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.

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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

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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

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


High melting point and chemical compatibility ($T_{\text{Solidus}} = 2,800^\circ C$, well above superalloys; tie line between ZrC and W)

Attributes of Co-Continuous ZrC/W Composites

- High melting point and chemical compatibility \( T_{\text{Solidus}} = 2,800^\circ\text{C} \), well above superalloys; tie line between ZrC and W
- Retention of stiffness and strength at 800° C \( (E \geq 28 \times 10^6 \text{ psi/193 GPa}; \sigma_F \geq 50 \times 10^3 \text{ psi/350 MPa at RT and at 800° C}) \)

Failure Strength of Current Optimized ZrC/W

- Room Temperature
- 800°C
- 800°C with cycling

Failure Strength (MPa)

- Previous ZrC/W

[Graph showing failure strength data at different temperatures and conditions.]
Failure Strength of Current Optimized ZrC/W

Average RT Failure Strength: 531 ± 14 MPa; 77.0 ± 2 ksi
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Enhanced toughness w.r.t. conventional monolithic ceramics ($K_{1C} = 9.4 \pm 2.3 \text{ MPa}\cdot\text{m}^{1/2}$ vs. $\leq 0.8 \text{ MPa}\cdot\text{m}^{1/2}$ for Pyrex, $\leq 1.4 \text{ MPa}\cdot\text{m}^{1/2}$ for concrete, $\leq 4.8 \text{ MPa}\cdot\text{m}^{1/2}$ for Hexoloy SiC)

• http://www.refractories.saint-gobain.com/hexoloy/hexoloy-grades
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- **Thermal expansion match** (W: $4.5 \times 10^{-6}/^\circ C - 9.2 \times 10^{-6}/^\circ C$ from RT - 2700$^\circ C$; ZrC: $4.0 \times 10^{-6}/^\circ C - 10.2 \times 10^{-6}/^\circ C$ from RT - 2700$^\circ C$)

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- **High thermal conductivity** \( (\kappa = 66.0 \text{ W/m-K at 800}^\circ C \text{ vs.} 22.1 \text{ W/m-K for IN740H,} 24.4 \text{ W/m-K for H230}) \)

Thermal shock resistance and thermal cyclability
(ZrC/W nozzles have survived $>10^3\,^\circ C/\text{sec}$ heatup to 2500$^\circ C$ in a Pi-K rocket test; thermal cycling at 10$^\circ C$/min from RT to 800$^\circ C$ has not resulted in a decrease in fracture strength at 800$^\circ C$)

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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°C; PCT/U.S. patent application)

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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 application⁴)

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• K. H. Sandhage, et al., *U.S. Patents No. 6,833,337, No. 6,598,656, No. 6,407,022.*
Project Objectives

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  - 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
**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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  - fabricating thin (≤3 mm) channeled ZrC/W-based HEX plates with integral headers
  - 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.
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

Channeled Porous WC Preform Plate

Fabricate porous WC preform plates

Schematic illustrations of porous WC preform plates

Secondary electron image of a fractured cross-section

20 μm
Manufacturing of ZrC/W HEX Plates

Channeled Porous WC Preform Plate

→ Reactive Conversion

Channeled ZrC/W Plate

Fabricate porous WC preform plates

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

ZrC/W plate with molten salt channels

ZrC/W plate with sCO₂ channels

Schematic illustrations of dense-wall ZrC/W HEX plates
Displacive Compensation of Porosity

\[ \text{WC(s)} + \{\text{Zr}\} \rightarrow \text{Infiltrated} \]
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\[ \text{WC}(s) + \{\text{Zr}\} \rightarrow \text{ZrC}(s) + \text{W}(s) \]

Infiltrated Partial Rxn
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where \( V_m[\text{ZrC} + \text{W}] = 2.01 V_m[\text{WC}] \)

Infiltrated  Partial Rxn  Complete Rxn
Cu-Zr Phase Diagram


$T_{\text{fus}(\text{Zr})} = 1855^\circ\text{C}$
Melt Preparation and Infiltration Equipment

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

Cold-wall, Induction-heated Melt Infiltration System
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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
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\textsubscript{4}C/B\textsubscript{4}C-TiO\textsubscript{2} composite produced by tape casting of layers of B\textsubscript{4}C and B\textsubscript{4}C-TiO\textsubscript{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.)
Diffusion Bonding of Cu Layers

Cu layers on surfaces for sCO₂

Massachusetts Institute of Technology

Vacuum Process Engineering

PURDUE UNIVERSITY
Diffusion Bonding of Cu Layers

Cu layers on surfaces for sCO₂
Diffusion Bonding of HEX Assembly

ZrC/W header plate

ZrC/W side panels for stiffening

Ni alloy tubes

Gas pressure test assembly (inlet tubes only)
Standard methods for modelling convection (including compressibility) at 750°C (far from the CO₂ critical point) will be used:
- Reynold’s Averaged Navier Stokes equations
- k-omega model for turbulent sCO₂ flow
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FLUENT and/or COMSOL software will be used to model steady-state flow through the HEX channels for each fluid to calculate pressure drops
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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
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
ZrC/W cermets provide an attractive combination of high-temperature properties relative to state-of-the-art metal alloys
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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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 MWth ZrC/W HEX for Phase 3 of the Gen3 CSP program.
Questions?
Suggestions?