Processing and Properties of Robust Ceramic/Metal Composites for Heat Exchangers Operating at $\geq$750^{o}C with Supercritical CO_2

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Oak Ridge National Laboratory

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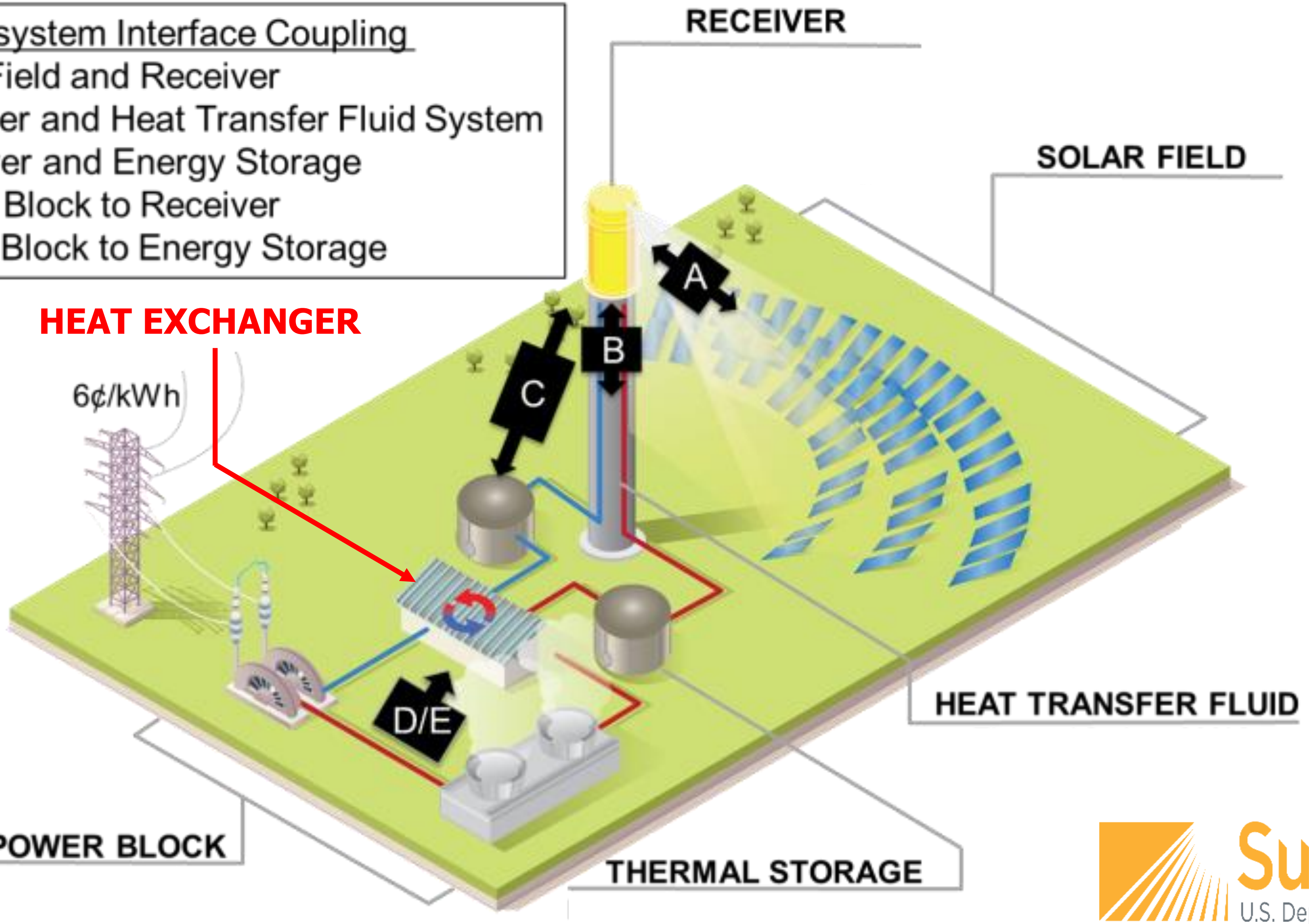
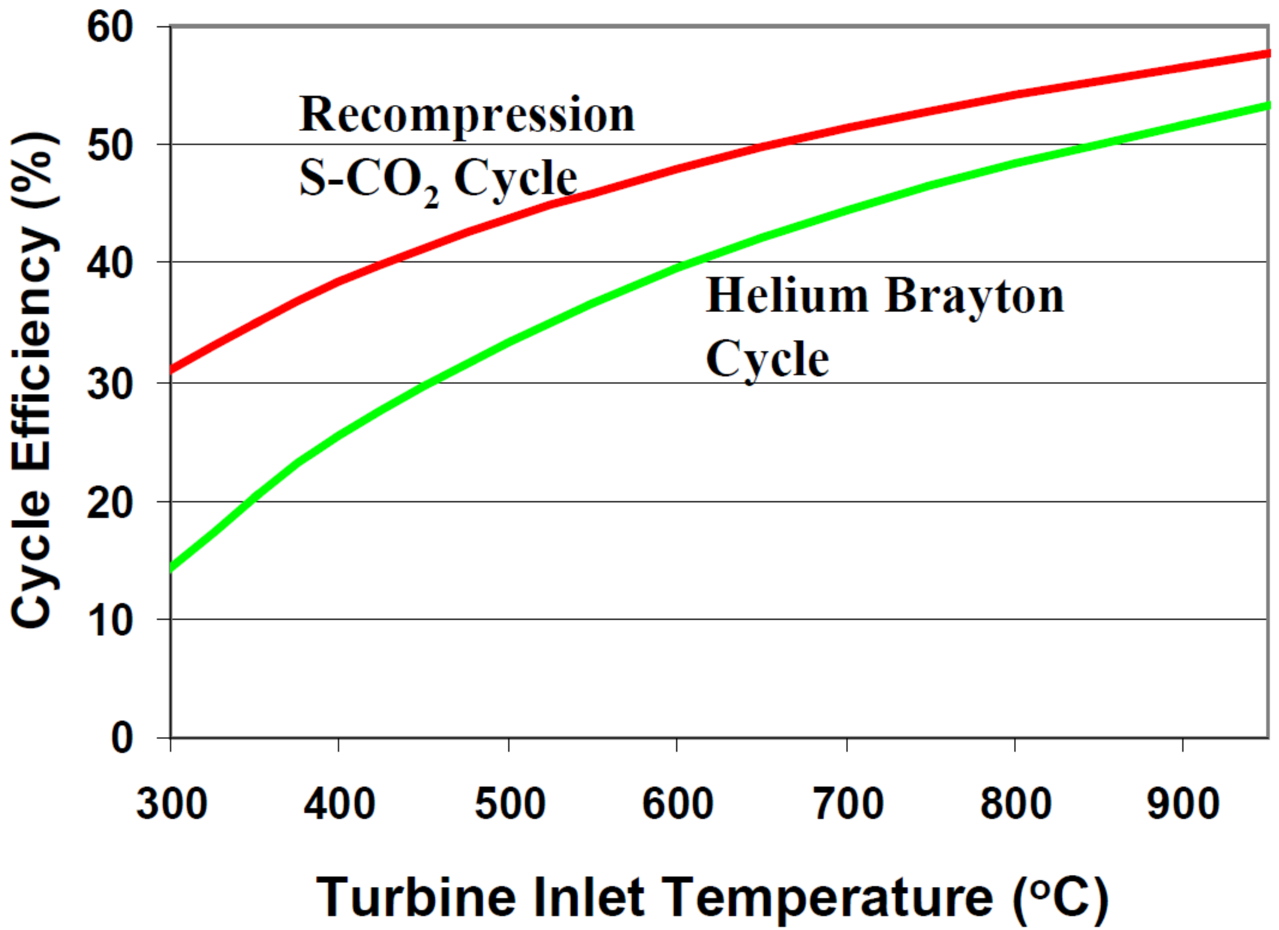
Concentrated Solar Power Tower

CSP Subsystem Interface Coupling
A: Solar Field and Receiver
B: Receiver and Heat Transfer Fluid System
C: Receiver and Energy Storage
D: Power Block to Receiver
E: Power Block to Energy Storage



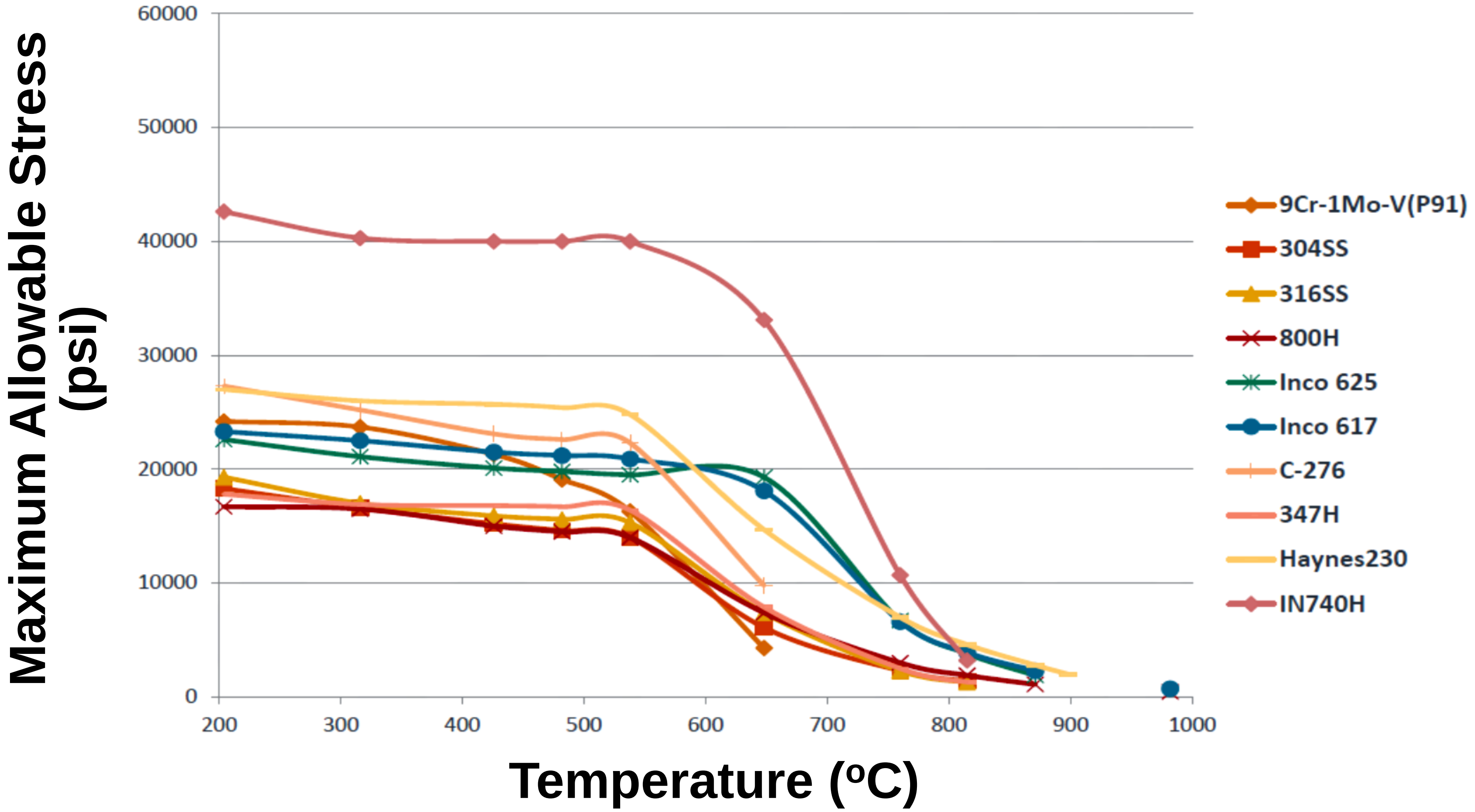
SunShot
U.S. Department of Energy

Push for Higher Turbine Inlet Temperatures



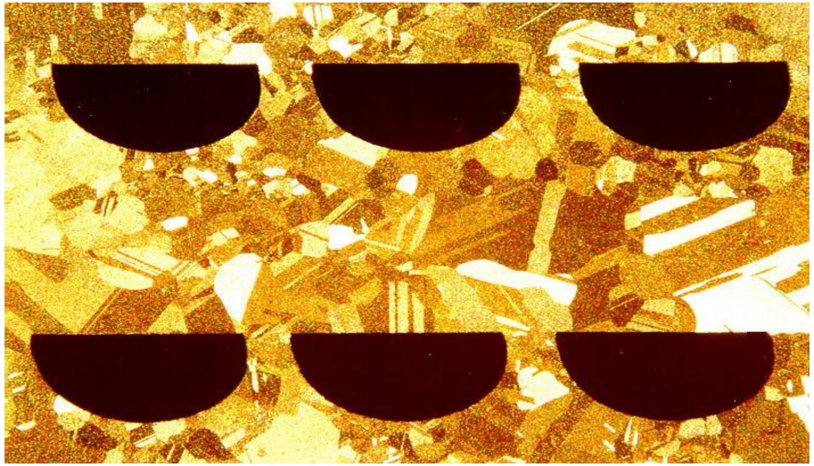
V. Dostal, M. J. Driscoll, P. Hejzlar, N. E. Todreas, "A Supercritical CO$_2$ Gas Turbine Power Cycle for Next-Generation Nuclear Reactors," *Proc. 10th Intl. Conf. Nuclear Engineering*, ICONE 10, Arlington, VA, 2002; V. Dostal, P. Hejzlar, M. J. Driscoll, "The Supercritical Carbon Dioxide Power Cycle: Comparison to Other Advanced Cycles," *Nuclear Technol.*, 154, 283-301 (2006).

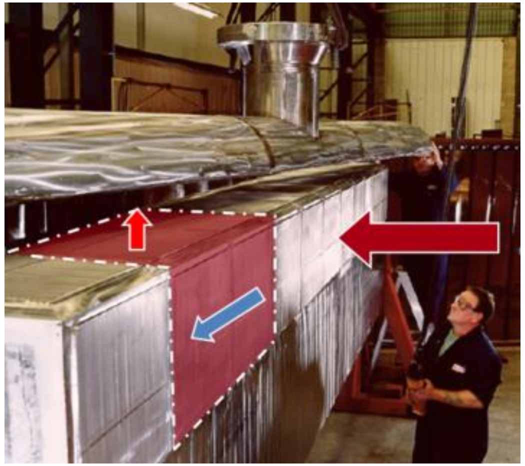
State of the Art: Metal Alloy Printed Circuit HEXs



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

State of the Art: Metal Alloy Printed Circuit HEXs





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.

Current Technology:

- Printed Circuit HEXs: patterned etching of channels into metal alloy plates, then diffusion bonding
- Alloy mechanical properties degrade significantly above 650°C

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 $\geq$ 750°C

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

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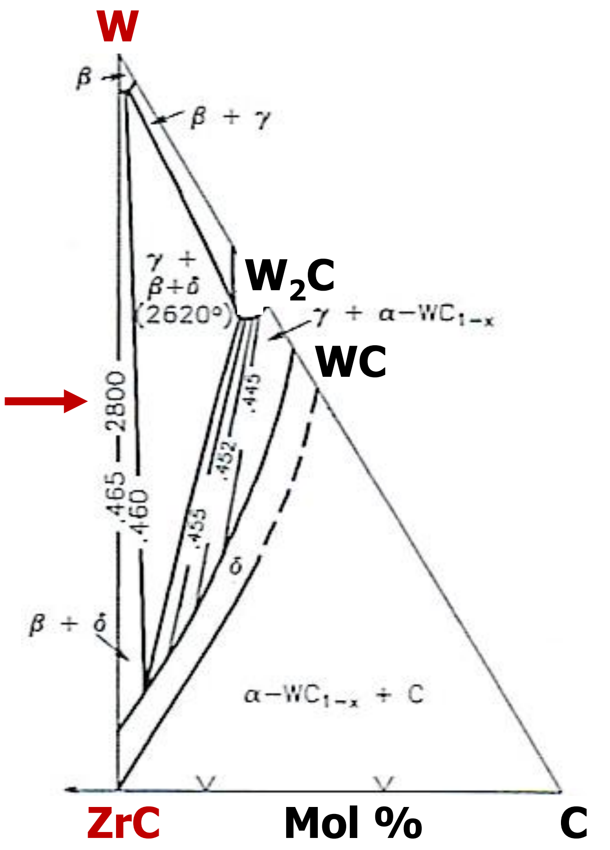
Attributes of Co-Continuous ZrC/W Composites

- **High melting point and chemical compatibility**

  ($T_{Solidus} = 2{,}800^{o}C$, well above superalloys; tie line between ZrC and W)



1. 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°C, well above superalloys; tie line between ZrC and W)
- **Retention of stiffness and strength at 800°C**
  ($E \geq 28\text{x}10^6$ psi/193 GPa; $\sigma_F \geq 50\text{x}10^3$ psi/350 MPa at RT and at 800°C)
- **Enhanced toughness w.r.t. conventional monolithic ceramics**
  ($K_{1C} = 9.4$ MPa·m$^{1/2}$ vs. ≤ 0.8 MPa·m$^{1/2}$ for Pyrex, ≤ 1.4 MPa·m$^{1/2}$ for concrete, ≤ 4.8 MPa·m$^{1/2}$ for Hexoloy SiC)
- **Thermal expansion match**
  (W: $4.5\text{x}10^{-6}$/°C - $9.2\text{x}10^{-6}$/°C from RT - 2700°C; ZrC: $4.0\text{x}10^{-6}$/°C - $10.2\text{x}10^{-6}$/°C from RT - 2700°C)
- **High thermal conductivity at 800°C**
  (κ = 66.0 W/m·K vs. 22.1 W/m·K for IN740H[1], 24.4 W/m·K for H230[2], $\leq$ 45 W/m·K for SiC[3-5])

1. http://www.specialmetals.com/files/PCC%20EG%20740H%20White%20Paper.pdf
2. http://www.hightempmetals.com/techdata/hitempHaynes230data.php
3. 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).
4. D.-M. Liu, B.-W. Lin, "Thermal Conductivity in Hot-Pressed Silicon Carbide," *Ceram. Int.*, 22, 407-414 (1996).
5. 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 °C/sec heatup to 2500°C in a Pi-K rocket test[1]; thermal cycling at 10°C/min from RT to 800°C has not resulted in a decrease in fracture strength at 800°C)

- **Oxidation resistance**
  (Tailoring of the ZrC/W surface and the sCO_2 fluid has rendered ZrC/W composites resistant to oxidation by the sCO_2-based fluid at 750°C/20 MPa; PCT/US patent application[2])

- **Cost-effective fabrication of ZrC/W-based HEX plates**
  (Scalable, low-cost forming and shape/size-preserving DCP reaction processing[3] of ZrC/W-based plates with tailorable channels and headers for HEXs; PCT/US patent application[4])

1. 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).
2. K. H. Sandhage, "Method for Enhancing Corrosion Resistance of Oxidizable Materials and Components Made Therefrom," *PCT/US Patent Application*, 2017; *US Provisional Patent Application*, 2016.
3. K. H. Sandhage, et al., *U.S. Patents No. 6,833,337, No. 6,598,656, No. 6,407,022.*
4. A. Henry, K. H. Sandhage, "Methods for Manufacturing Ceramic and Ceramic Composite Components and Components Made Thereby," *PCT/US Patent Application*, 2017; *US Provisional Patent Application*, 2016.

Displacive Compensation of Porosity (DCP) Process

(K. H. Sandhage, et al., ***U.S. Patents No. 6,833,337;***
No. 6,598,656; No. 6,407,022)

DCP Reaction for ZrC/W Composites

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

where {Zr} refers to zirconium dissolved in a liquid solution

- **Thermodynamically-favored reaction**

  $\Delta G°_{rxn}$ = -150.8 to -143.3 kJ/mole (1000-2000°C[1])

- **Several congruently-melting Zr-Cu compositions exist with modest melting points (<1115°C)[2].**
- **The molar volume of ZrC is 24.5% larger than the molar volume of WC (i.e., more ceramic volume is created than is consumed by this reaction)**

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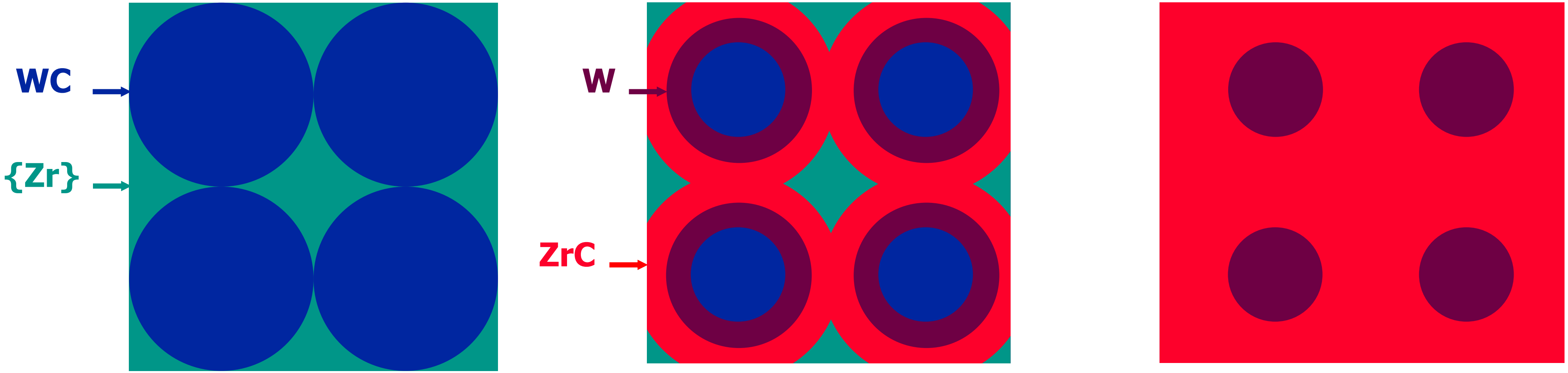
1. I. Barin, *Thermochemical Data of Pure Substances*, 3rd Edn, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1995.
2. D. Arias, J. P. Abriata, *Bull. Alloy Phase Diagrams*, 11 (5) 452 (1990).

Displacive Compensation of Porosity (DCP) Process

$$\mathrm{WC(s)} + \{\mathrm{Zr}\} => \mathrm{ZrC(s)} + \mathrm{W(s)}$$

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

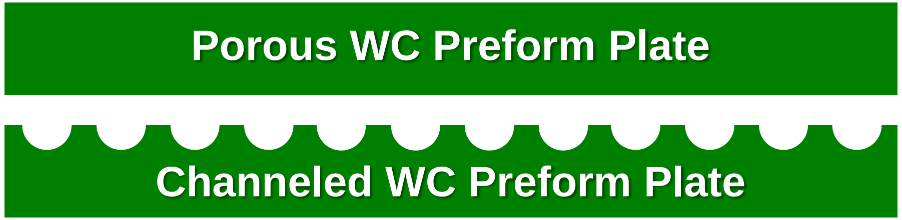


Infiltrated

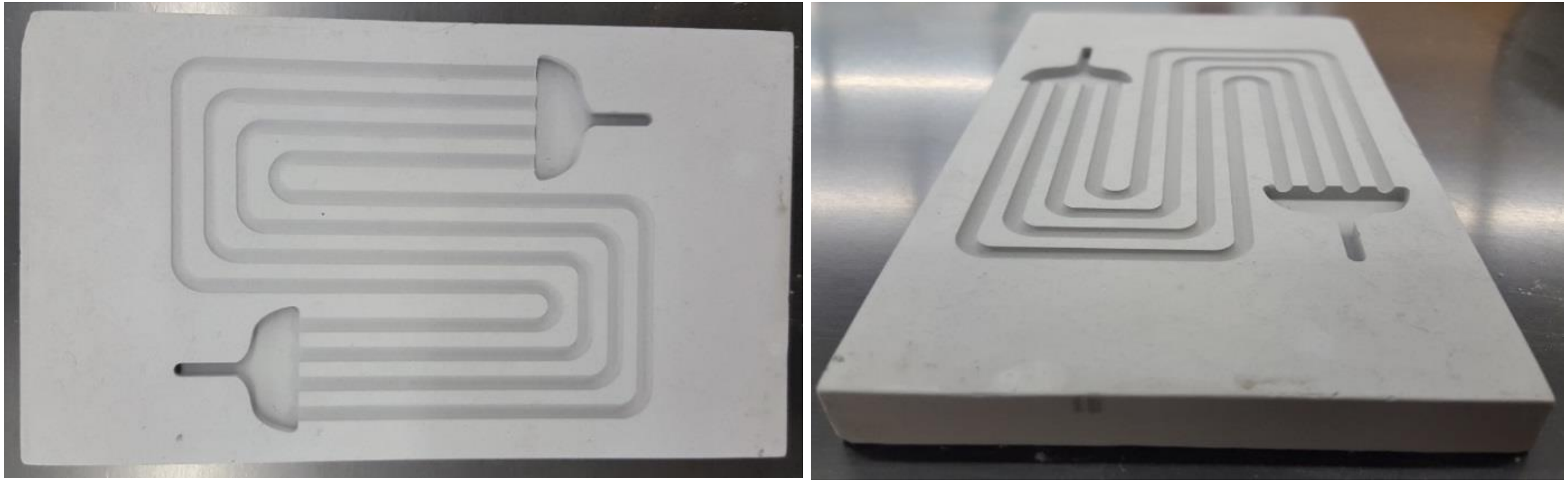
Partial Rxn

Complete Rxn

Fabrication of ZrC/W Heat Exchangers

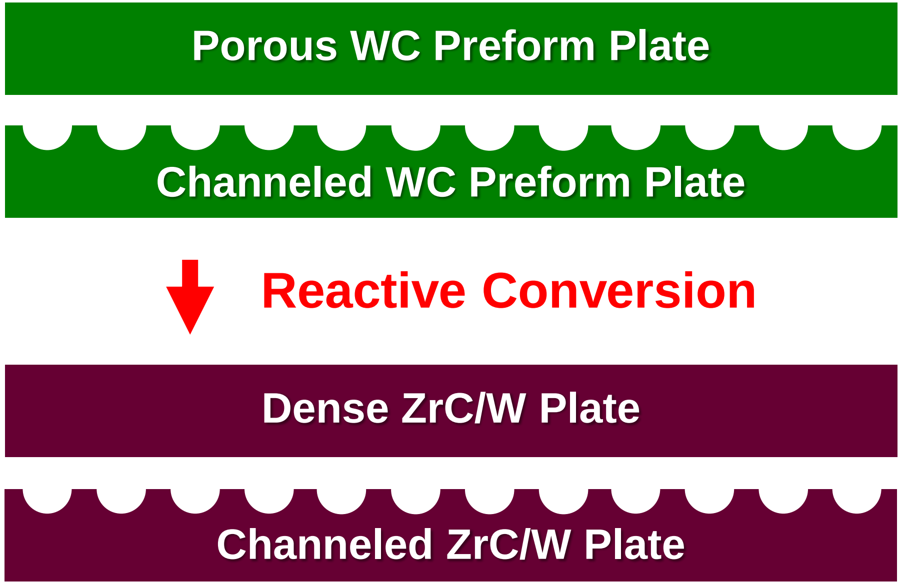


Fabricate pairs of porous WC preform plates (one with patterned channels)



Green Machined Porous WC Preform Plates

Fabrication of ZrC/W Heat Exchangers



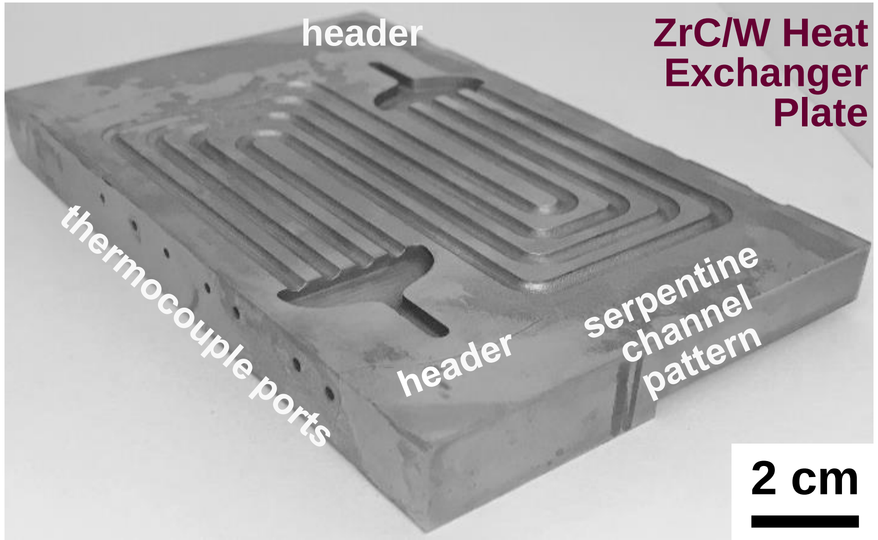
Porous WC Preform Plate

Channeled WC Preform Plate

Reactive Conversion

Dense ZrC/W Plate

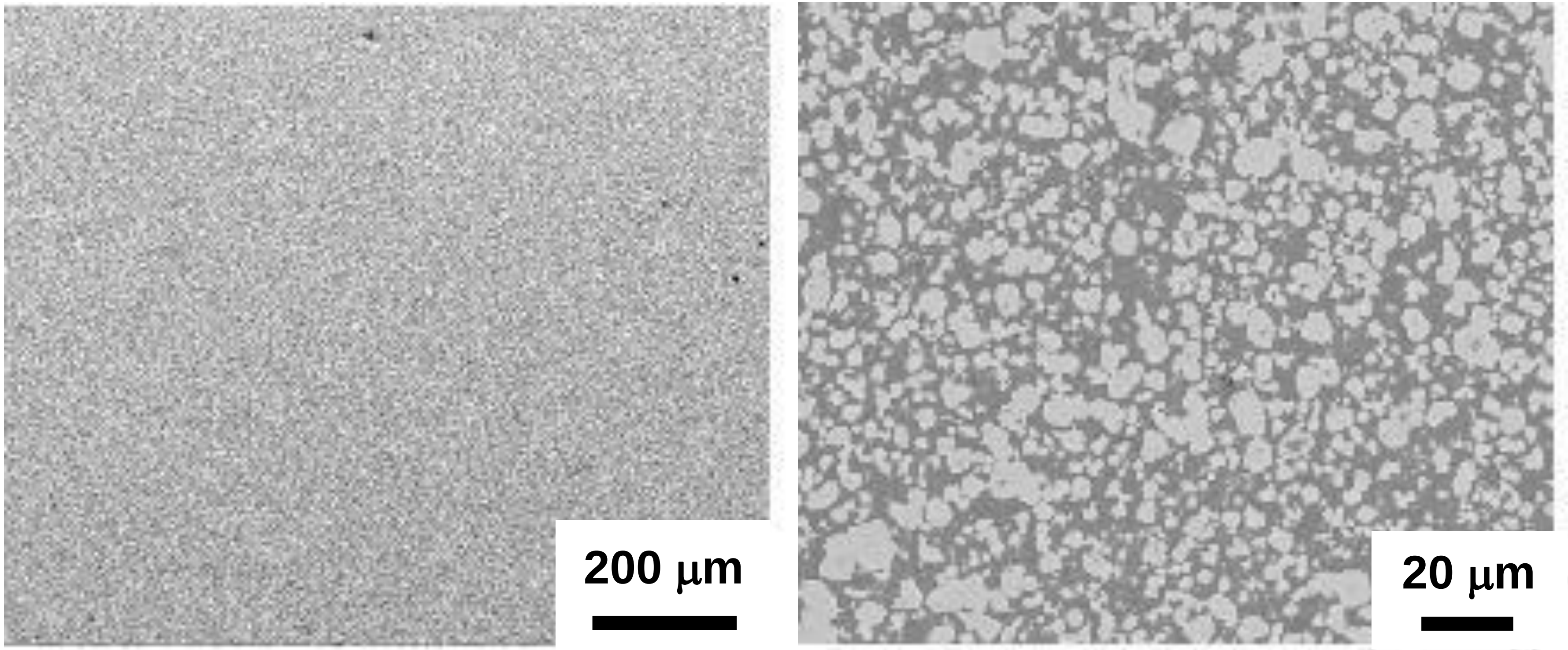
Channeled ZrC/W Plate



Fabricate pairs of porous WC preform plates (one with patterned channels)

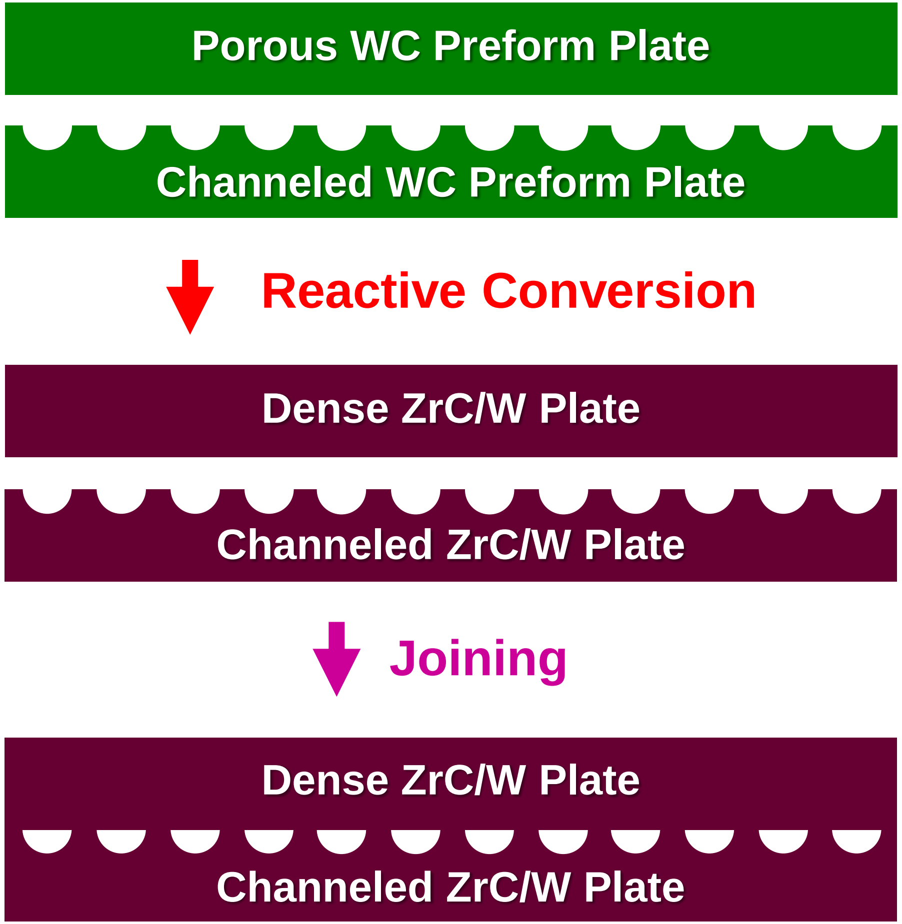
Generate net-shape/size dense ZrC/W plates via DCP reaction process

Fabrication of ZrC/W Heat Exchangers



Backscattered electron images of polished cross-sections of dense DCP-derived ZrC/W composites

Fabrication of ZrC/W Heat Exchangers



Porous WC Preform Plate

Channeled WC Preform Plate

Reactive Conversion

Dense ZrC/W Plate

Channeled ZrC/W Plate

Joining

Dense ZrC/W Plate

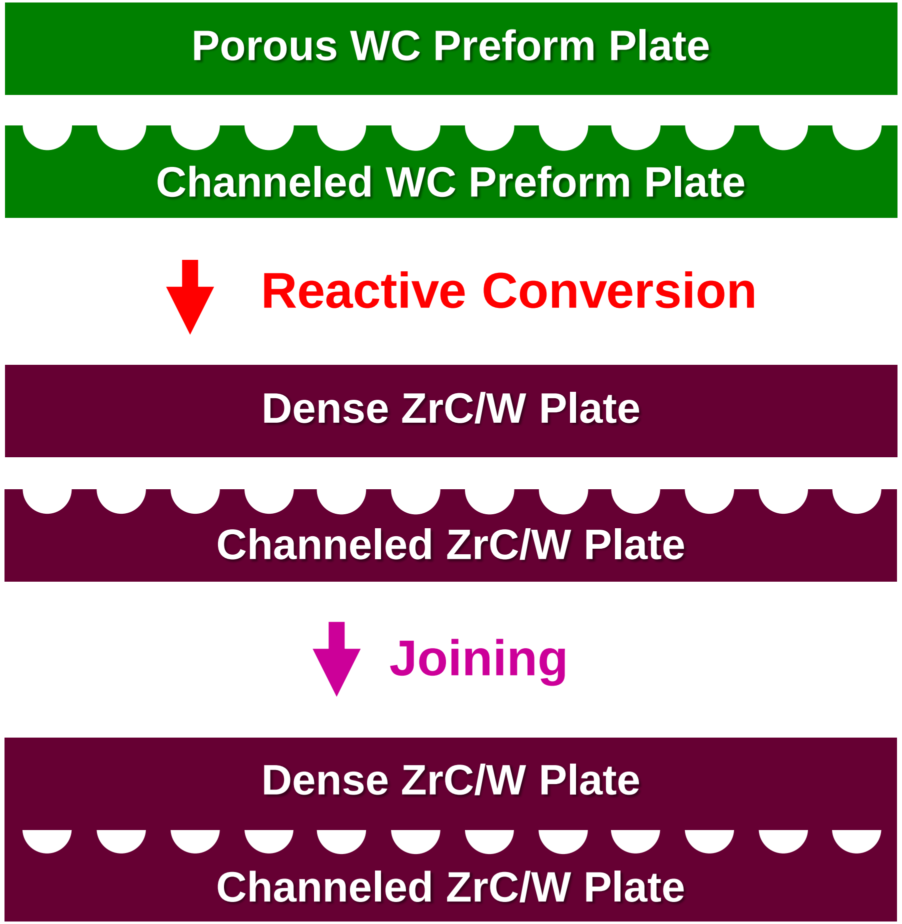
Channeled ZrC/W Plate

Fabricate pairs of porous WC preform plates (one with patterned channels)

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

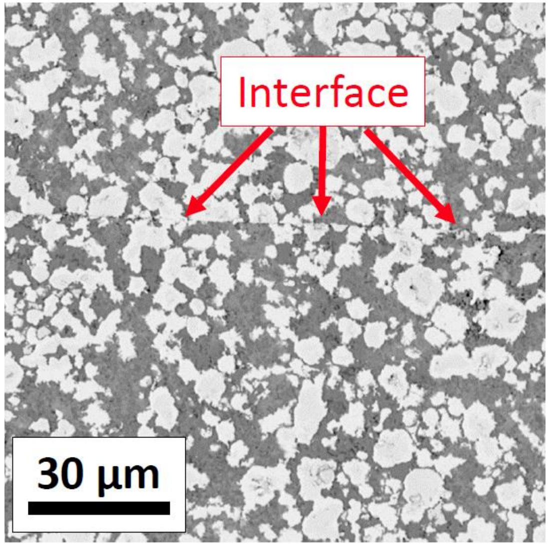
Diffusion bond pairs of ZrC/W plates; connect to headers and tubing

Fabrication of ZrC/W Heat Exchangers



Fabricate pairs of porous WC preform plates (one with patterned channels)

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



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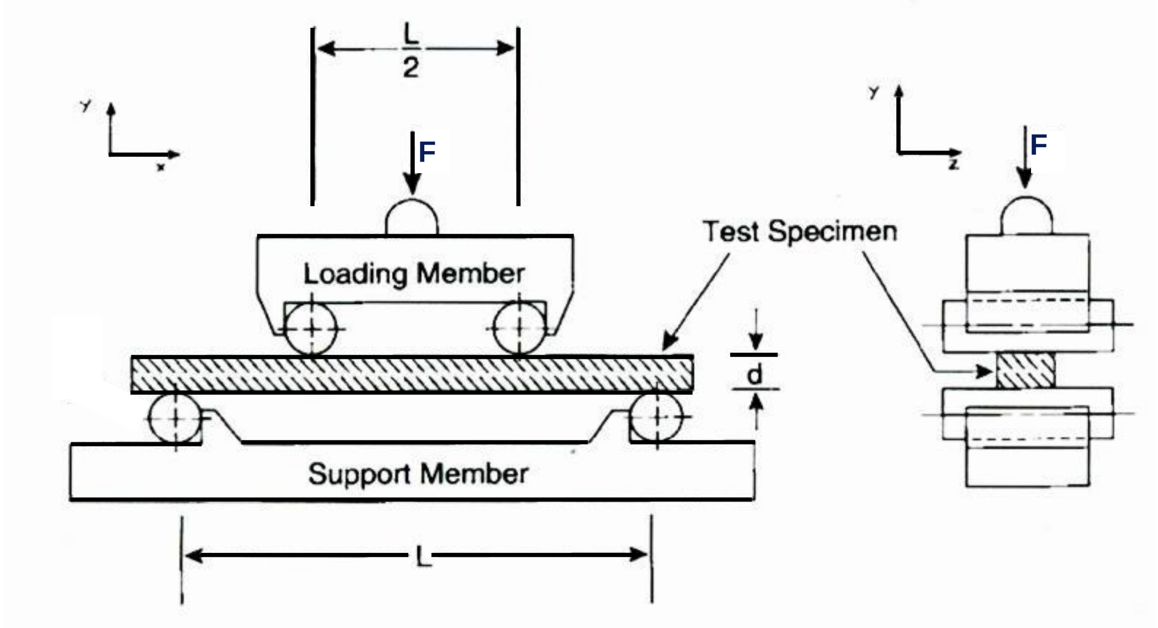
High-Temperature Mechanical Testing of ZrC/W

- The average fracture strength of DCP-derived, co-continuous ZrC/W composites has been evaluated with four point bend tests conducted at room temperature, at 800ºC, and at 800ºC after thermal cycling (High Temperature Materials Laboratory, Oak Ridge National Laboratory) as per ASTM standards E1161-18 and E1211-18



$$\sigma_f = (3L/4bd^2)F$$

where:

σ_f = fracture strength
L = 20 mm
b = 2.0 mm
d = 1.5 mm
F = applied force at fracture

1. “Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature,” *ASTM E1161-18*, ASTM International, 2013.
2. “Standard Test Method for Flexural Strength of Advanced Ceramics at Elevated Temperatures,” *ASTM E1211-18*, ASTM International, 2013.

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- ZrC/W rectangular bars (configuration A: 2.0 mm x 1.5 mm x 25 mm) were diamond ground and chamfered as per ASTM standards C1161-18 and C1211-18
- The specimens were heated at 10ºC/min to 800ºC and held for 1 h prior to bend testing (thermal cycling was also conducted at 10ºC/min to 800ºC, with 10 cycles)
- Fracture strength values (average of 10 tests, 95% confidence range):

$\sigma_F(25^oC) = 348 \pm 23$ MPa (50.5 ± 3.3 ksi) $\sigma_F(800^oC) = 369 \pm 11$ MPa (53.5 ± 1.6 ksi)

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Purdue University

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σ_F(800°C) = 369±11 MPa (53.5±1.6 ksi)

σ_F(800°C w/10 cycles): 387±7 MPa (56.1 ksi)

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High-Temperature Mechanical Testing of ZrC/W

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- The specimens were heated at 10ºC/min to 800ºC and held for 1 h prior to bend testing (thermal cycling was also conducted at 10ºC/min to 800ºC, with 10 cycles)
- Unlike stainless steels or Ni-based alloys, the ZrC/W failure strength was not strongly temperature dependent (for RT vs. 800ºC)

High-Temperature Mechanical Testing of ZrC/W

- The average fracture strength of DCP-derived, co-continuous ZrC/W composites has been evaluated with four point bend tests conducted at room temperature, at 800ºC, and at 800ºC after thermal cycling (High Temperature Materials Laboratory, Oak Ridge National Laboratory) as per ASTM standards E1161-18 and E1211-18
- ZrC/W rectangular bars (configuration A: 2.0 mm x 1.5 mm x 25 mm) were diamond ground and chamfered as per ASTM standards C1161-18 and C1211-18
- The specimens were heated at 10ºC/min to 800ºC and held for 1 h prior to bend testing (thermal cycling was also conducted at 10ºC/min to 800ºC, with 10 cycles)
- The ZrC/W failure strength was also not degraded by thermal cycling between RT and 800ºC (10 cycles)

High-Temperature Thermal Conductivity of ZrC/W

- The thermal diffusivity (α) and heat capacity (C_p) values have been obtained for DCP-derived ZrC/W composite samples at 800°C using laser flash analyses (as per ASTM standard E1461) and differential scanning calorimetry (as per ASTM standard E1269)
- ZrC/W disks were prepared for laser flash (12.5 mm diameter x 3.0 mm thick) and heat capacity (4.9 mm diameter x 11.4 mm thick) analyses at 800°C at the Orton Ceramic Foundation
- The values of thermal diffusivity (α = 0.201 cm^2/sec), and heat capacity (C_p = 3.28 J/cm^3-K) were used to calculate the thermal conductivity:

$$\kappa \text{ (W/m-K)} = 100\alpha C_p$$

- The κ value for ZrC/W at 800°C was 66.0±5.3 W/m-K, which is 2-3 times larger than for stainless steels and Ni-based superalloys at 800°C[1-3]

1. http://www.specialmetals.com/files/PCC%20EG%20740H%20White%20Paper.pdf
2. http://www.hightempmetals.com/techdata/hitempHaynes230data.php
3. Y. S. Touloukian, R. W. Powell, C. Y. Ho, PP. G. Klemens, *Thermal Conductivity. Metallic Elements and Alloys. Thermophysical Properties of Matter.* Vol. 1, Plenum Press, NY, 1970.

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High-Temperature Thermal Conductivity of ZrC/W

- A simple effective medium (rule of mixtures) model has been used to predict the thermal conductivity of DCP-derived ZrC/W composites
- Thermal conductivity values of W and ZrC at 800°C are reported to be 119 W/m-K and 34.6 W/m-K, respectively[1,2]
- The calculated rule-of-mixtures thermal conductivity value for an equimolar mixture of ZrC and W in a DCP-derived composite is 66.7 W/m-K at 800°C, which is similar to the measured value obtained at this temperature (66.0±5.3 W/m-K)
- Hence, this simple effective medium model may be used to estimate thermal conductivity values of DCP-derived ZrC/W composites at other temperatures

Georgia Institute of Technology

1. Y. S. Touloukian, R. W. Powell, C. Y. Ho, PP. G. Klemens, *Thermal Conductivity. Metallic Elements and Alloys. Thermophysical Properties of Matter.* Vol. 1, Plenum Press, NY, 1970.
2. R. E. Taylor, “Thermal Conductivity of Zirconium Carbide at High Temperatures,” *J. Am. Ceram. Soc.,* 45 (7) 353-354 (1962).

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High-Temperature Corrosion Resistance to sCO_2

- **ZrC/W cermets (and other oxidizable materials, such as stainless steels or other metallic alloys) can be endowed with high-temperature corrosion resistance in sCO_2-based fluids via use of a new concept (K. H. Sandhage, PCT/U.S. Patent Application[1]):**

  a supercritical buffered (reducing) CO-CO_2 fluid

- **Modest CO additions to CO_2 can dramatically lower the equilibrium oxygen fugacity, f_{O2}, of the CO_2-based fluid:**

$$2CO + O_2 = 2CO_2$$

  ⇒ the addition of just 10 ppm CO in CO_2 at 750°C yields an equilibrium f_{O2} value of only 1.7×10^{-10} atm (at 1 atm total pressure)[2]

- **For equilibrium at higher total pressures at 750°C (e.g., at 20 MPa/197.4 atm), the Gibbs free energy change for this reaction should become more negative, with a negative volume change upon reaction ($\partial\Delta G_{rxn}/\partial P|_T = \Delta V_{rxn}$)**

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1. 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.
2. I. Barin, *Thermochemical Data of Pure Substances*, 3rd Edn, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1995.

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High-Temperature Corrosion Resistance to sCO_2

- Hence, the f_{O_2} associated with CO-CO_2 mixtures should decrease as total pressure increases
- Consequently, supercritical CO-CO_2 (sCO/CO_2) mixtures with sufficient CO contents can act as reducing (non-oxidizing) fluids to otherwise oxidizable materials
- Relatively noble metals can be rendered inert in sCO/CO_2 fluids with modest CO contents
- The f_{O_2} required to oxidize Cu to form Cu_2O at 750°C is 2.6×10^{-10} atm[1], which corresponds to a CO/CO_2 mixture containing only 8.1×10^{-6} (8.1 ppm) CO
- Hence, a Cu surface layer exposed to sCO/CO_2 fluids containing >10 ppm CO at 750°C should be thermodynamically stable (inert)[2]

1. I. Barin, *Thermochemical Data of Pure Substances*, 3rd Edn, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1995.
2. 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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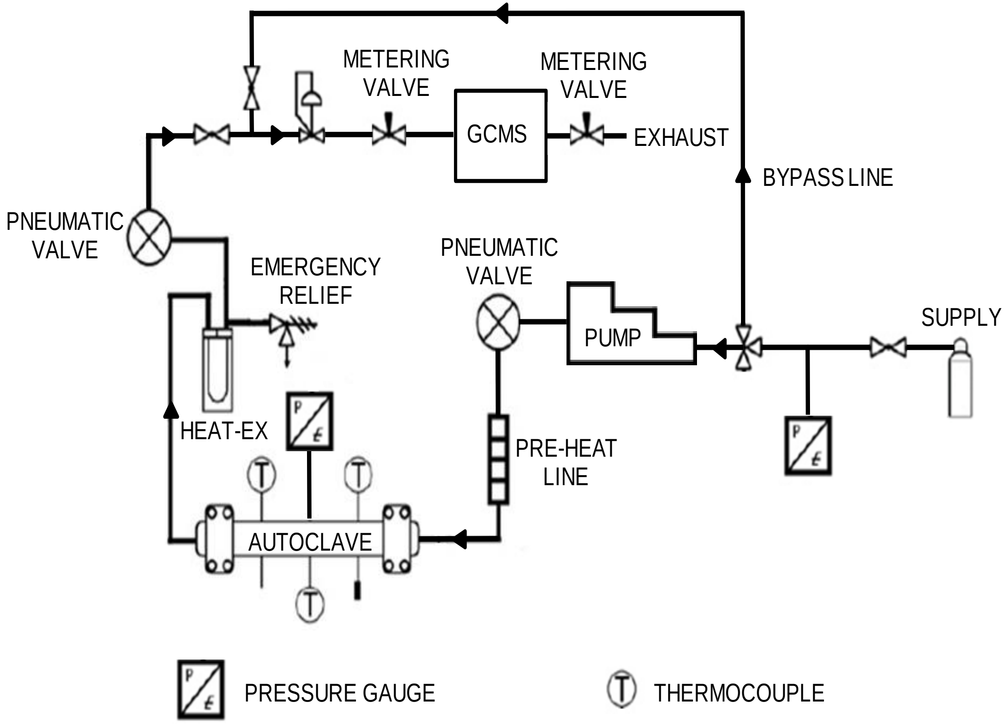
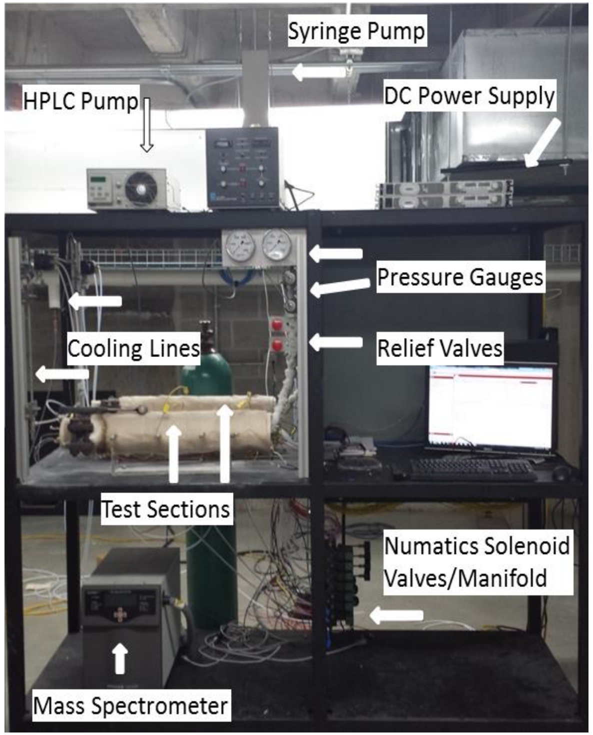
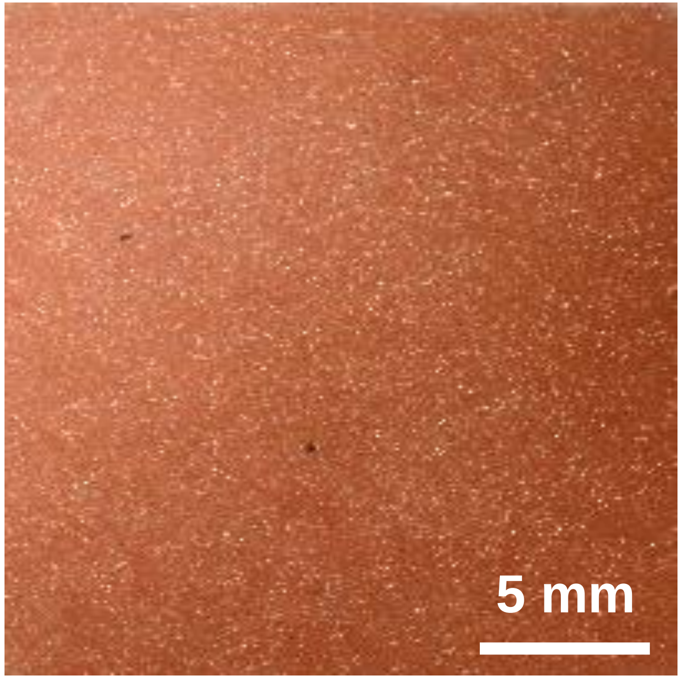
High-Temperature Corrosion Resistance to sCO$_2$

- A U.S. Occupational Safety and Health Administration guideline limits human exposure to 50 ppm of CO for 8 h in an enclosed space
- To test this reducing sCO/CO$_2$ concept, 5 Cu-layer-bearing ZrC/W specimens were exposed to a flowing (~0.1 kg/hr) mixture of 50±10 ppm CO in CO$_2$ at 750°C and 20 MPa for up to 1000 h





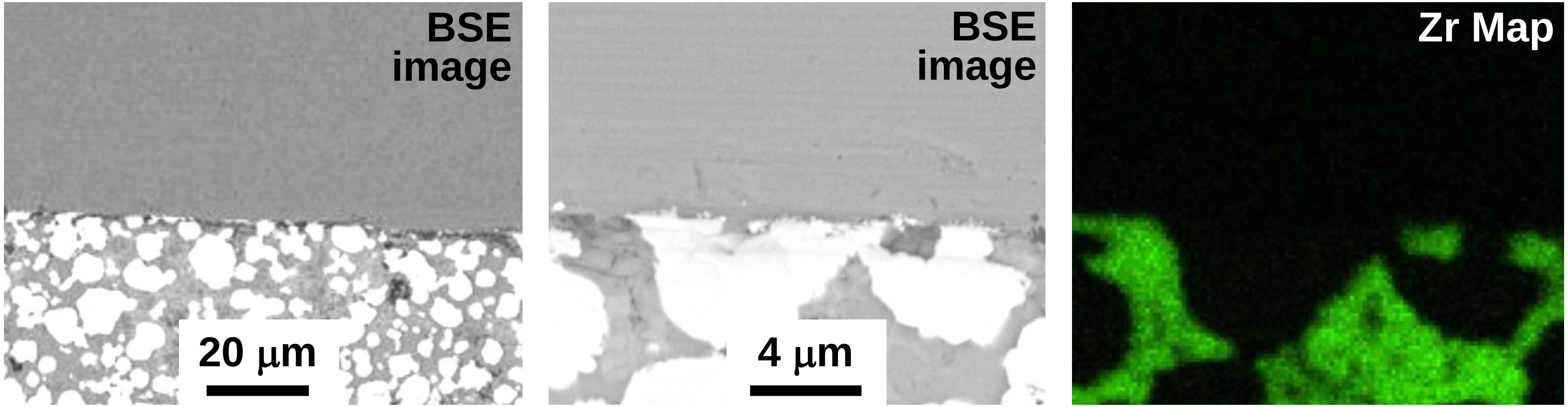
High-Temperature Corrosion Resistance to sCO_2



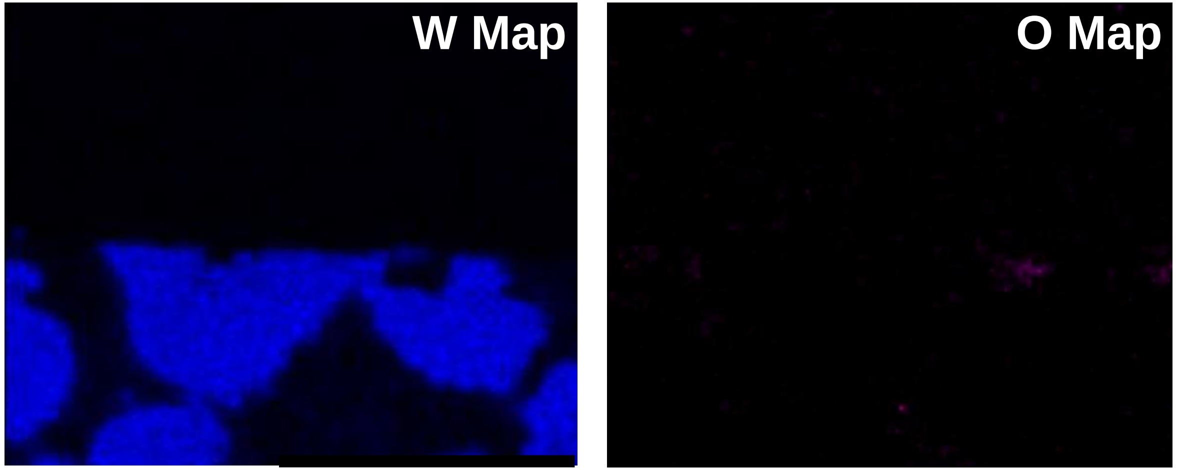
Photograph of a Cu-layer-bearing ($\geq$1 mm thick Cu) ZrC/W specimen after 1000 h in 50 ppm sCO/SCO_2 at 750°C/20 MPa

- The tan color of the copper was retained after such sCO/CO_2 exposure
- No mass gains were detected after such exposure for five Cu-layer-bearing ZrC/W specimens

High-Temperature Corrosion Resistance to sCO_2



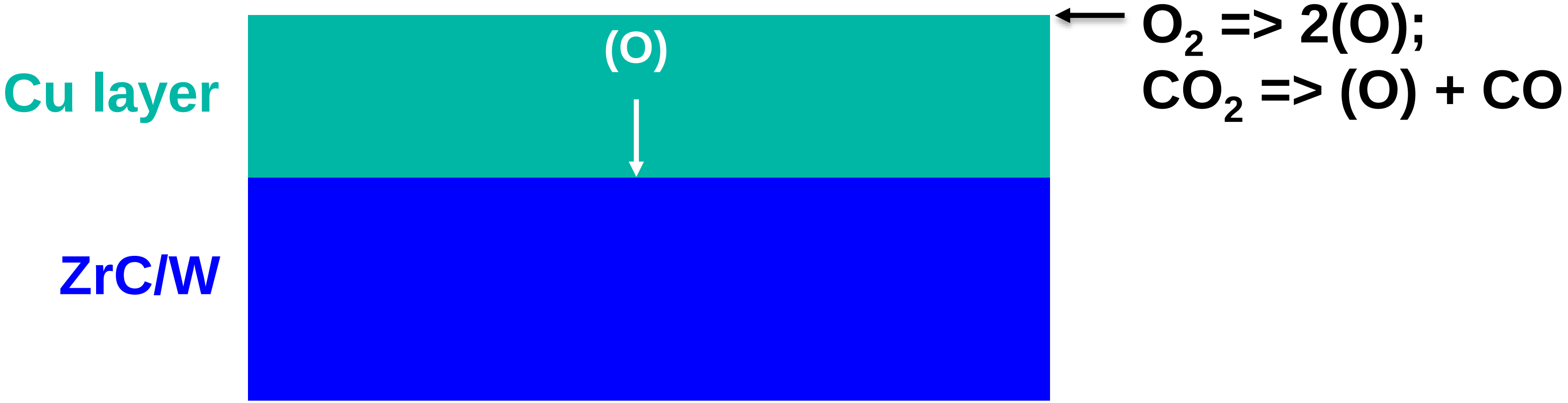
Cu:ZrC/W interface after 1000 h of exposure to 50 ppm CO in CO_2 at 750°C and 20 MPa



1. 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.

High-Temperature Corrosion Resistance to sCO_2

- **While Cu should be stable (inert) in a 50 ppm CO/CO_2 mixture at 750ºC, it is possible for oxygen to migrate through a Cu layer to the Cu:ZrC/W interface and then oxidize the ZrC/W cermet**
- **The oxygen flux through a Cu layer exposed to a 50 ppm CO/CO_2 mixture at 750ºC may be calculated from the oxygen solubility, X_o, and oxygen diffusivity, D_O, in Cu[1]**



$O_2 \Rightarrow 2(O)$;

$CO_2 \Rightarrow (O) + CO$

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[1] M. L. Narula, V. B. Tare, W. L. Worrell, "Diffusivity and Solubility of Oxygen in Solid Copper Using Potentiostatic and Potentiometric Techniques," *Metall. Trans. B*, 14B, 673-677 (1983).

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- **The *maximum oxygen flux* would occur if it is assumed that the mole fraction of oxygen dissolved in Cu at the Cu/ZrC-W interface is essentially zero, and is given by:**

$$J_O \text{ (moles O/cm}^2\text{-sec)} = D_O X_O / \{L V_m(\text{Cu})\}$$

with X_O = atom fraction of oxygen dissolved in Cu at the Cu:CO-CO_2 interface; L = Cu thickness; V_m(Cu) = Cu molar volume

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High-Temperature Corrosion Resistance to sCO_2

- The maximum oxygen flux through a 1 mm thick Cu layer is:

$$J_O = (4.25\text{x}10^{-6}\ \text{cm}^2/\text{sec})(5.75\text{x}10^{-7})/[(0.1\ \text{cm})(7.113\ \text{cm}^3/\text{mole})]$$

$$= 3.44\text{x}10^{-12}\ \text{moles O/cm}^2\text{-sec}$$

- In 1000 h ($3.60\text{x}10^6$ sec), $1.24\text{x}10^{-5}$ moles of O per cm^2 (or $6.19\text{x}10^{-6}$ moles of $O_2/\text{cm}^2 = 9.90\text{x}10^{-5}$ g/cm^2) would migrate through such a Cu layer

- If all of this oxygen was used to generate ZrO_2 by the oxidation of ZrC, then a ZrC recession of 1.0 μm should occur (the ZrO_2 and ZrC molar volumes are 21.2 cm^3/mole and 15.6 cm^3/mole, respectively)

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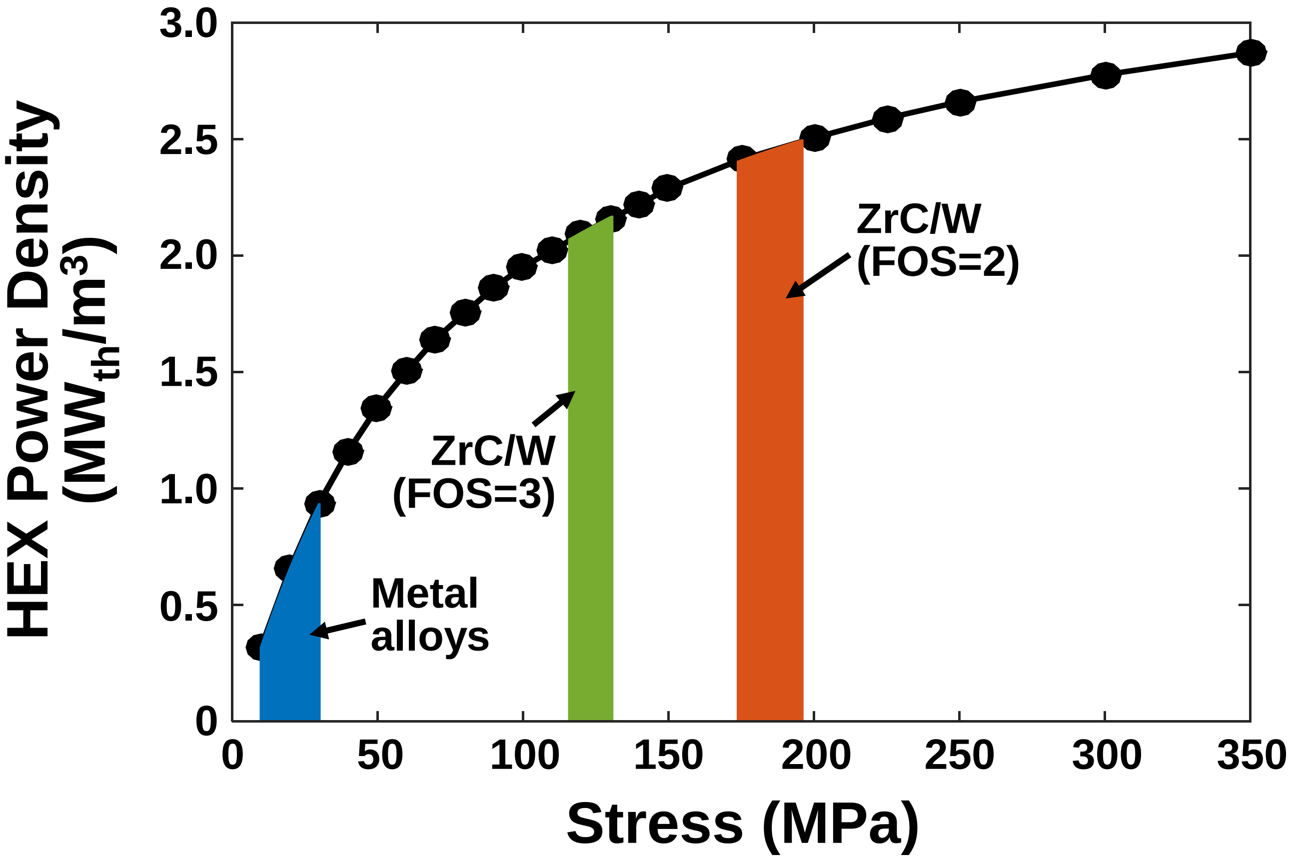
- In 1 year (3.15×10^{7} sec), the corresponding ZrC recession would be < 8.4 μm

Heat Exchanger Performance Simulation



For a 10 MW_e HEX operating with 95% effectiveness for heat transfer at a peak temperature of 800°C to sCO_2 (400,000 straight channels, semi-circular cross-section, 2 mm diameter, 2.5 m long)

Summary

- **Co-continuous ZrC/W composites possess an attractive and unusual combination of thermomechanical properties for high-temperature (≥750ºC) heat exchangers:**
  - **retention of stiffness and strength at elevated temperature (well above values for stainless steels and nickel-based alloys at ≥750ºC)**
  - **high toughness relative to monolithic ceramics**
  - **high thermal conductivity at elevated temperatures (greater than for SS, Ni-based alloys, and Hexoloy SiC)**
  - **modest thermal expansion coefficients for both ZrC and W (unlike for other ceramic/metal composites)**
  - **excellent thermal shock resistance (>10^3 ºC/sec Pi-K solid-fuel rocket tests)**

1. A. Henry, K. H. Sandhage, "Methods for Manufacturing Ceramic and Ceramic Composite Components and Components Made Thereby," *PCT/US Patent Application*, 2017; *US Provisional Patent Application*, 2016.

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Summary

- ZrC/W composites (and other oxidizable materials, including metal alloys) can be endowed with corrosion resistance in supercritical CO_2-based fluids via use of a new concept (PCT/U.S. Patent Application[1]):

  a supercritical buffered (reducing) CO/CO_2 fluid

- Cu:ZrC/W layered composites exhibited excellent resistance to corrosion after exposure for 1000 h to a flowing mixture of 50 ppm CO in CO_2 at 750°C and 20 MPa
- ZrC/W HEX plates with tailorable channels and internal headers can be fabricated by cost-effective forming and shape/size-preserving reactive conversion (DCP process)
- Simulations indicate that compact ZrC/W HEXs can operate with relatively high power densities for heat transfer to sCO_2 at 800°C

1. 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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Ongoing and Future Work

- Fabrication of high-temperature metallic alloy header/tube assemblies
- Diffusion bonding of metallic alloy header/tube assemblies to ZrC/W-based HEX plate stacks
- Setup of an 800^{o}C/20 MPa sCO_2 test loop (at the Georgia Institute of Technology)
- Evaluation of ZrC/W HEX performance in the 800^{o}C/20 MPa sCO_2 test loop
- Further testing of ZrC/W properties (thermomechanical, chemical) with DOE laboratory partners
- Development of scaled-up HEX fabrication processes (forming, reactive conversion, diffusion bonding) with manufacturing partners

Georgia Institute of Technology

Oak Ridge National Laboratory

Purdue University

Recent Publication

- **More details of this work can be found in the following recent journal publication:**

  "Ceramic-metal composites for heat exchangers in concentrated solar power plants," M. Caccia[#], M. Tabandeh-Khorshid[#], G. Itskos[#], A. R. Strayer[#], A. S. Caldwell, S. Pidaparti, S. Singnisai, A. D. Rohskopf, A. M. Schroeder, D. Jarrahbashi, T. Kang, S. Sahoo, N. R. Kadasala, A. Marquez-Rossy, M. H. Anderson, E. Lara-Curzio, D. Ranjan, A. Henry, K. H. Sandhage*, *Nature*, 562 (7727), 406-409 (2018).

  [#] These authors contributed equally.

  ***Correspondence and requests for materials should be addressed to K.H.S.**

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Questions?

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