C in a Pi-K rocket test; thermal cycling at 10^{o}C/min from RT to 800^{o}C has not resulted in a decrease in failure strength at 800^{o}C)

- **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**

  (Addition of 50 ppm CO to sCO_2 with Cu bonded to the ZrC/W surface, and purification of the molten $MgCl_2$-KCl salt, have rendered ZrC/W composites resistant to corrosion at 750^{o}C)

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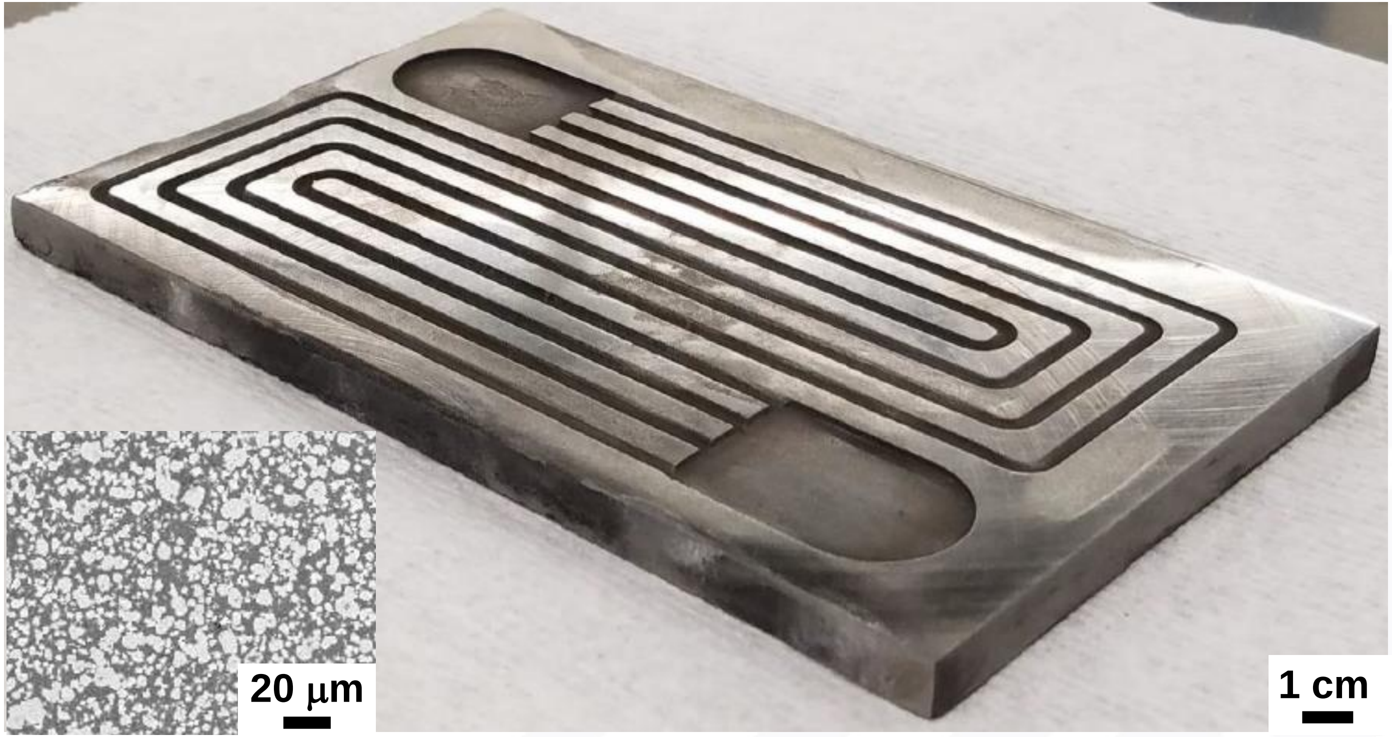
- **Cost-effective fabrication of ZrC/W-based HEX plates**

  (Scalable, low-cost forming and shape/size-preserving DCP reaction processing of ZrC/W-based plates with tailorable channels and headers for HEXs)

- 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.

ZrC/W Heat Exchanger Plates

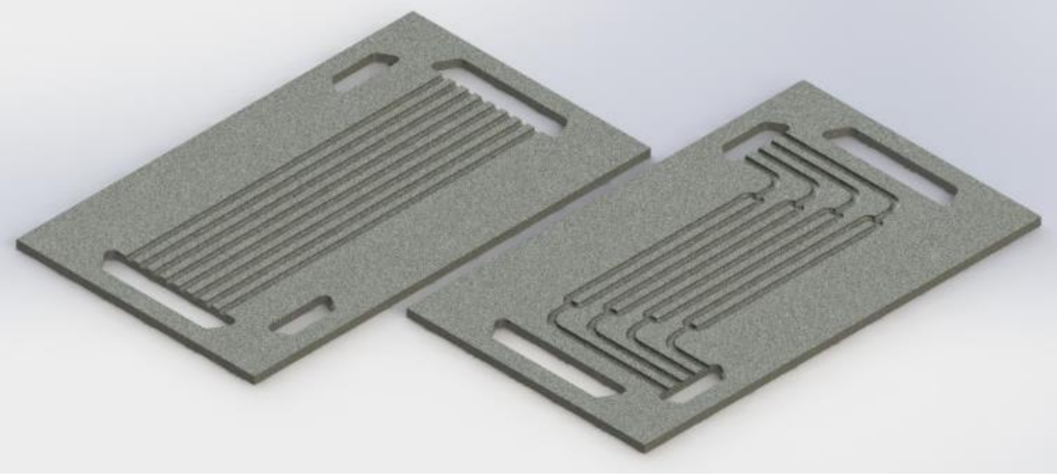


Dense channeled ZrC/W plate generated by shape/size-preserving reactive melt infiltration (DCP process) of a porous WC plate

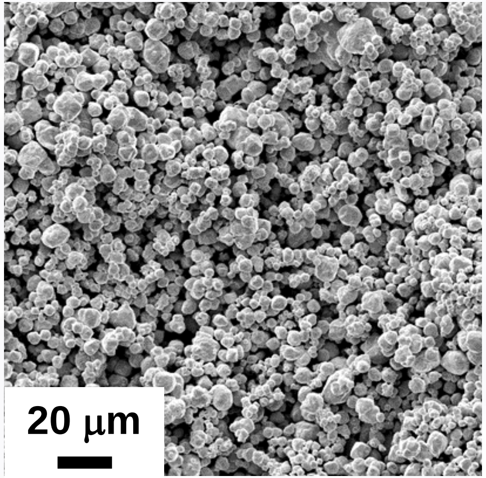
Manufacturing of ZrC/W Heat Exchanger Plates

Channeled Porous WC Preform Plate

Fabricate porous WC preform plates



Schematic illustrations of porous WC preform plates

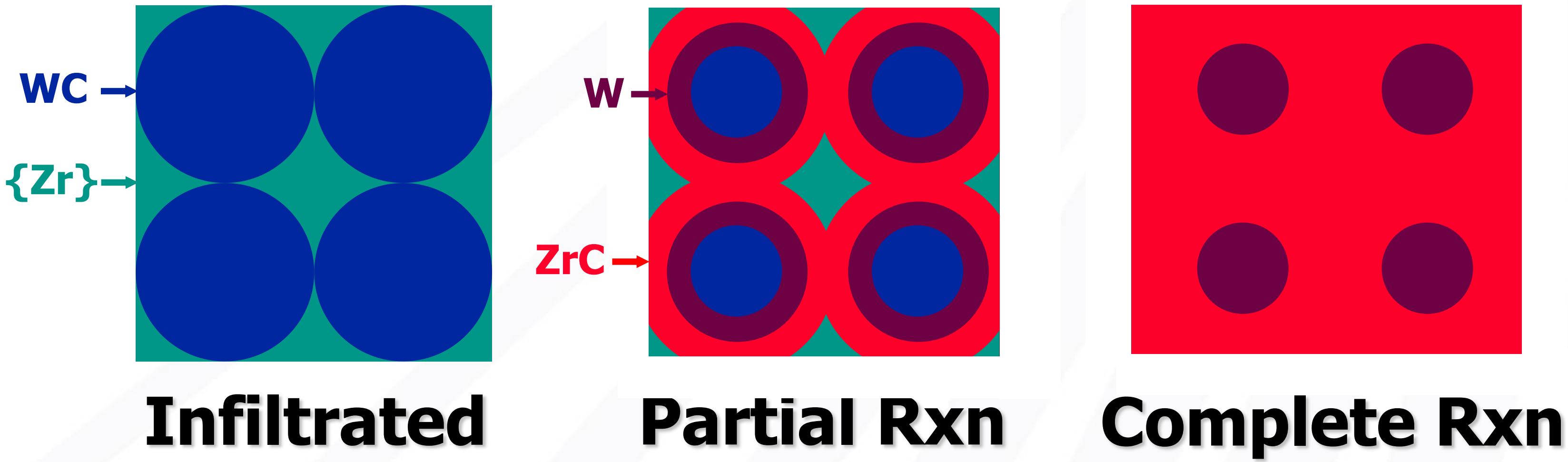


Secondary electron image of a polished cross-section

Displacive Compensation of Porosity (DCP)

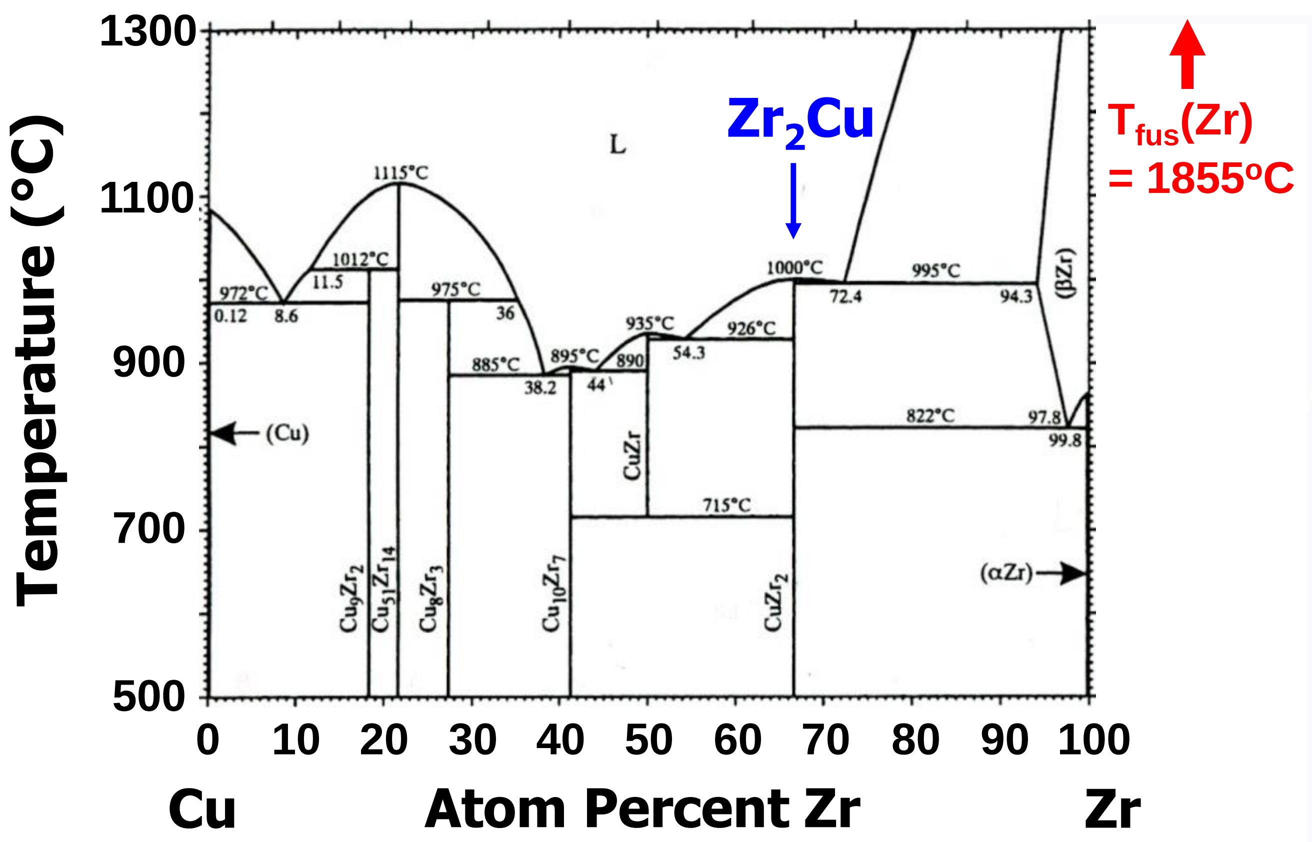
$$WC(s) + \{Zr\} \Rightarrow ZrC(s) + W(s)$$

$$\text{where } V_m[ZrC + W] = 2.01V_m[WC]$$



- K. H. Sandhage, et al., *U.S. Patents 6,833,337; 6,598,656; 6,407,022*
- A. Henry, K. H. Sandhage, *PCT/U.S. Patent Application*, 2017

Cu-Zr Phase Diagram

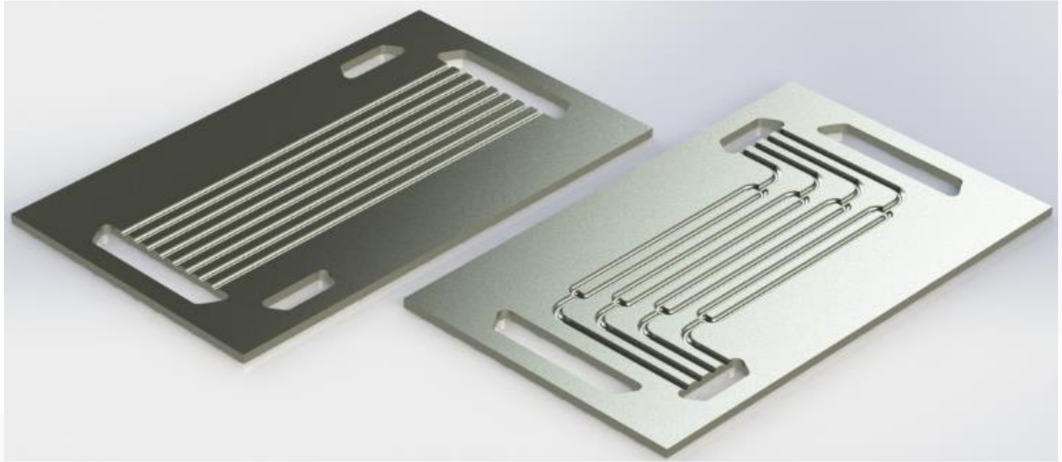


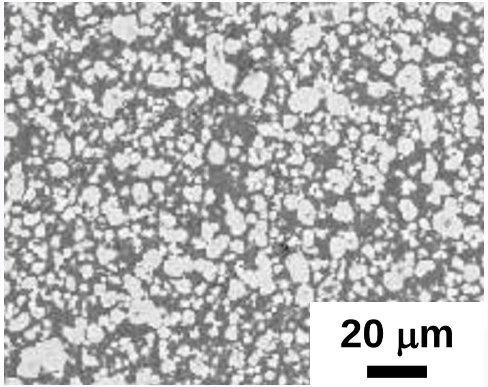
D. Arias, J. P. Abriata, *Bull. Alloy Phase Diagrams*, 11 (5) 452 (1990).

Manufacturing of ZrC/W Heat Exchanger Plates

Fabricate porous WC preform plates

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





Backscattered electron image of a polished cross-section

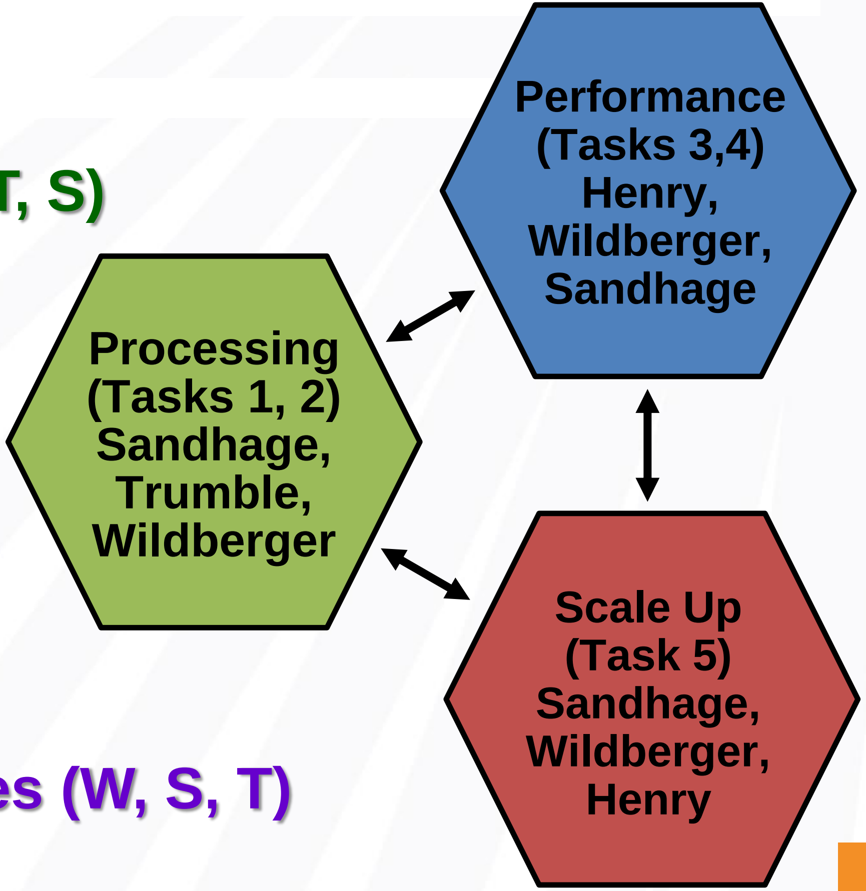
Project Objectives

- **To design a robust ZrC/W-based heat exchanger with tailored performance (effectiveness, pressure drop)**
- **To demonstrate scalable methods for:**
  - **fabricating thin (≤ 3 mm) channeled ZrC/W-based HEX plates with integral headers**
  - **assembling such plates into HEX stacks connected to metal alloy headers/tubes**
- **To develop a manufacturing pathway for a 2 MW_{th} ZrC/W-based compact (printed circuit-like) heat exchanger**

Thrusts and Expertise

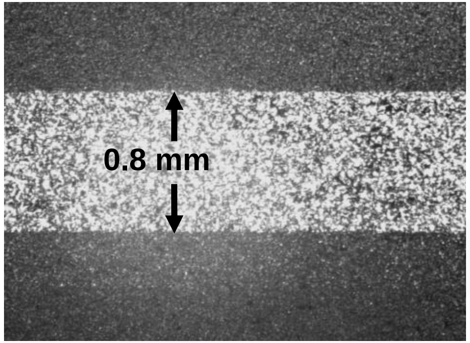
Areas of Expertise:

- Ceramic forming (T)
- Thermal processing of ceramics (T, S)
- Reactive melt infiltration (S)
- *Near net-shape* processing (S)
- Joining (S, W, H)
- High-temperature corrosion (S)
- Modeling and design of components for high-temperature thermal systems (W, H)
- Industrial manufacturing processes (W, S, T)



Thinner ZrC/W Heat Exchanger 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-TiO_2 composite generated by tape casting and thermal treatment (Trumble, et al.)

  - powder compaction

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

Heat Exchanger Design, Performance Modeling

- **Standard methods for modelling conjugate heat transfer and convection (including compressibility) at 750ºC (far from the CO_2 critical point) are being used:**
  - **- Reynold's Averaged Navier Stokes equations**
  - **- k-ε RANS model for turbulent sCO_2 flow**
- **FE analyses are being used to evaluate interfacial stresses**
- **Multiphysics modelling software (COMSOL) is being used for simulations of fluid flow, heat transfer, and stresses**
- **The geometries and dimensions of the HEX channels, and vias/headers are being tailored to simultaneously optimize the effectiveness, pressure drops, and thermomechanical reliability**

Melt Preparation and Infiltration Equipment

Cold-wall, Induction-heated Melt Infiltration System

A. Intermediate oil-based HEX for cooling of the 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

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 ZrC/W HEX plates with tailorable channel patterns
- Scalable strategies for manufacturing robust ZrC/W-based HEX assemblies are being examined
- Work with Vacuum Process Engineering, Inc. and other partners/ vendors is being conducted to develop a manufacturing pathway to a 2 MW_{th} ZrC/W heat exchanger

Questions?

Suggestions?

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