Gen3 CSP Summit 2021

Robust, High-Temperature, Chloride Salt Heat Exchanger Materials

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Massachusetts Institute of Technology

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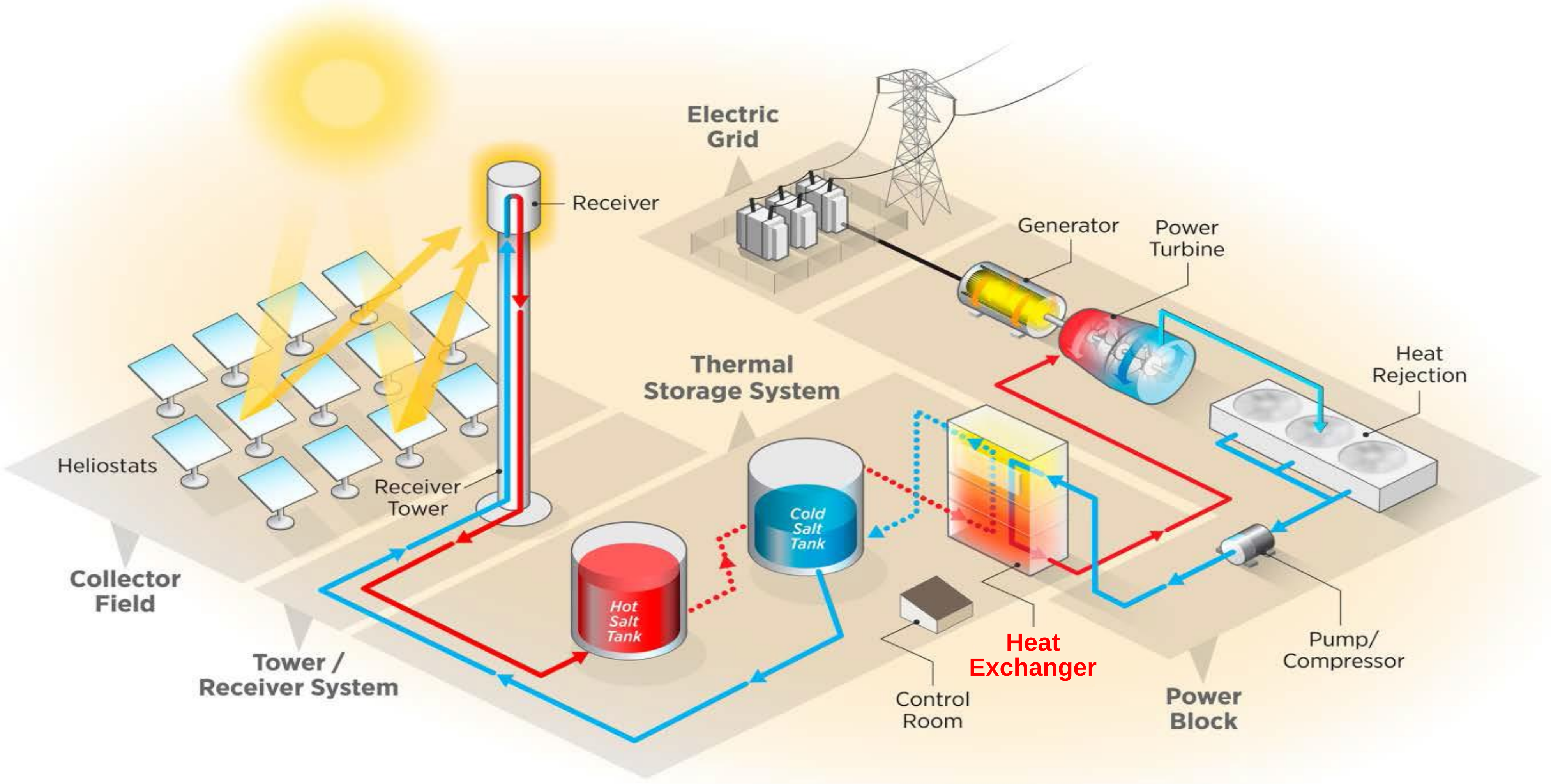
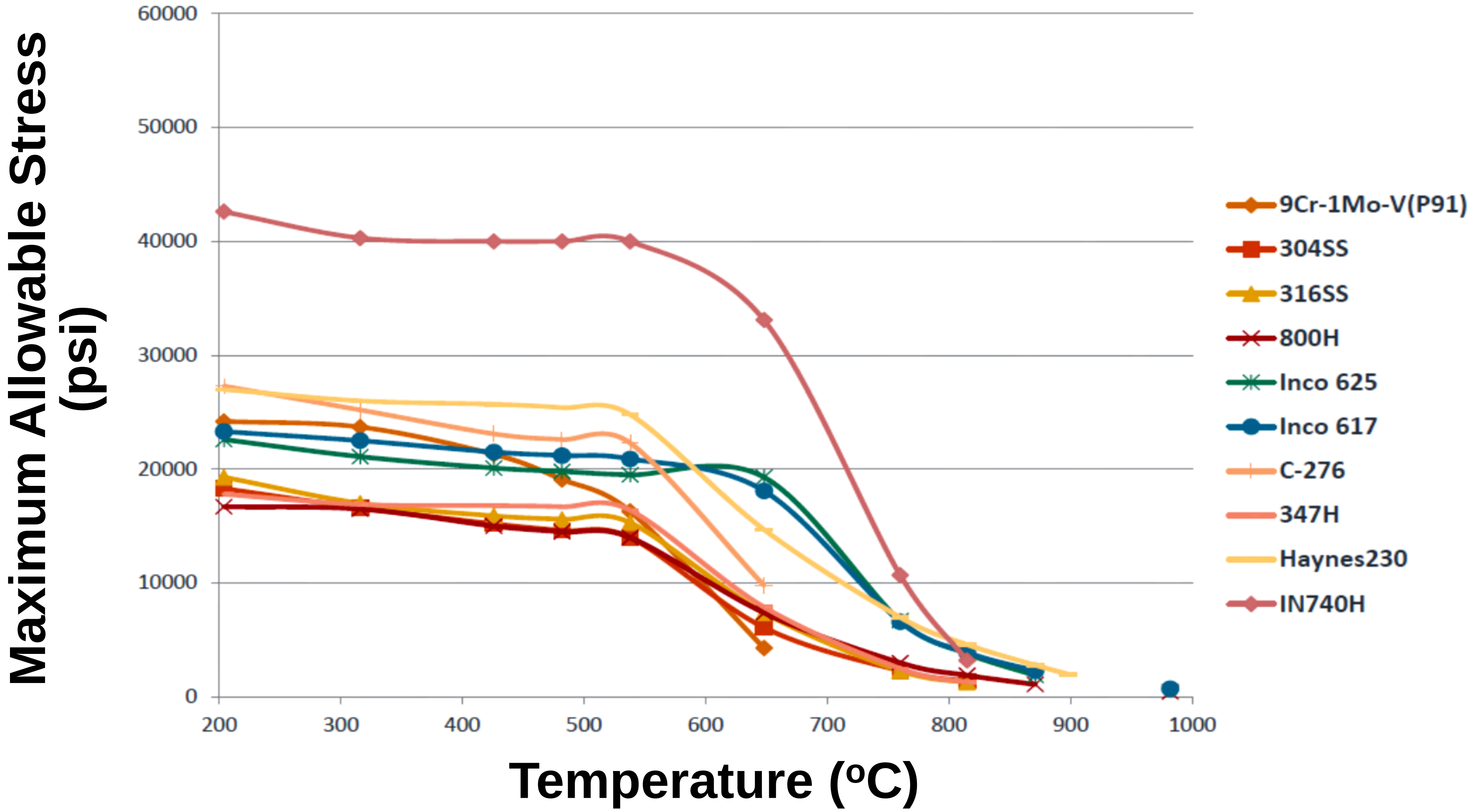
Power Tower Concept for Concentrated Solar Power



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

Temperature Limits of Metal Alloy Printed Circuit HEXs

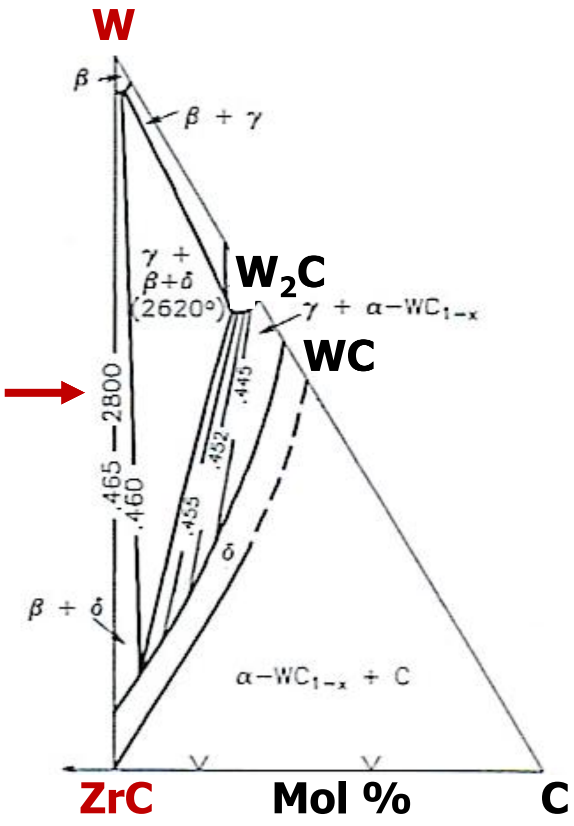


2010 ASME Boiler Pressure Vessel Code, Sec. II, from Tables 1A and 1B, July 1, 2010, New York, NY (compiled by Mark Anderson)

Attributes of ZrC/W-based Composites

◆ **Chemical compatibility at high temperatures**

(No new compounds form between ZrC and W[1])



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[1] V. N. Eremenko, T. Y. Velikanova, L. V. Artyukh, G. M. Aksel'rod, A. S. Vishnevskii, *Phase Diagrams for Ceramists*, Vol. X, C-W-Zr System (Fig. 9034), Ed. A. E. McHale, The American Ceramic Society, 1994.

Attributes of ZrC/W-based Composites

- **Chemical compatibility at high temperatures**
  (No new compounds form between ZrC and W)
- **Tailorable for corrosion resistance**
  (ZrC/W cermets have been found to be resistant to corrosion in dry, oxygen-purified $MgCl_2$ (31.9 mol%)-KCl-based salt at 750^{o}C in UHP Ar, with a projected recession of <12 μm/yr)

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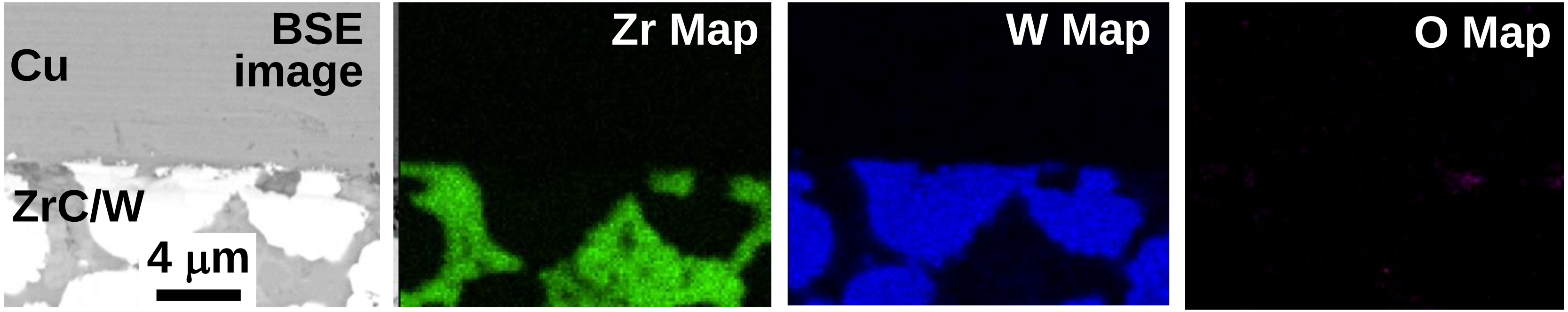

Cu:ZrC/W interface after 1000 h in 50 ppm CO in CO_2 at 750°C, 20 MPa[2]

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1. K. H. Sandhage, "Method for Enhancing Corrosion Resistance of Oxidizable Materials and Components Made Therefrom," *P.C.T./U.S. Patent Application*, 2017; *U.S. Provisional Patent Application*, 2016.
2. M. Caccia, M. Tabendeh-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, "Ceramic/Metal Composites for Heat Exchangers in Concentrated Solar Power Plants," *Nature*, 562 (7727) 406-409 (2018).

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- ◆ **High thermal conductivity at 800^{o}C**

  (κ = 66.0 W/m·K[1] vs. 22.1 W/m·K for IN740H[2] and $\leq$ 45 W/m·K for SiC[3-5])

1. M. Caccia, M. Tabendeh-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, "Ceramic/Metal Composites for Heat Exchangers in Concentrated Solar Power Plants," *Nature*, 562 (7727) 406-409 (2018).
2. http://www.specialmetals.com/files/PCC%20EG%20740H%20White%20Paper.pdf
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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◆ **Resistance to thermal cycling and thermal shock**

(at RT: CTE W = 4.5x10^{-6}/°C and CTE ZrC = 4.0x10^{-6}/°C; at 2700°C, CTE W = 9.2x10^{-6}/°C and CTE ZrC = 10.2x10^{-6}/°C; No σ_f reduction after 10 cycles from RT - 750°C)

1. Y. S. Touloukian, R. K. Kirby, R. K., R. E. Taylor, P. D. Desai, *Thermophysical Properties of Matter*. Vol. 12. Thermal Expansion of Metallic Elements and Alloys, Plenum Press, New York, NY, USA, 1975.
2. Y. S. Touloukian, R. K. Kirby, R. E. Taylor, T. Y. R. Lee, *Thermophysical Properties of Matter*. Vol. 13. Thermal Expansion of Nonmetallic Solids, Plenum Press, New York, NY, USA, 1977.
3. M. Caccia, M. Tabendeh-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, "Ceramic/Metal Composites for Heat Exchangers in Concentrated Solar Power Plants," *Nature*, 562 (7727) 406-409 (2018)
4. 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 ZrC/W-based rocket nozzle liners via the displacive compensation of porosity (DCP) method," *J. Mater. Sci.* 39, 6005-6015 (2004).

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- **High thermal conductivity at 800ºC**
  (κ = 66.0 W/m·K vs. 22.1 W/m·K for IN740H and ≤ 45 W/m·K for SiC)
- **Resistance to thermal cycling and thermal shock**
  (<u>at RT</u>: CTE W = $4.5x10^{-6}$/°C and CTE ZrC = $4.0x10^{-6}$/°C; <u>at 2700°C</u>, CTE W = $9.2x10^{-6}$/°C and CTE ZrC = $10.2x10^{-6}$/°C; No σ_f reduction after 10 cycles from RT - 750ºC)
- **Enhanced toughness w.r.t. conventional monolithic ceramics**
  (K_{1C} = 9.4±2.4 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[1-3])

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1. Y. W. Zhao, Y. J. Wang, X. Y. Jin, P. Jia, L. Chen, Y. Zhou, G. M. Song, J. P. Li, Z. H. Feng, "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).
2. W. D. Callister, *Materials Science and Engineering - An Introduction*, 6th Edn., John Wiley & Sons, 2003.
3. http://www.refractories.saint-gobain.com/hexoloy/hexoloy-grades

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- **Enhanced toughness w.r.t. conventional monolithic ceramics**
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- **High stiffness and retention of strength at 800°C**
  (E = 44±16 x10^3 ksi/305±110 GPa; σ_F = 87±7 ksi/598±51 MPa at 800°C)

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- **Enhanced toughness w.r.t. conventional monolithic ceramics**
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- **High stiffness and retention of strength at 800°C**
  (E = 44±16 $\times 10^3$ ksi/305±110 GPa; σ_F = 87±7 ksi/598±51 MPa at 800°C)
- **Cost-effective fabrication of ZrC/W-based HEX plates**

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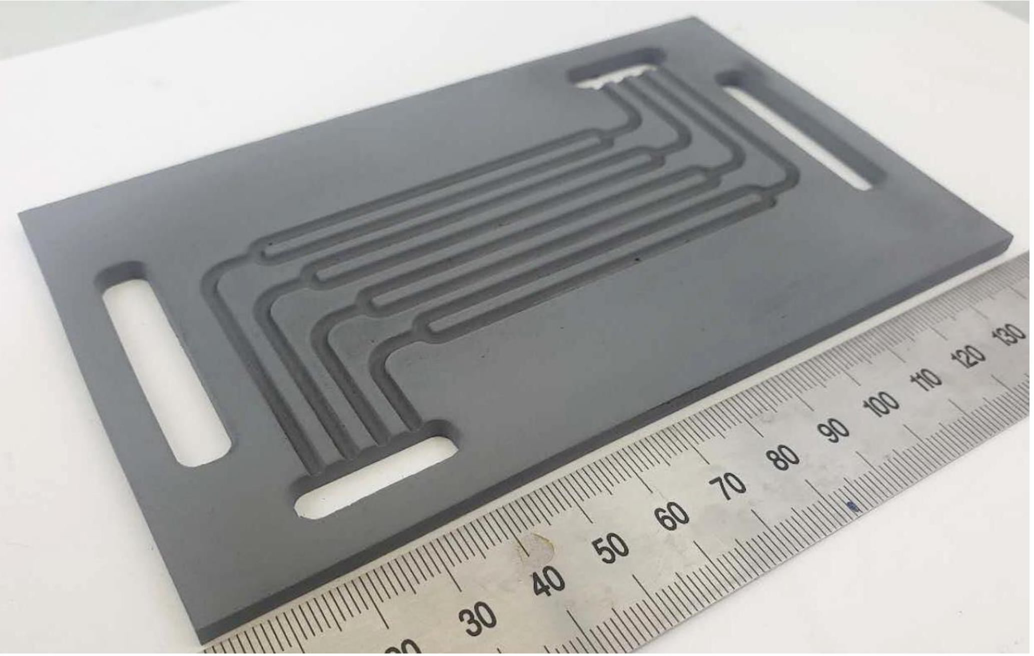
Fabrication of ZrC/W HEX Plates

Channeled Porous WC Preform Plate

Fabricate porous, channeled WC preform plates



Porous channeled WC preform plates (15 cm x 9 cm x 3 mm)
(pressing/stamping of WC/binder mixture, binder removal, light sintering)

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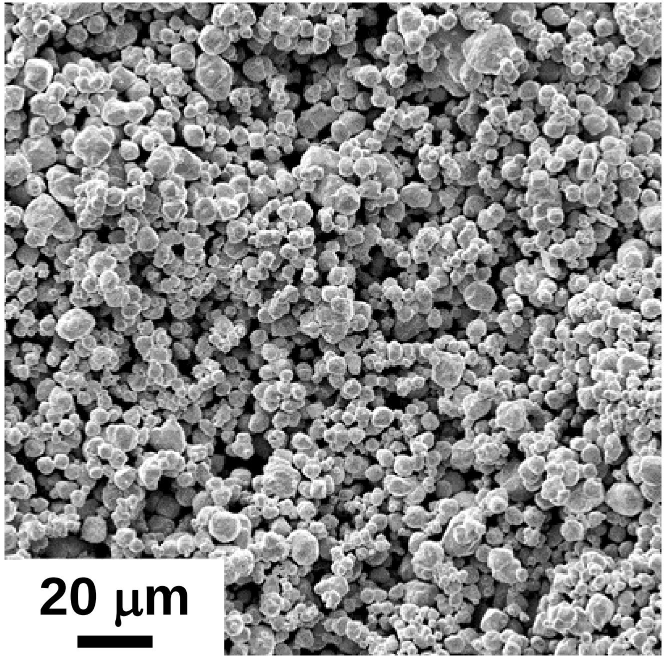

Secondary electron image of a fractured cross-section of a porous WC channeled preform plate

Porous channeled WC preform plates (15 cm x 9 cm x 3 mm) (pressing/stamping of WC/binder mixture, binder removal, light sintering)

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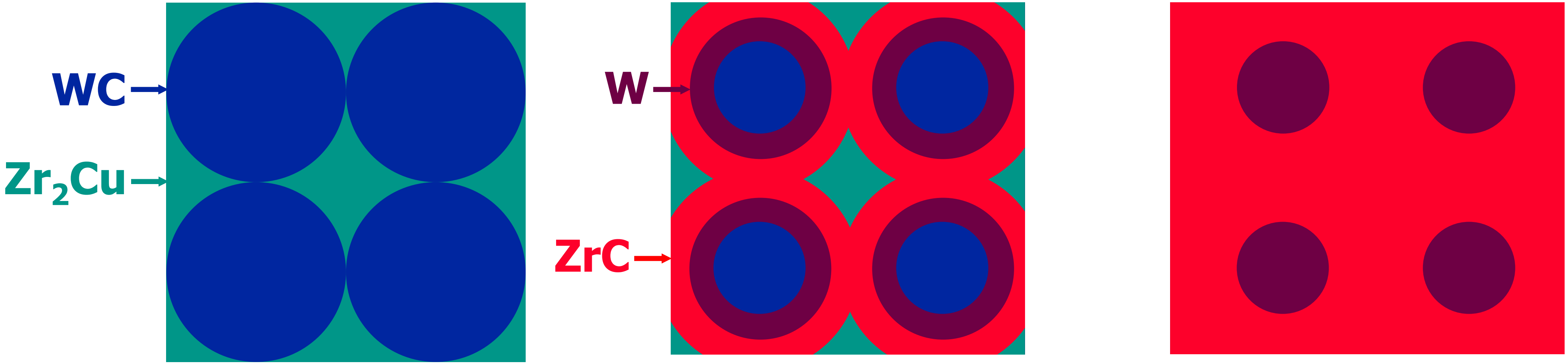
Displacive Compensation of Porosity (DCP) Process[1-3]

$$WC(s) + \tfrac{1}{2}Zr_2Cu(l) \Rightarrow ZrC(s) + W(s) + \tfrac{1}{2}Cu(l)$$

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



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

1. K. H. Sandhage, et al., *U.S. Patents* No. 6,833,337, 2004; No. 6,598,656, 2003; No. 6,407,022, 2002.
2. K. H. Sandhage, A. S. Henry, *U.S. Patent Appln.*, No. 16/094,262, 2017; *U.S. Provisional Patent Appln.*, 2016.
3. K. H. Sandhage, M. R. Caccia, *U.S. Patent Appln.*, No. 16/503,117, 2019; *U.S. Provisional Patent Appln.*, 2018.

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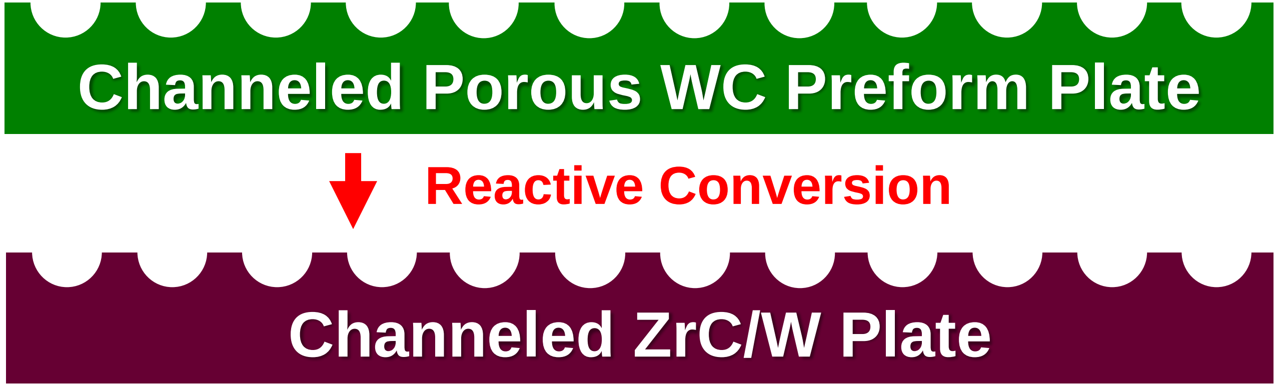
Fabrication of ZrC/W HEX Plates



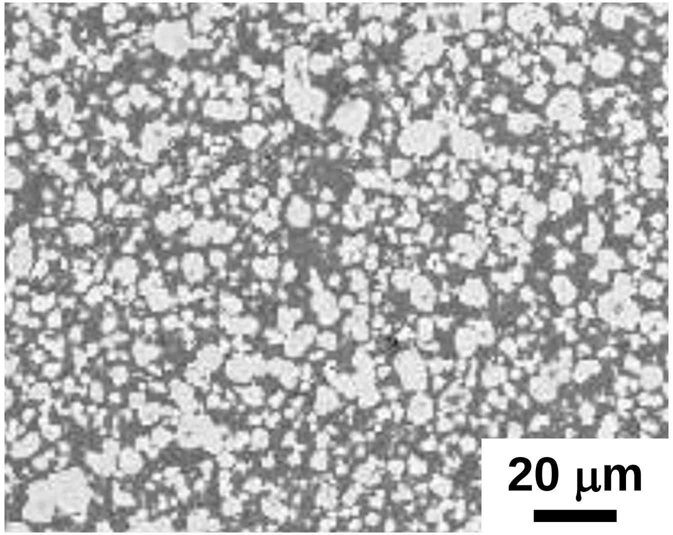
Channeled Porous WC Preform Plate

Reactive Conversion

Channeled ZrC/W Plate

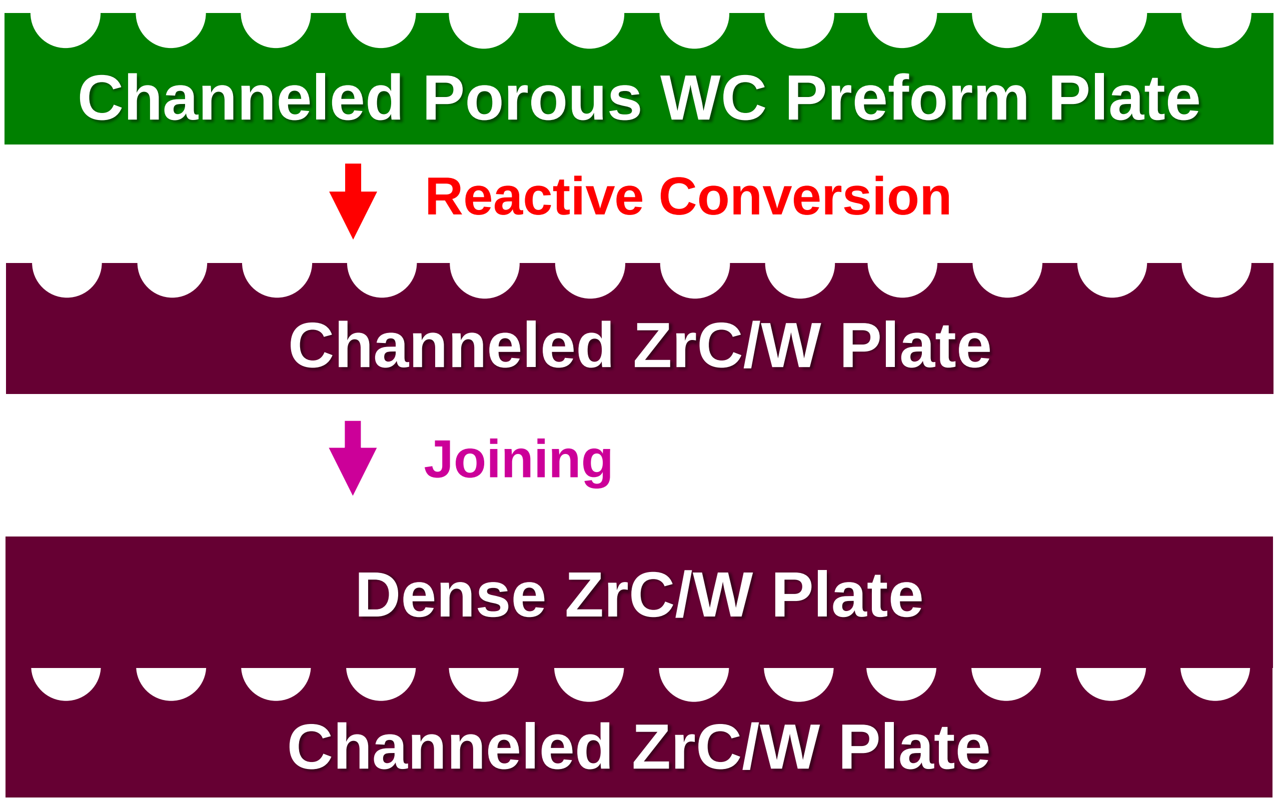
Fabricate porous, channeled WC preform plates

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



Backscattered electron image of a polished cross-section of a dense, ZrC/W channeled plate

Fabrication of ZrC/W HEX Plates



Channeled Porous WC Preform Plate

Reactive Conversion

Channeled ZrC/W Plate

Joining

Dense ZrC/W Plate

Channeled ZrC/W Plate

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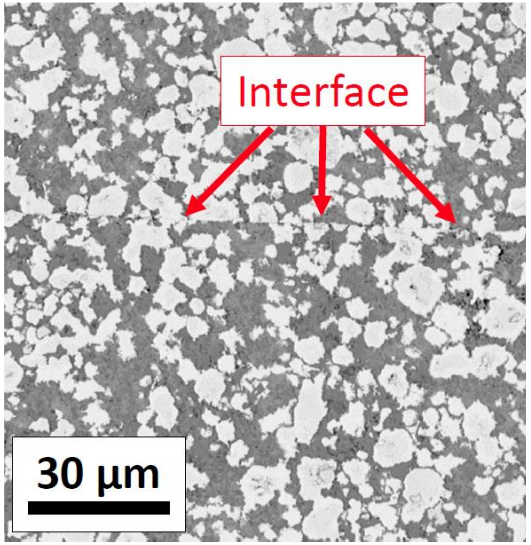
Generate dense, net-size channeled ZrC/W plates via the DCP process



BSE image of a diffusion-bonded ZrC/W plate pair (1600ºC, 2 h, 10 MPa)

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Summary and Ongoing Work

◆ **ZrC/W-based cermets provide an unusual and attractive combination of high-temperature mechanical and thermal properties relative to Fe- and Ni-based alloys**

◆ **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[1,2]:**

a supercritical buffered (reducing) CO/CO_2 fluid

1. K. H. Sandhage, "Method for Enhancing Corrosion Resistance of Oxidizable Materials and Components Made Therefrom," *P.C.T./U.S. Patent Application*, 2017; *U.S. Provisional Patent Application*, 2016.
2. M. Caccia, M. Tabendeh-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, "Ceramic/Metal Composites for Heat Exchangers in Concentrated Solar Power Plants," *Nature*, 562 (7727) 406-409 (2018).

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- **ZrC/W-based cermets provide an unusual and attractive combination of high-temperature mechanical and thermal properties relative to Fe- and Ni-based alloys**
- **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:**

a supercritical buffered (reducing) CO/CO_2 fluid

- **Scalable, 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**
- **Diffusion bonding of ZrC/W plates, and brazing of Cu to Ni alloy headers, can provide high-pressure seals for use with sCO/CO_2-bearing fluids at 720ºC**

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Attributes of Al_2O_3/Cr-based Composites

- **Chemical compatibility at high temperatures**

  (Al_2O_3 and Cr do not undergo a displacement rxn; $T_m[Al_2O_3]$ = 2054°C; $T_m[Cr]$ = 1863°C)

- **Creep resistance**

  (Al_2O_3 is quite creep resistant at 750°C; cermets with a continuous Al_2O_3 matrix have exhibited negligible creep at 1000°C, 20 MPa)

- **Failure strength and toughness**

  (Four-point-bend σ_F (64 vol% Al_2O_3/36 vol% Cr) = 47×10^3 psi/320 MPa at 750°C; K_{1C} = 7.2 $MPa \cdot m^{1/2}$ at RT)

- **Thermal expansion match**

  ($100 \cdot \Delta L/L_o$ from 25°C to 750°C: Cr = 0.71%, Al_2O_3 = 0.63%)

- **Thermal conductivity**

  (ROM κ(64 vol% Al_2O_3/36 vol% Cr) = 28 W/m-K at 750°C vs. 23.4 W/m-K for H230)

- **Oxidation resistance**

  (slow parabolic kinetics at 750°C in CO_2 and air[1])

[1] T. D. Nguyen, M. Caccia, C. K. McCormack, G. Itskos, K. H. Sandhage, "Corrosion of Al_2O_3/Cr and Ti_2O_3/Cr Composites in Flowing Air and CO_2 at 750°C," *Corros. Sci.*, 179, 109115-1 to 109115-12 (2021)

Acknowledgements

- **This work has been supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), Solar Energy Technologies Office (SETO) under Awards Number DE-EE0008369, DE-EE0008527, and DE-EE0008998**
- **Matching support has also been provided by Purdue University and the Massachusetts Institute of Technology**