What Universities Can Do To Help Make sCO_2 a Commercial Reality?

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Exploration of Robust, High-Temperature Ceramic Composites

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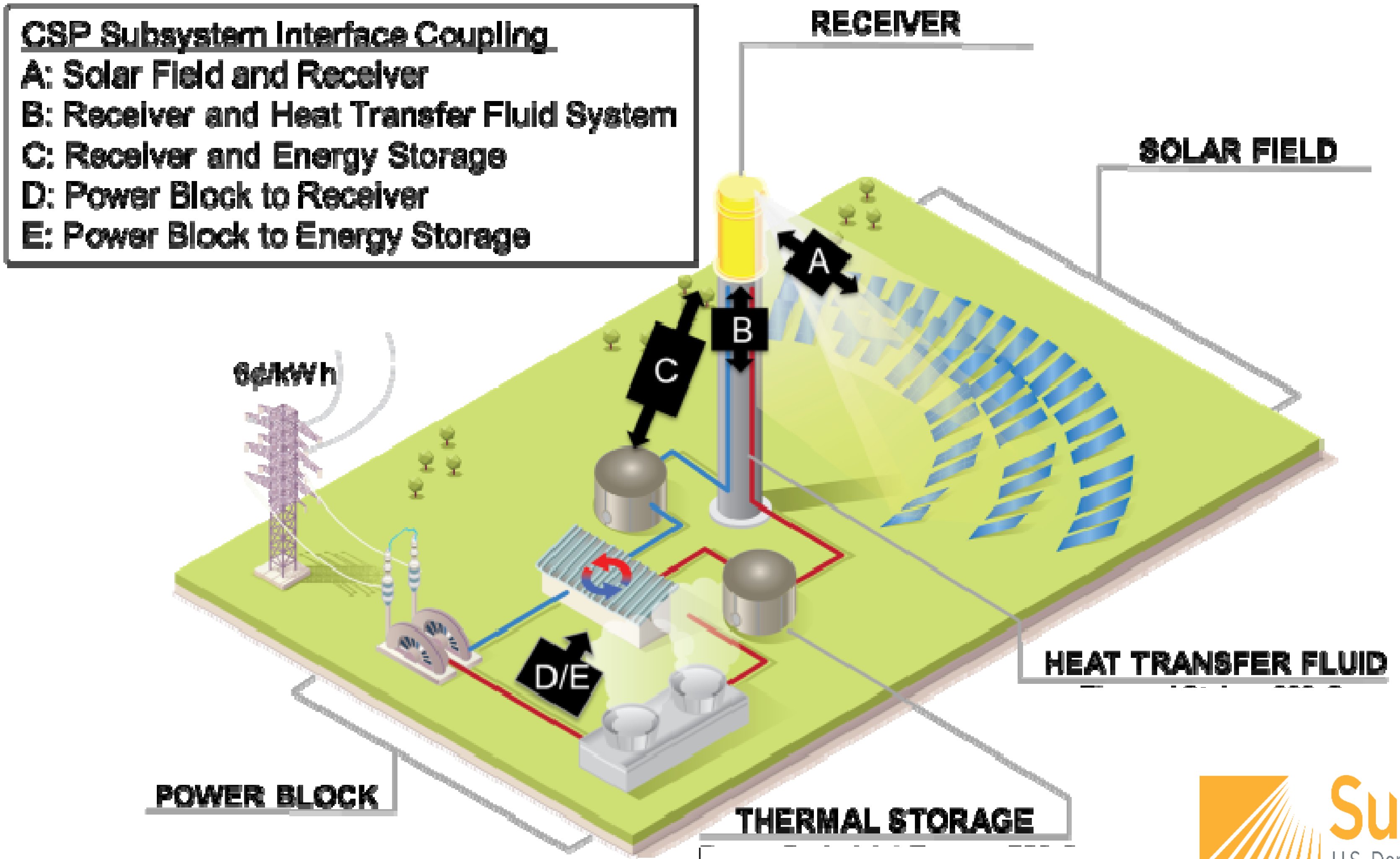
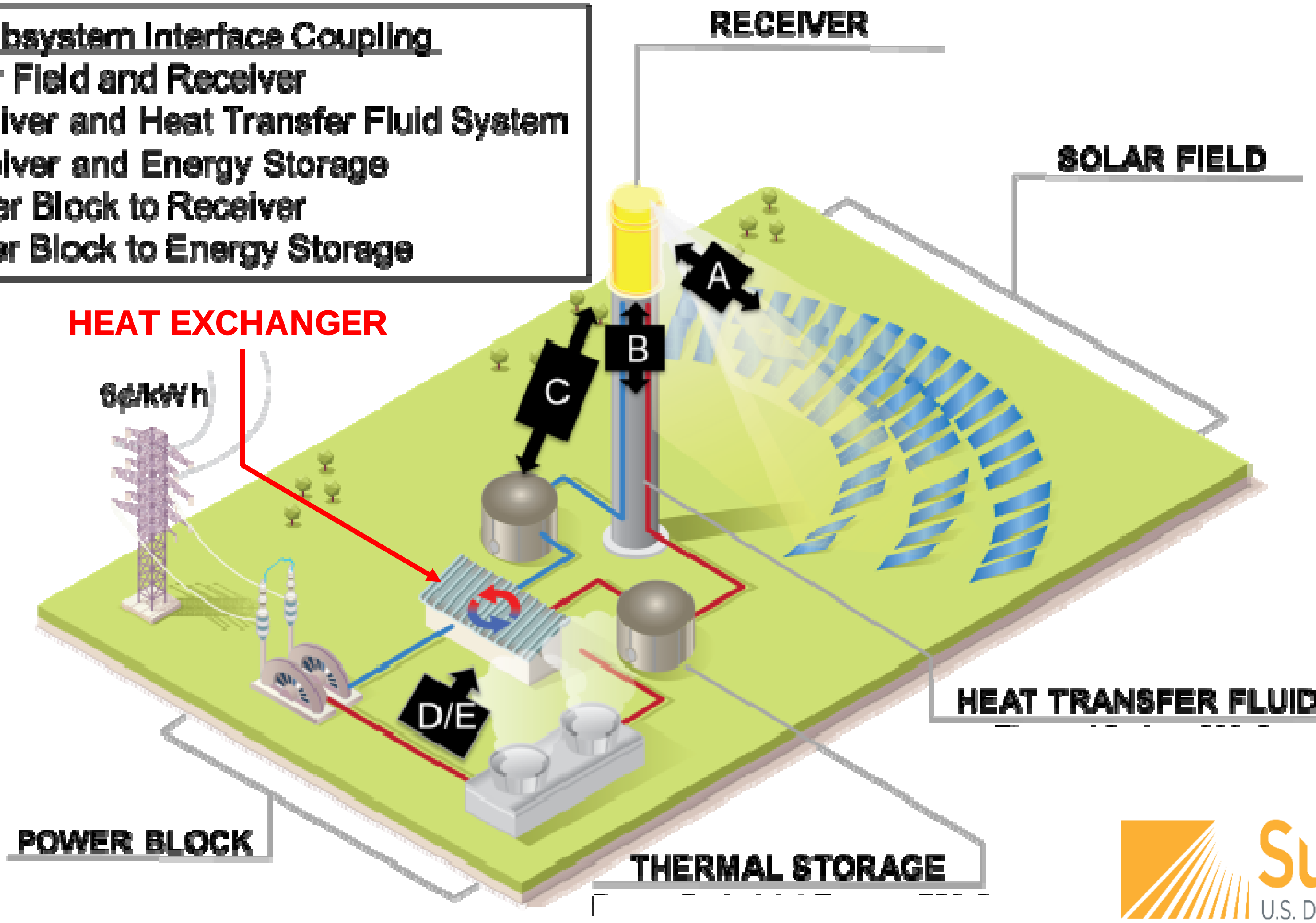
Concentrated Solar Power Tower



SunShot
U.S. Department of Energy

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



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Some Limitations of Fe-, Ni-based Alloys

- **Modest melting points**
  (T$_{Solidus}$ ≤ 1400°C for IN617/Ni-Cr-Co-Mo[1], IN740H/Ni-Cr-Co[2], 304SS/Fe-Cr-Ni-Mn[3], 316SS/Fe-Cr-Ni-Mo-Mn[4])
- **Significant strength decline at >650°C**
  (10,000 h rupture strength decreases from 345 MPa at 600°C to 116 MPa at 760°C to 69 MPa at 815°C for IN617[1])

1. http://www.specialmetals.com/assets/smc/documents/alloys/inconel/inconel-alloy-617.pdf.
2. http://www.specialmetals.com/assets/smc/documents/alloys/inconel/inconel-alloy-740-h.pdf
3. http://asm.matweb.com/search/SpecificMaterial.asp?bassnum=mq304a
4. http://asm.matweb.com/search/SpecificMaterial.asp?bassnum=mq316a
5. 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, 1975.

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- **Modest thermal conductivities at 800°C**
  (at 800°C, κ = 25.6 W/m-K for IN617[1], 22.1 W/m-K for IN740H[2], 26.3 for 304SS[5], and 23.4 W/m-K for 316SS[5])

1. http://www.specialmetals.com/assets/smc/documents/alloys/inconel/inconel-alloy-617.pdf.
2. http://www.specialmetals.com/assets/smc/documents/alloys/inconel/inconel-alloy-740-h.pdf
3. http://asm.matweb.com/search/SpecificMaterial.asp?bassnum=mq304a
4. http://asm.matweb.com/search/SpecificMaterial.asp?bassnum=mq316a
5. 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, 1975.

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- **Photochemical etching of channel patterns can be a relatively slow and expensive process for mass production of standardized patterns**
  (compared to fast forming processes, such as stamping[6-8])

6. D. M. Allen, "Photochemical Machining: From "Manufacturing's Best Kept Secret" to a $6 Billion per Annum, Rapid Manufacturing Process," *CIRP Ann.*, 53 (2) 559-572 (2004).
7. D. M. Allen, H. J. A. Almond, F. Gaben, S. Impey, "The Causes and Prevention of Smut on Etched AISI 300 Stainless Steels," *CIRP Ann.*, 54 (1) 187-190 (2005).
8. P. N. Rao, D. Kunzru, "Fabrication of Microchannels on Stainless Steel by Wet Chemical Etching," *J. Micromech. Microeng.*, 17, N99-N106 (2007).

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Some Limitations of Monolithic Ceramics

- **Modest fracture toughness**
  (K_{1C} = 3 MPa·m$^{1/2}$ for $\geq$ 95% dense, 7 μm (ave.) $Al_6Si_2O_{13}$ (mullite)[1]; 3-5 MPa·m$^{1/2}$ for $\geq$ 90% dense, 4-8 μm Al_2O_3[2]; 3.9-4.6 MPa·m$^{1/2}$ for $\geq$ 94% dense, 4-10 μm Hexoloy SiC[3])

1. Superior Technical Ceramics, https://www.ceramics.net/sites/default/files/files/Mullite%20Material%20Property%20Chart%201page.pdf.
2. CoorsTek, https://www.coorstek.com/media/1715/advanced-alumina-brochure.pdf
3. Saint-Gobain Ceramic Materials, https://www.refractories.saint-gobain.com/sites/imdf.hpr.com/files/hexoloy-norbide-noralide-alnimax-products-en-1027-bro.pdf

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- **Low-to-modest thermal conductivity at 800°C**
  (κ $\leq$ 4 W/m-K for $\geq$ 89% dense $Al_6Si_2O_{13}$[4,5], $\leq$ 7 W/m-K for $\geq$ 92% dense polycrystalline Al_2O_3[5], $\leq$ 45 W/m-K for dense sintered polycrystalline SiC[6])
- **Poor-to-fair thermal shock resistance**
  (Al_2O_3 and $Al_6Si_2O_{13}$ are worse than SiC[7,8])

4. B. Hildmann, H. Schneider, "Thermal Conductivity of 2/1-Mullite Single Crystals," *J. Am. Ceram. Soc.*, 88 (10) 2879-2882 (2005).
5. W. D. Kingery, J. Francl, R. L. Coble, T. Vasilos, "Thermal Conductivity: X, Data for Several Pure Oxide Materials Corrected to Zero Porosity," *J. Am. Ceram. Soc.*, 37 (2) 107-110 (1954).
6. L. Sigl, "Thermal Conductivity of Liquid Phase Sintered Silicon Carbide," *J. Euro. Ceram. Soc.*, 23, 1115-1122 (2003).
7. H. Wang, R. N. Singh, "Thermal Shock Behavior of Ceramics and Ceramic Composites," *Int. Mater. Rev.*, 39 (6) 228-244 (1994).
8. W. D. Kingery, "Factors Affecting Thermal Stress Resistance of Ceramic Materials," *J. Am. Ceram. Soc.*, 38 (1) 3-15 (1955).

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- **Poor-to-fair thermal shock resistance**
  (Al_2O_3 and $Al_6Si_2O_{13}$ are worse than SiC[7,8])
- **Fabrication of dense ceramics in complex, tailorable, and precise shapes is non-trivial and can be expensive**
  (high firing temperatures; sintering shrinkage and distortion[9])

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9. A. Sommers, Q. Wang, X. Han, C. Tjoen, Y, Park, A. Jacobi, "Ceramics and Ceramic Matrix Composites for Heat Exchangers in Advanced Thermal Systems - A Review," *Appl. Thermal Eng.*, 30, 1277-1291 (2010).

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Ceramic/Metal Composites:

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    (ave. linear CTEs for RT-1000°C: 16.3×10^{-6}/°C for IN617/Ni-Cr-Co-Mo, 9.0×10^{-6}/°C for Al_2O_3; 4.8×10^{-6}/°C for SiC)

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  - **thermal conductivities**
- **Mechanical compatibility**
  (continuity of ceramic phase for high-temperature stiffness and creep resistance; high metallic content for toughness)
- **Cost-effective processing capable of generating complex, tailorable, and precise shapes**
  (*liquid metal processing*: poor wetting of the ceramic by the liquid metal, metal melting temperature; *powder processing*: high sintering temperatures, shrinkage and distortion)

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Robust Cost-Effective ZrC/W Composites

- **High melting point and chemical compatibility**
  (Tie line between ZrC and W, limited mutual solubility, $T_{Solidus}$ = 2,800°C)

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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, 23.4 W/m-K for 316SS, 26.3 W/m-K for 304SS, $\leq$ 45 W/m-K for SiC)

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- **Retention of stiffness and strength at 800°C**
  (E $\geq$ 28x10^6 psi/193 GPa; $\sigma_F \geq$ 50x10^3 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. $\leq$ 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)

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- **Formable porous preforms, net-shape/size reactive conversion process**
  (pressing, green machining, 3-D printing, stamping, casting; pressureless reactive melt infiltration at $\leq$ 1350°C)

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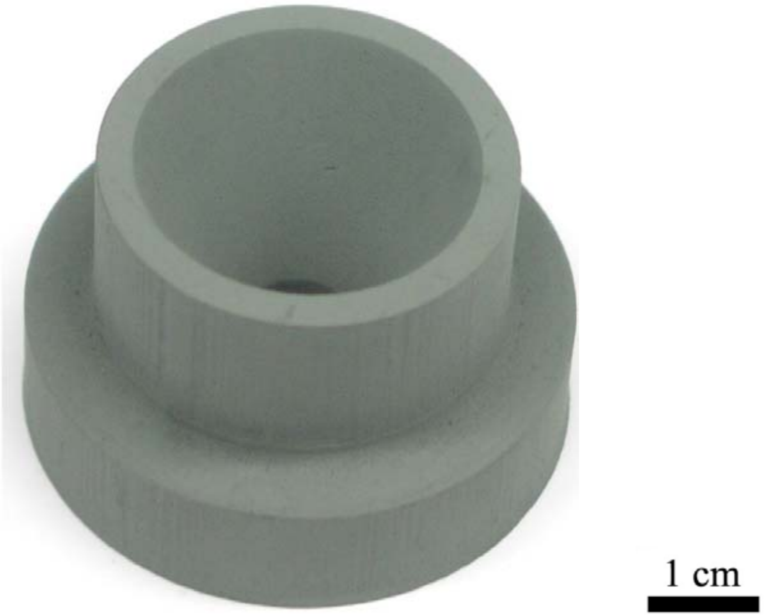
Near Net-Shape/Net-Size Reactive Conversion



CNC-Machined 50% Porous WC Nozzle

CNC Machining of a Porous WC Preform

Model 7300 Prototyping and Production Mill
(Flashcut CNC, Deerfield, IL)

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3-D Printing of a Porous WC Preform

Model 310 3-D Printer, Z-Corp., Burlington, MA

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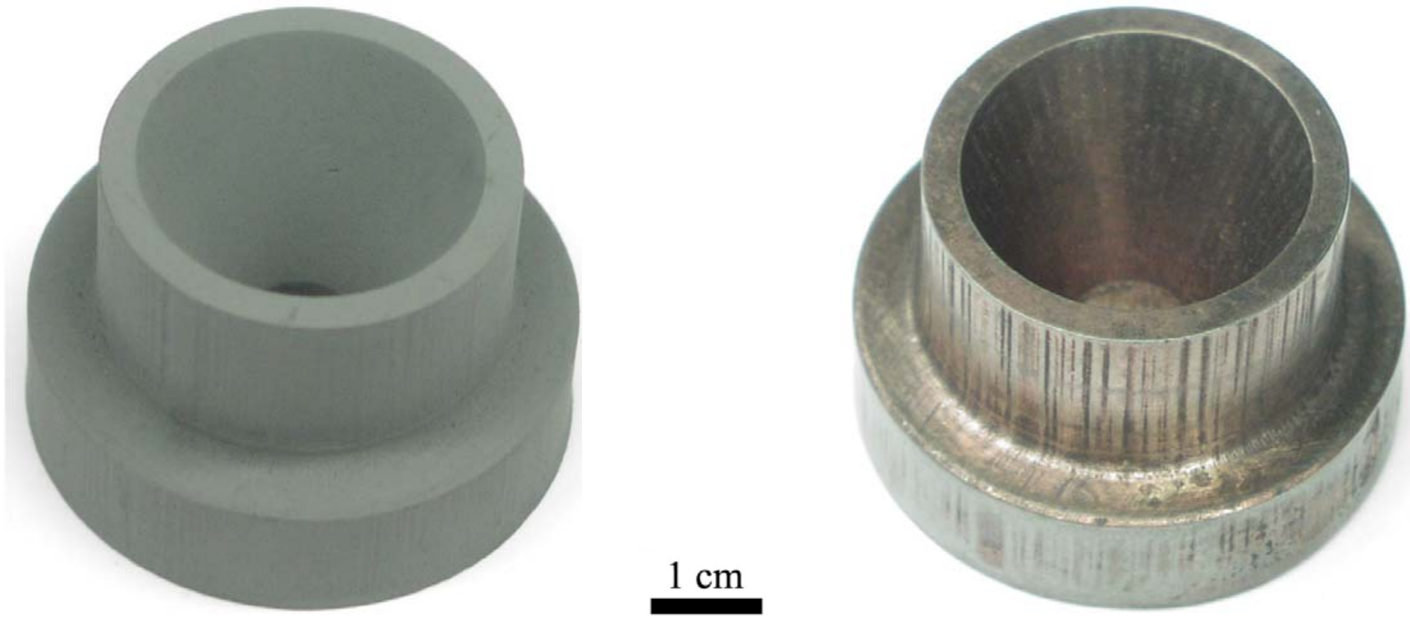
Near Net-Shape/Net-Size Reactive Conversion



CNC-Machined 50%
Porous WC Nozzle

Dense ZrC/W Nozzle

Shape- and size-preserving reactive melt infiltration:

WC + {Zr} => ZrC + W

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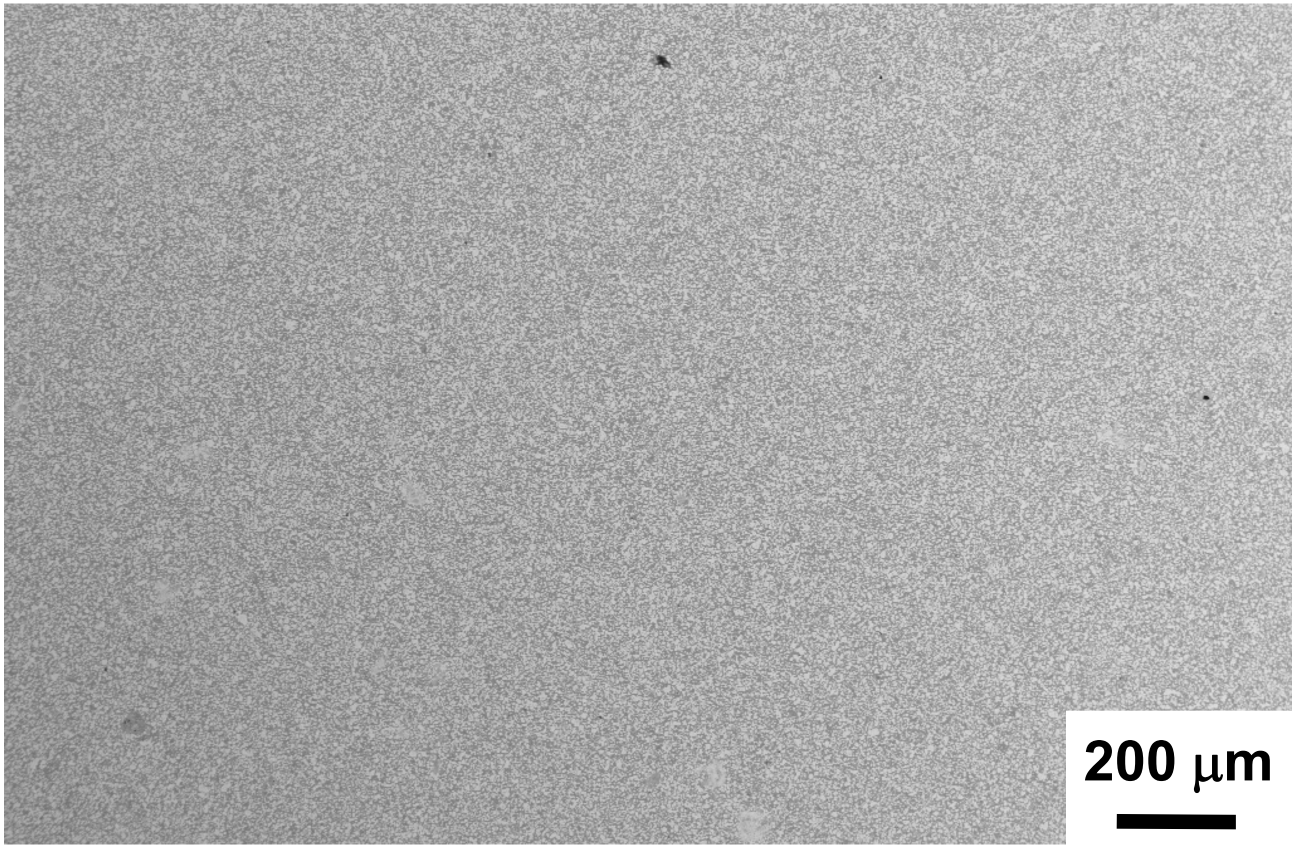
Dense DCP-derived ZrC/W Composite



Backscattered electron images

Polished cross-section of a dense, reactively-converted ZrC/W composite

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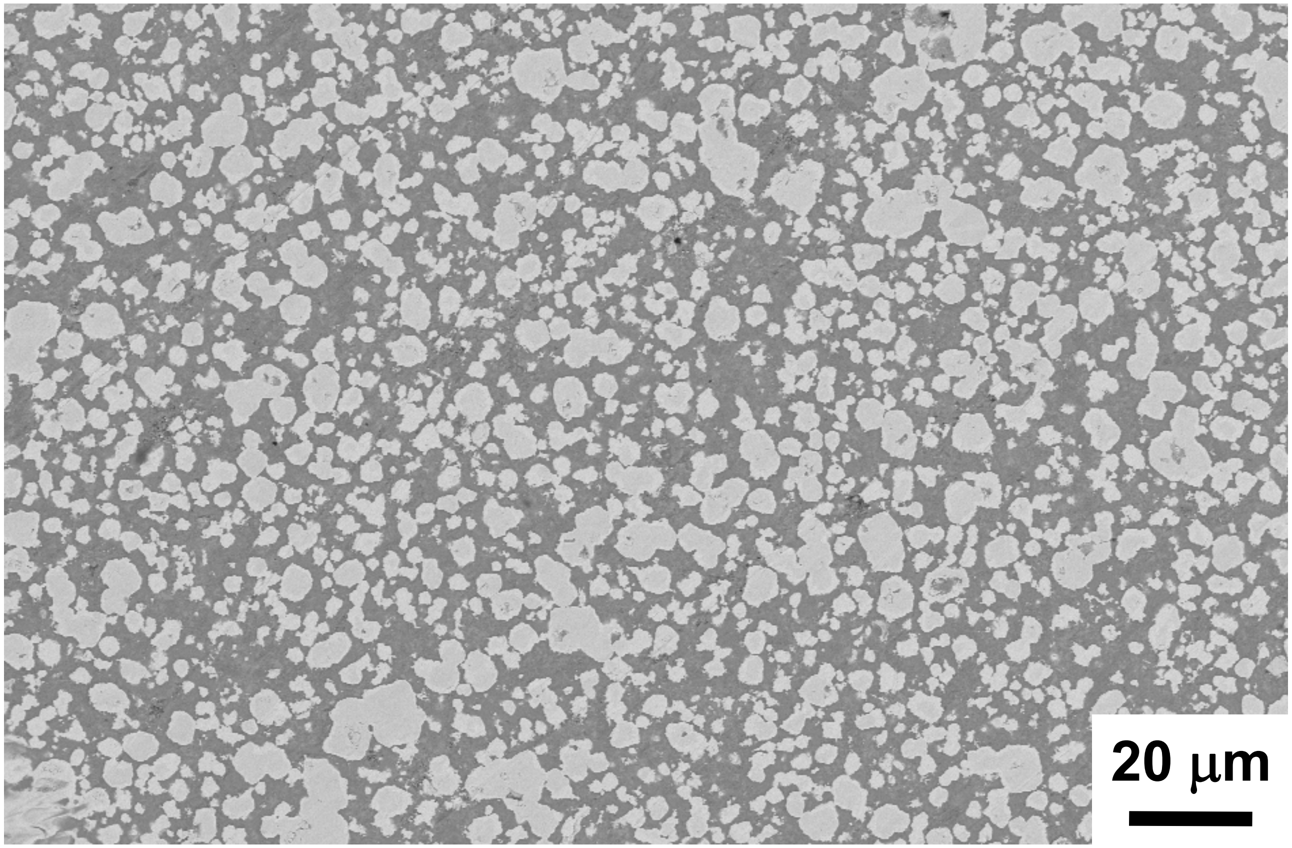
Dense DCP-derived ZrC/W Composite



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Polished cross-section of a dense, reactively-converted ZrC/W composite

Near Net-Shape/Net-Size Reactive Conversion

1 cm

Specimen	Nozzle Exit Outer Diameter	Nozzle Entrance Outer Diameter	Nozzle Height
WC Preform (left)	50.65±0.09 mm	37.50±0.08 mm	32.13±0.22 mm
ZrC/W Nozzle (right)	50.32±0.16 mm	37.23±0.07 mm	32.00±0.30 mm
	$\Delta D/D_o$: -0.6±0.1%	$\Delta D/D_o$: -0.7±0.1%	$\Delta H/H_o$: -0.4±0.2%

Solid Fuel Rocket Nozzles

- **Temperatures in excess of 2500^{o}C within 1 sec**
- **Al_2O_3(l) and gas products traveling at supersonic speeds ($\geq$2,500 m/s)**
- **New materials that are:**
  - **high melting**
  - **thermal shock resistant**
  - **erosion resistant**
  - **lightweight**
  - **non-porous**
  - **inexpensive (raw material, nozzle fabrication)**

  are needed

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Gel Casting of Porous WC Preforms

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Gel Casting of Porous WC Preforms

Gel Casting of Porous WC Preforms

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Rigid, Porous WC Nozzle Insert Preforms

Dense ZrC/W-based Rocket Nozzle Inserts

($\Delta D/D_o$ = -0.4% $\pm$ 0.2%:
9.65 to 9.63 cm, 3.05 to 3.03 cm)

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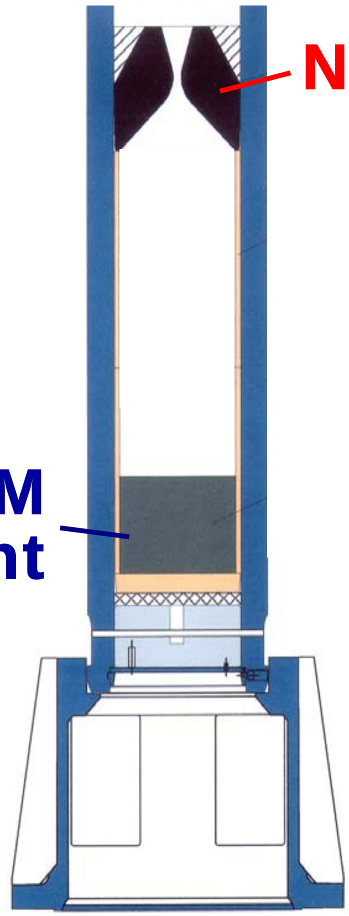
Pi-K Rocket Nozzle Test (Edwards AFB)



(19 wt% Al propellant,
burn pressure = 3.5 MPa)

(with Wes Hoffman, EAFB)

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Pi-K Rocket Nozzle Test (Edwards AFB)

(19 wt% Al propellant, burn pressure = 3.5 MPa)

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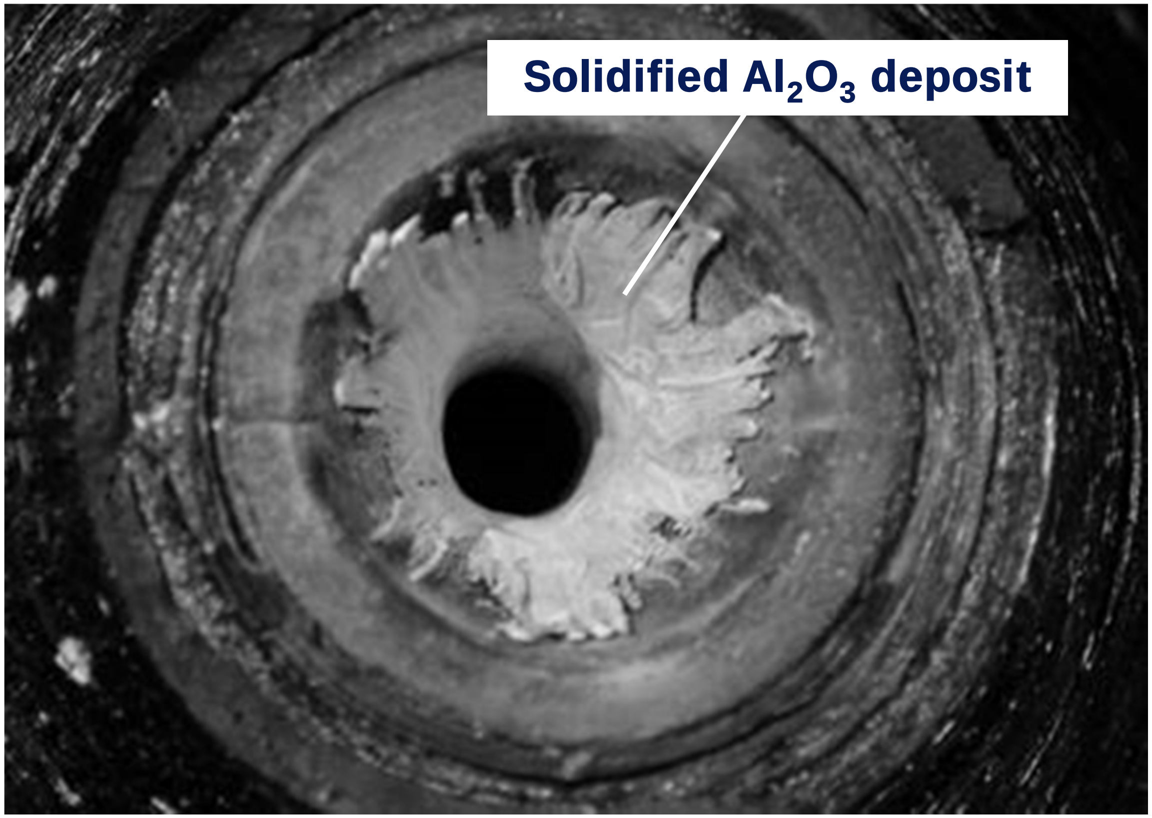
Pi-K Rocket Nozzle Test (Edwards AFB)



Top-down view into ZrC/W nozzle after the Pi-K rocket test

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Future sCO_2/Cermet Research (University+)

- **Design and fabrication of robust net-shape/net-size cermet components tailored for other sCO_2 systems**
  (collaborative research for nuclear, natural gas, other power systems)

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- **Further thermomechanical testing, and coding, of high-temperature cermets**
  (with National Laboratory, industry, and government partners)

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- **Interface design and integration of high-temperature cermets components with structural metal alloys**
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  (chemical/structural tailoring of robust interfaces; development of bonding methods)
- **Scaleup of cermet component manufacturing and systems testing**
  (forming, reactive conversion, bonding; with product development, manufacturing, and application partners)

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Processing and Properties of Robust Ceramic/Metal Composites for Heat Exchangers Operating at ≥750°C with Supercritical CO_2

Mario Caccia[1], Meysam Tabandeh-Khorshid[1], Grigoris Itskos[1], Alex R. Strayer[1], Adam S. Caldwell[1], Sandeep Pidaparti[2], Supattra Singnisai[1], Andrew D. Rohskopf[2], Anthony M. Schroeder[3], Andres M. Rossy[4], Dorrin Jarrahbashi[2], Taegyu Kang[2], Seshadev Sahoo[1], Ioanna Itskou[1], Edgar Lara-Curzio[4], Mark H. Anderson[3], Asegun Henry[2], Devesh Ranjan[2], Kenneth H. Sandhage[1]

[1] *School of Materials Engineering, Purdue University, W. Lafayette, IN USA*
[2] *School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA USA*
[3] *Department of Engineering Physics, University of Wisconsin, Madison, WI USA*
[4] *Division of Materials Science and Technology, Oak Ridge National Laboratory, Oak Ridge, TN USA*

Questions?

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High-Temperature Corrosion Resistance to sCO_2

- Oxidizable materials (e.g., ZrC/W, stainless steels or other metal alloys) can be endowed with enhanced high-temperature oxidation resistance in sCO_2-based fluids via use of a new concept (PCT/U.S. Patent Appln[1]):

a supercritical buffered (reducing) CO-CO_2 fluid

- Modest CO additions to CO_2 can dramatically lower the equilibrium oxygen fugacity, f_{O_2}, of the CO_2-based fluid:

$$2CO + O_2 = 2CO_2$$

$\Rightarrow$ the addition of just 10 ppm CO in CO_2 at 750°C yields an equilibrium $f_{O_2} = 1.7 \times 10^{-10}$ atm (1 atm total pressure)[2]

- Relatively noble metals, such as copper, can be rendered inert in sCO/CO_2 fluids with modest CO contents

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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