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Ultra-High Temperature Thermal and Mechanical Properties of ZrB2-Based Ceramics

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Ultra-High Temperature Thermal and Mechanical Properties of ZrB_2-Based Ceramics

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Ultra-High Temperature Ceramics:
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Goals and Outline

- **Goals**
  - **Understand the role of impurities (i.e., C), additives (i.e., SiC), isotopes (^{10}B or ^{11}B in ZrB_2) on the thermal and mechanical properties of ZrB_2 based ceramics**

- **Outline**
  - **Thermal Conductivity of ZrB_2-based Ceramics**
    - **Historical studies vs. modern research studies**
    - **Missouri S&T studies – Thermal conductivity to 2000ºC+**
  - **Flexure Strength of ZrB_2-based Ceramics**
    - **Historical studies vs. modern research studies**
    - **Missouri S&T studies – Annealing; Flexure strength to 2300ºC+**
  - **Conclusions**

Thermal Conductivity of ZrB_2-Based UHTCs

Literature– ZrB_2 Thermal Conductivity

Reference	Year	Relative Density (%)	Test Temperatures (° C)	Special Considerations
Tye and Clougherty[1]	1970	100	100-1000	-
Tye and Clougherty[1]	1970	90	100-1000	"fluid energy milled"
Branscomb and Hunter[2]	1971	97.4	200-1300	0.92% impurity content
Fridlender et al.[3]	1980	92	1000-2200	vibrogrinding (60hrs)
Andrievskii et al.[4]	1980	95	100-900	-
Zimmermann et al.[5]	2008	100	25-1327	attrition milled w/WC
Zhang et al.[6]	2011	92.5	25-427	reaction processed (Zr+B)
Thompson et al.[7]	2012	100	400-2000	attrition milled w/WC

[1] Tye and Clougherty, *Proceeding of the Fifth Symposium of Thermophysical Properties,* 396-401, 1970

[2] Branscomb and Hunter*, Journal of Applied Physics*, 42, 2309-2315, 1971

[3] Fridlender, Neshpor, Ordan'yan, and Unrod, *Teplofizika Vysokikh Temperatur*, 17, 1210-1215, 1980

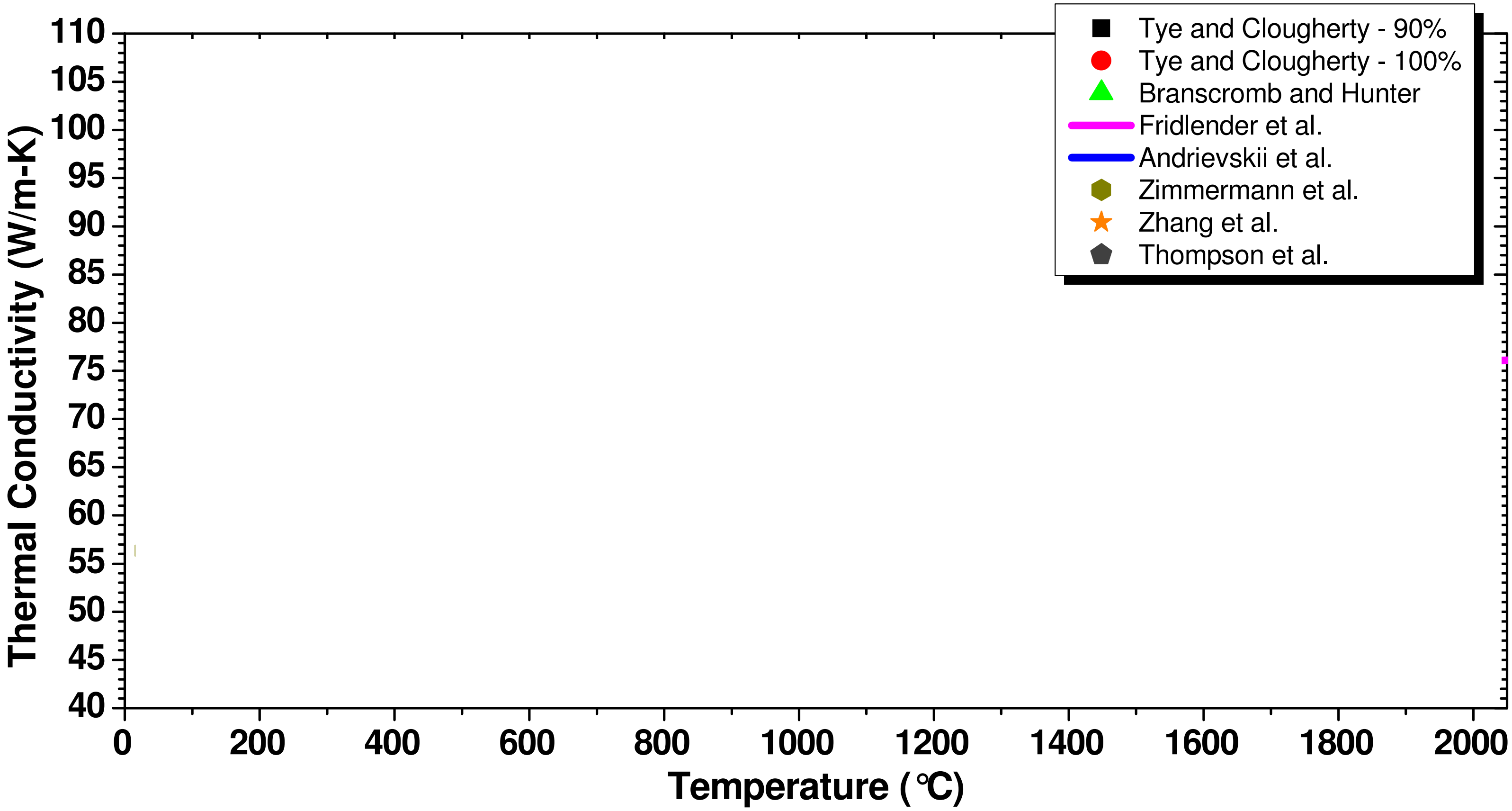
[4] Andrievskii, et al., *Soviet Powder Metallurgy and Metal Ceramics*, Vol 19(2), 27-29, 1980

[5] Zimmermann, Hilmas, Fahrenholtz, Dinwiddie, Porter, and Wang, *J. of the American Ceramic Society*, 91, 1405-1411, 2008

[6] Zhang, Pejaković, Marschall, and Gasch, *Journal of the American Ceramic Society*, 94, 2562-2570, 2011

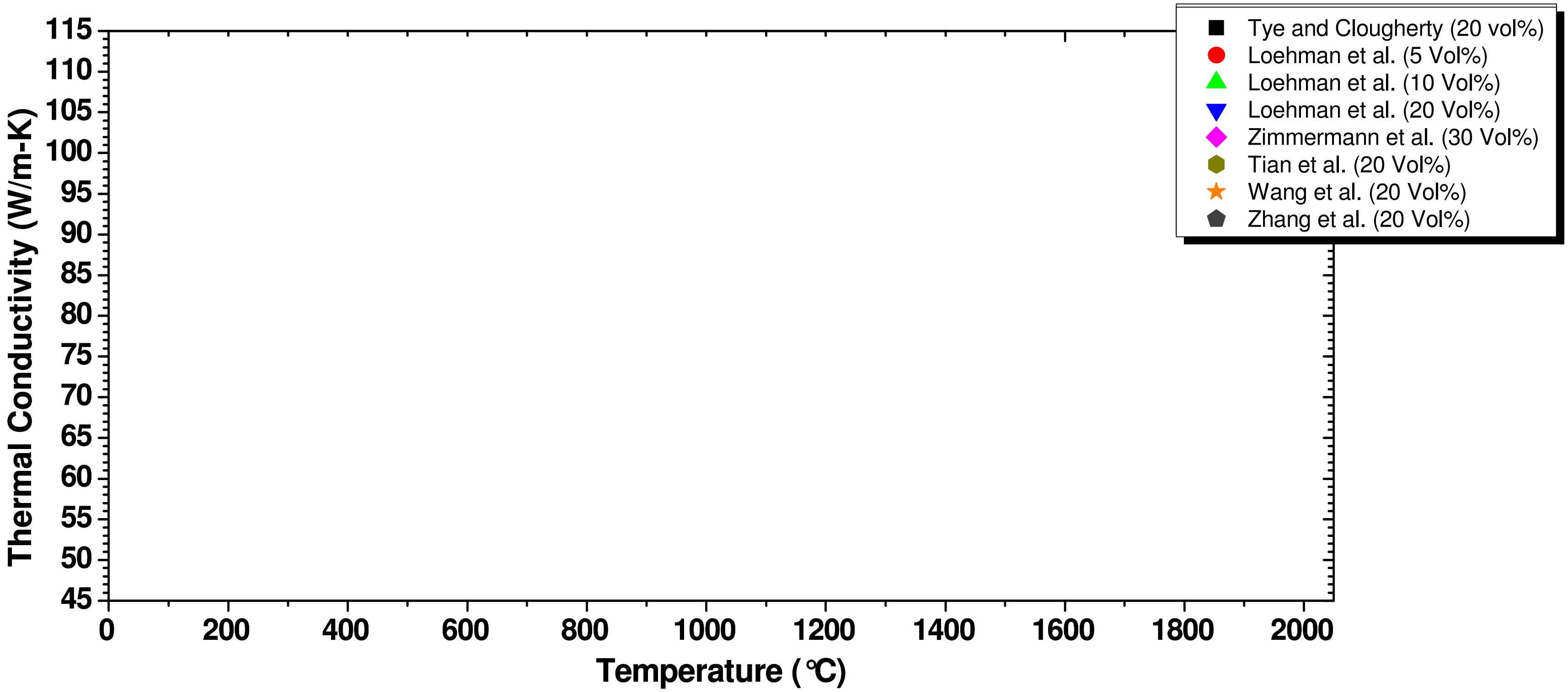
[7] Thompson, Fahrenholtz, and Hilmas, *Journal of the American Ceramic Society*, 95, 1077-1085, 2012

Literature– ZrB_2 Thermal Conductivity



- Broad range of reported conductivity values
- Slope of conductivity vs. temperature varies between positive and negative
  - Highest conductivities have negative slopes
  - Materials with positive slopes tend to have been milled (WC contamination)

Literature - ZrB_2+SiC Conductivity

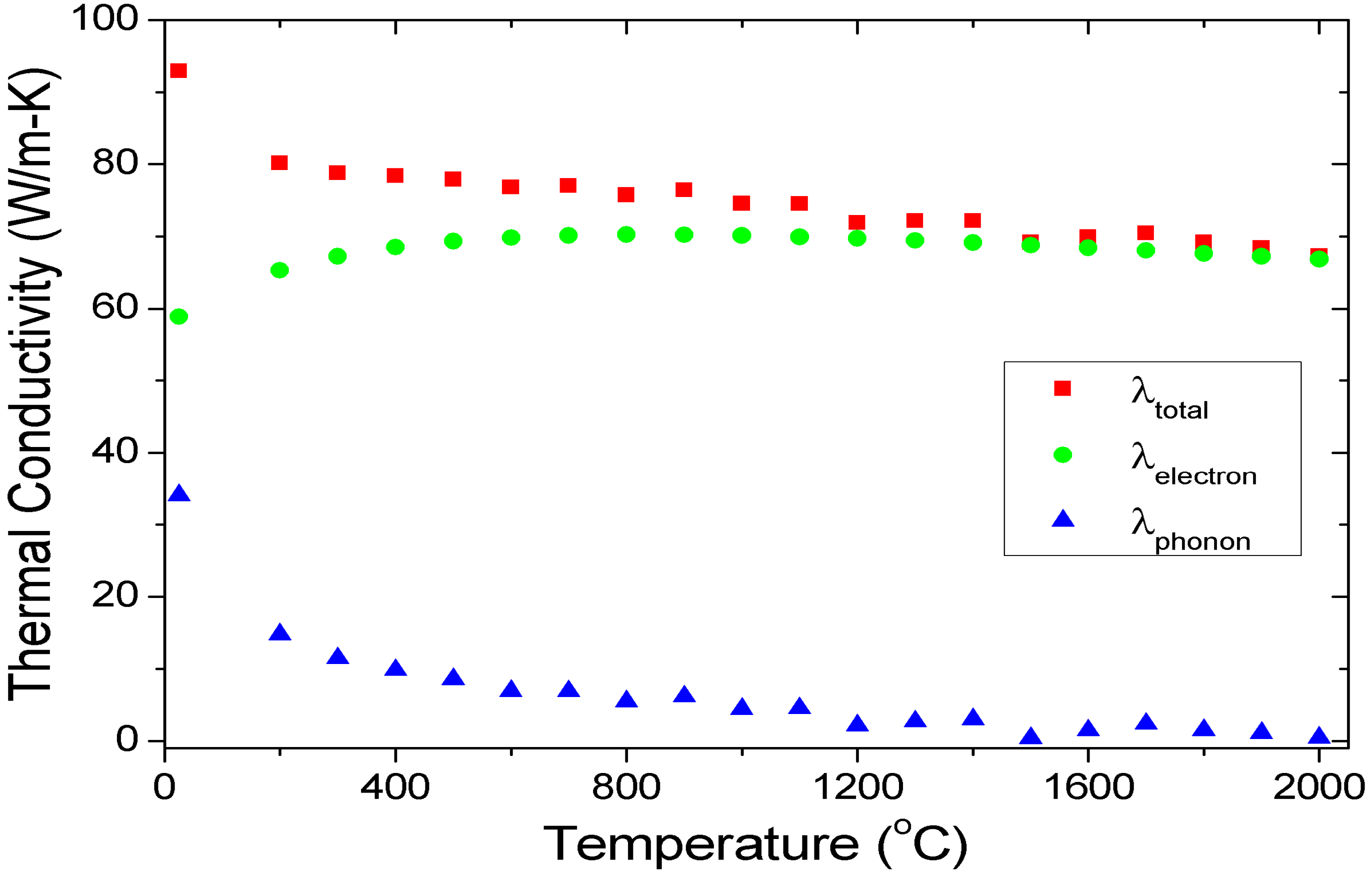


- Large variation in 20 vol% conductivity values
  - 35 W/m•K difference @ 200ºC
  - Multiple factors influencing overall conductivity
- Increasing SiC additions decrease thermal conductivity
- Decrease in conductivity w/temperature shows similar slope between different literature sources

Missouri S&T – λ Thermal Conductivity

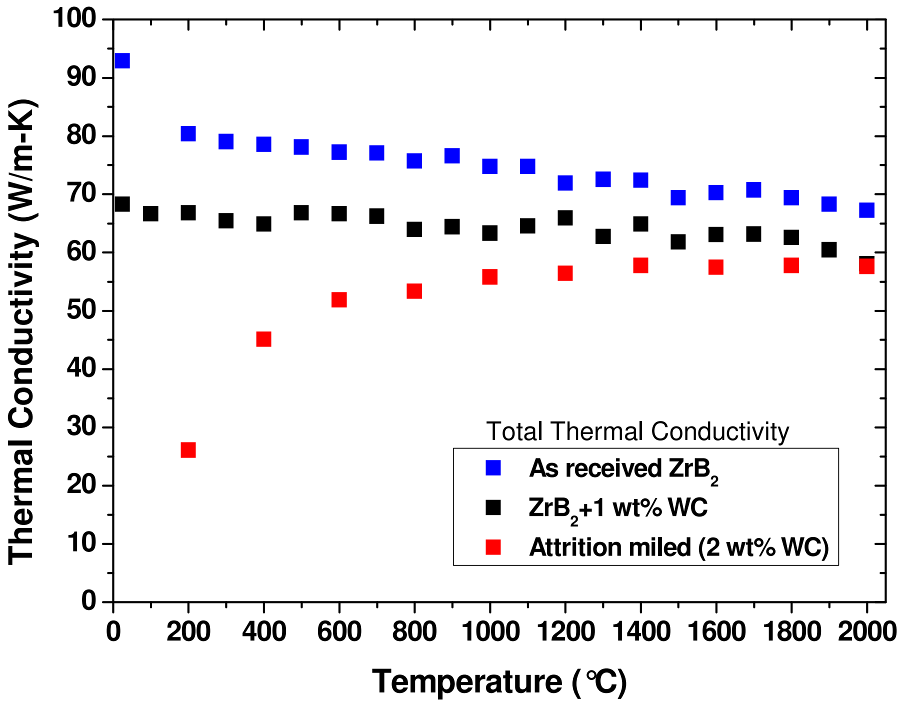
- Total thermal conductivity, $\lambda_{total} = D \cdot C_p \cdot \rho$
- Laserflash thermal analysis, 25 - 2000° C in Ar
  - Diffusivity (D) – evaluated using Clark and Taylor method
  - Heat capacity (C_p) – comparison method and/or NIST JANAF
  - Density (ρ) obtained using Archimedes' method + expansion w/ temp.
- Determine electronic ($\lambda_{electron}$) & phononic (λ_{phonon}) contributions
- $\lambda_{total} = \lambda_{electron} + \lambda_{phonon}$ where $\lambda_{electron} = 2.44\text{x}10^{-8}\sigma T$ (Wiedemann-Franz)
- Electrical conductivity (σ) measured at temp T by 4-point probe
- Tailor λ for UHTC applications
- Maximize λ
  - Hypersonic vehicle leading edges
  - Studying "phase pure" ZrB_2 (reactive processing and isotope affects)
- Minimize λ
  - Hypersonic thermal protection systems and high temperature refractories
  - Researching solid solution and second phase additives

λ for As-Received ZrB_2



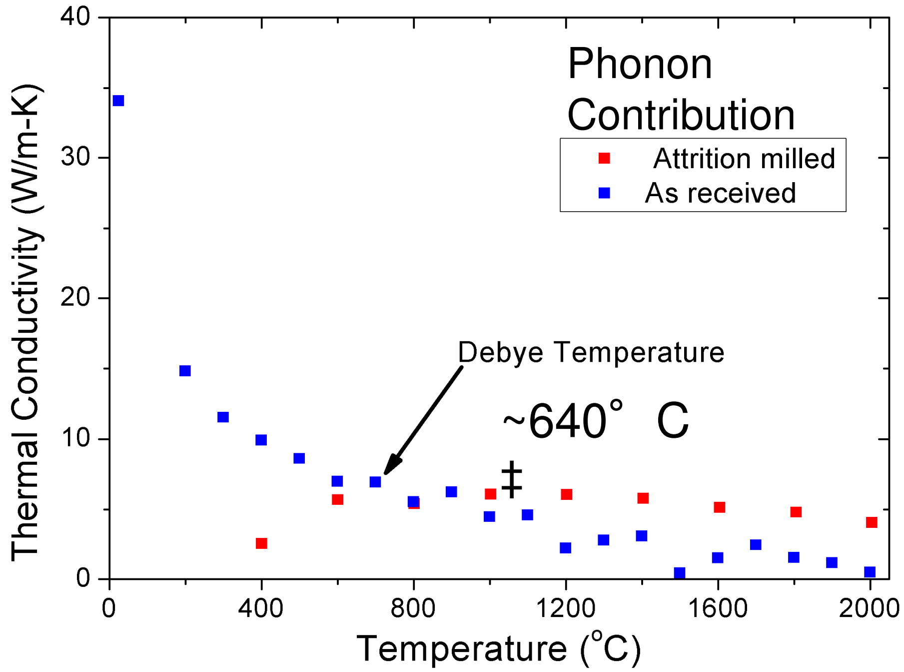
- **Hot pressed as-received ZrB_2 (H.C. Starck, Grade B)**
- **Electron contribution dominates thermal conductivity in ZrB_2**
- **Phonon contribution decreases to nearly zero above 1200ºC**

λ of As-Received ZrB_2 vs. ZrB_2 with WC



- WC additions decrease both $\lambda_{electron}$ and λ_{phonon} contributions to λ_{total} below the Debye temperature
- Above Debye, electron contribution is decreased by WC

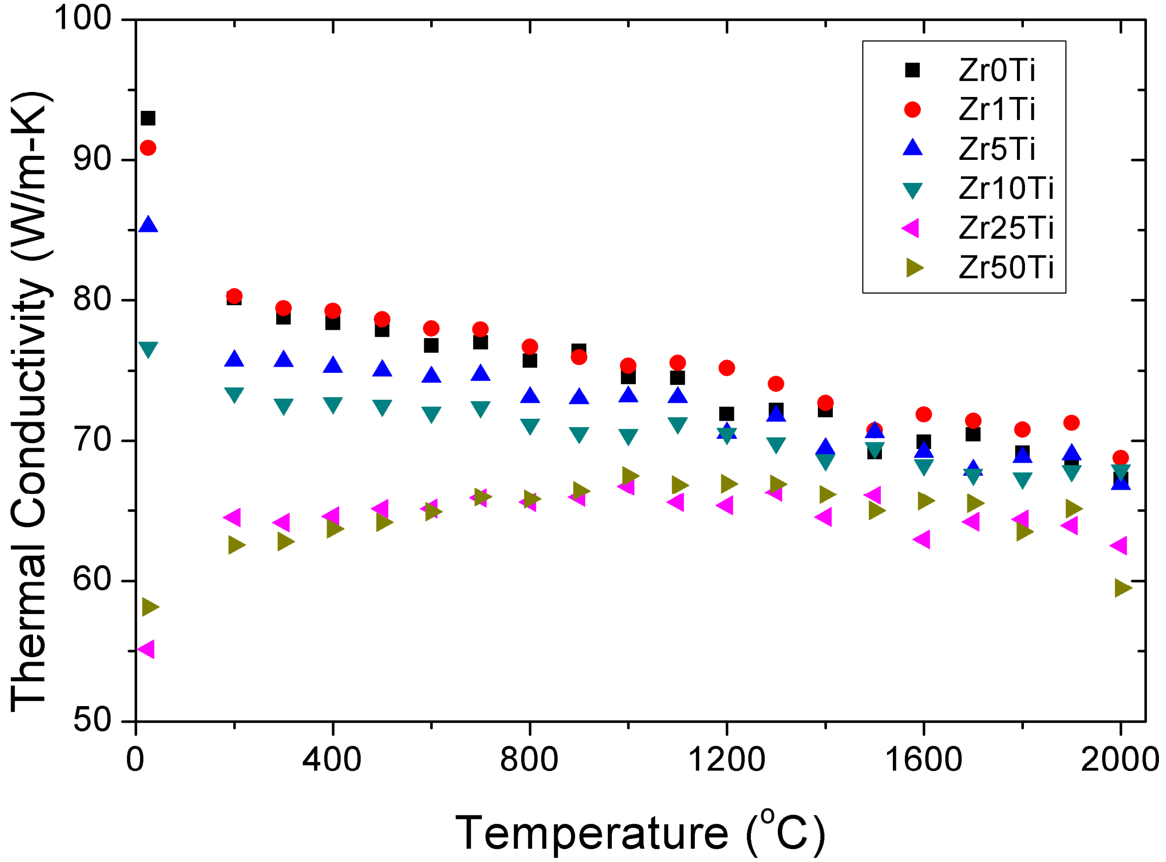
- WC contamination typically obtained when attrition milling
  - λ_{total} decreases for both 1 and 2 wt% WC additions
  - ~50 W/m-K decrease at 200° C
  - ~10 W/m-K decrease at 2000° C



*W seems to affect the electron contribution (↓ carrier concentration?)

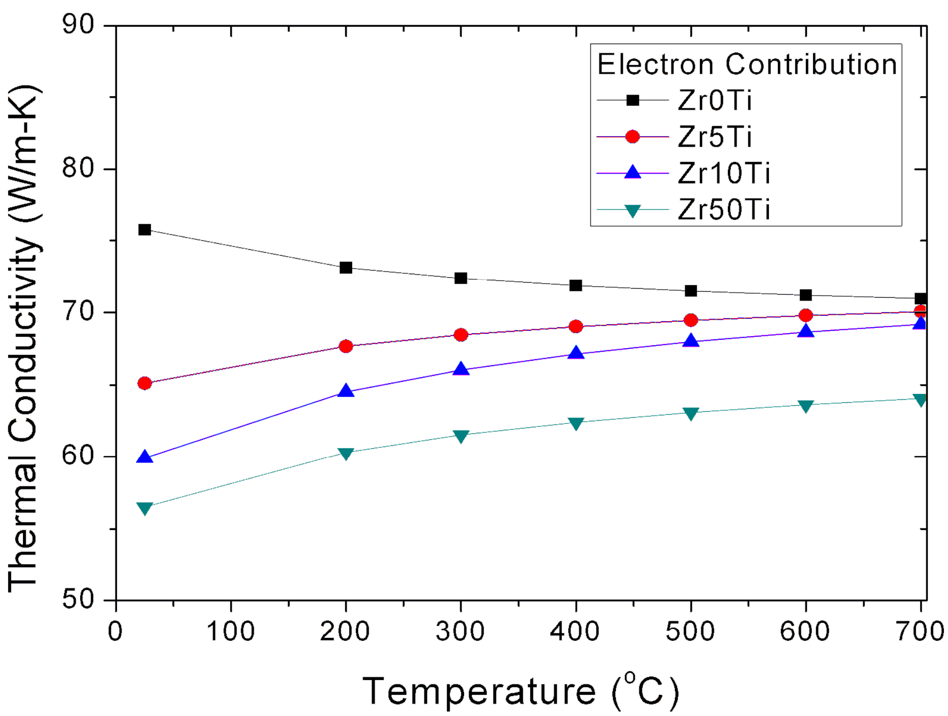
‡Wiley, Manning, and Hunter, *Journal of the Less Common Metals,* 18 [2], 149-57, 1969

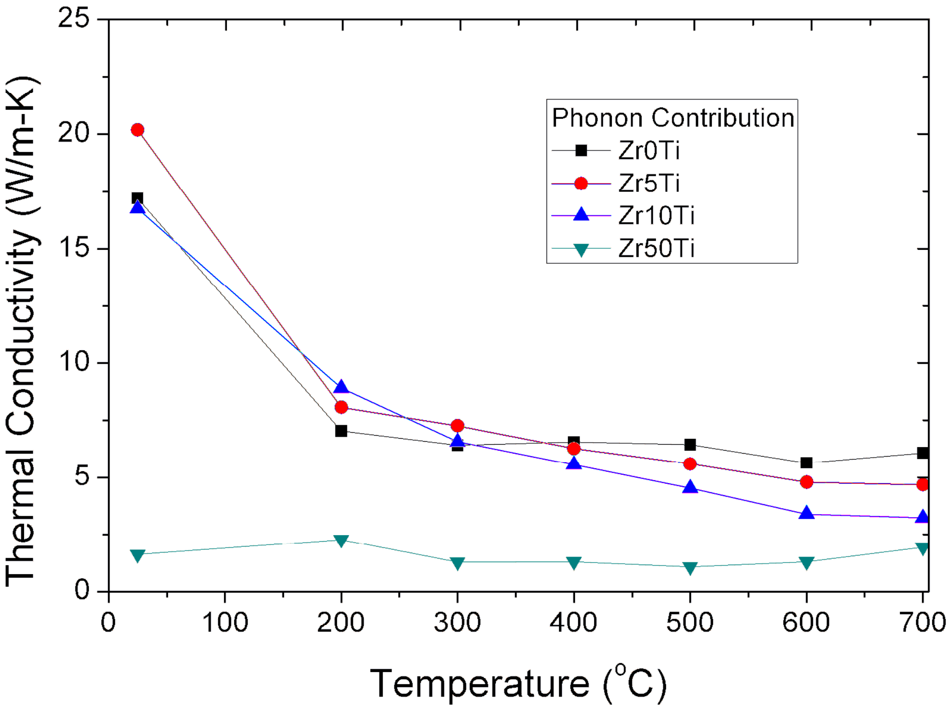
λ_{total} as a Function (Zr,Ti)B_2 (SS)



- (Zr,Ti)B_2 solid solution with 0 to 50 vol% TiB_2 additions
- λ_{total} decreases with increasing TiB_2 SS content
  - Largest effect seen below 1000ºC
  - Increase in λ with increasing temperature for 25 and 50 vol% TiB_2

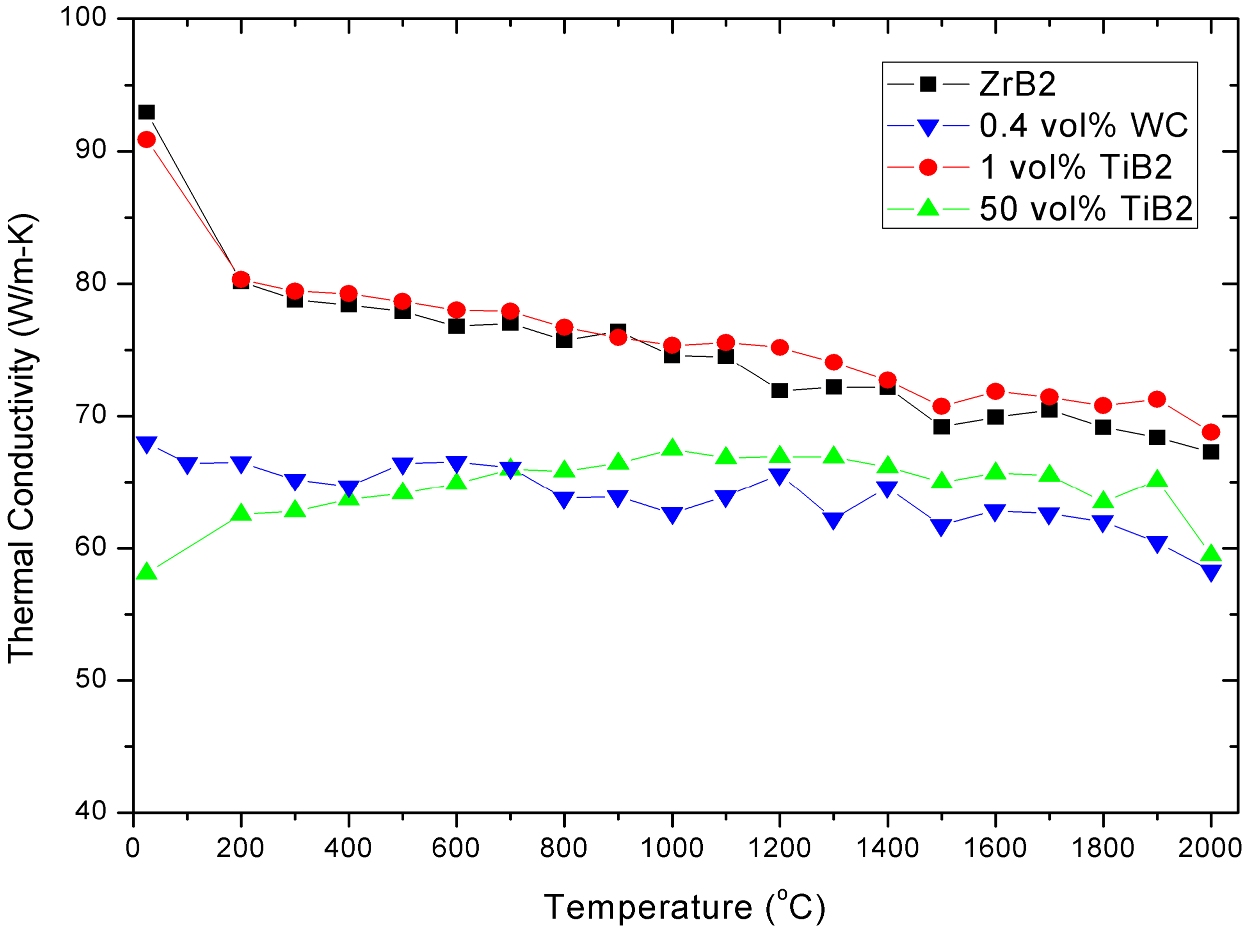
$\lambda_{electron}$ and λ_{phonon} for TiB_2 Additions





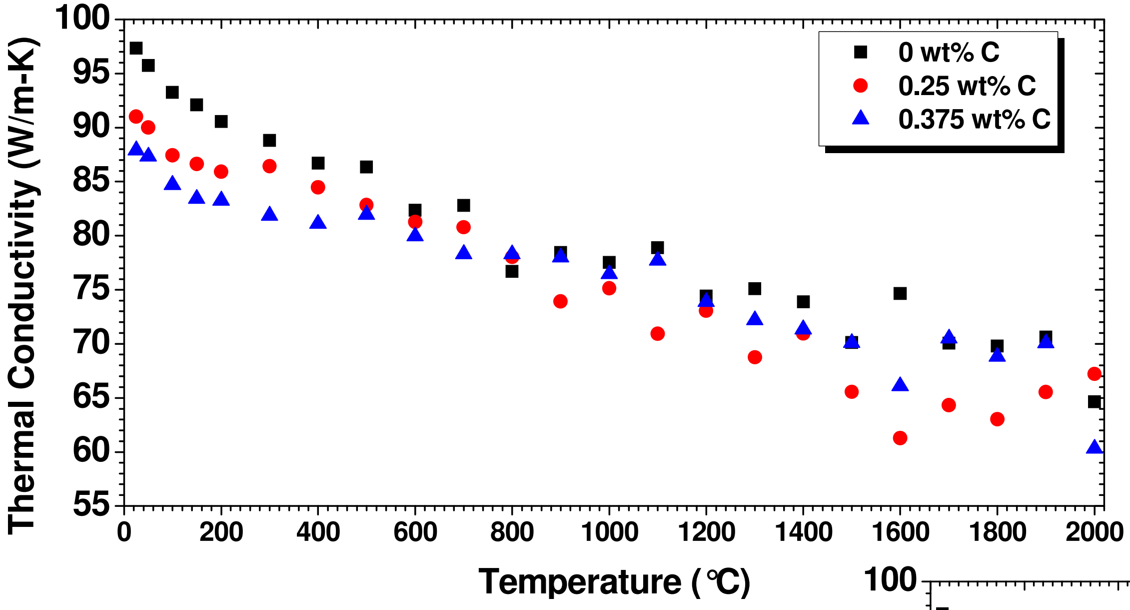
- **Steady decrease in electronic portion of λ_{total} with increasing TiB_2 SS**
- **Little change to phonon contribution up to 10 vol% TiB_2 addition but 50 vol% reduced phononic portion to nearly zero**

WC and TiB_2 Addition Comparison



- **Not all additions have the same affect**
  - **λ decreased significantly with WC addition compared to TiB_2**
  - **0.4 vol% WC provided similar λ as 50 vol% TiB_2**

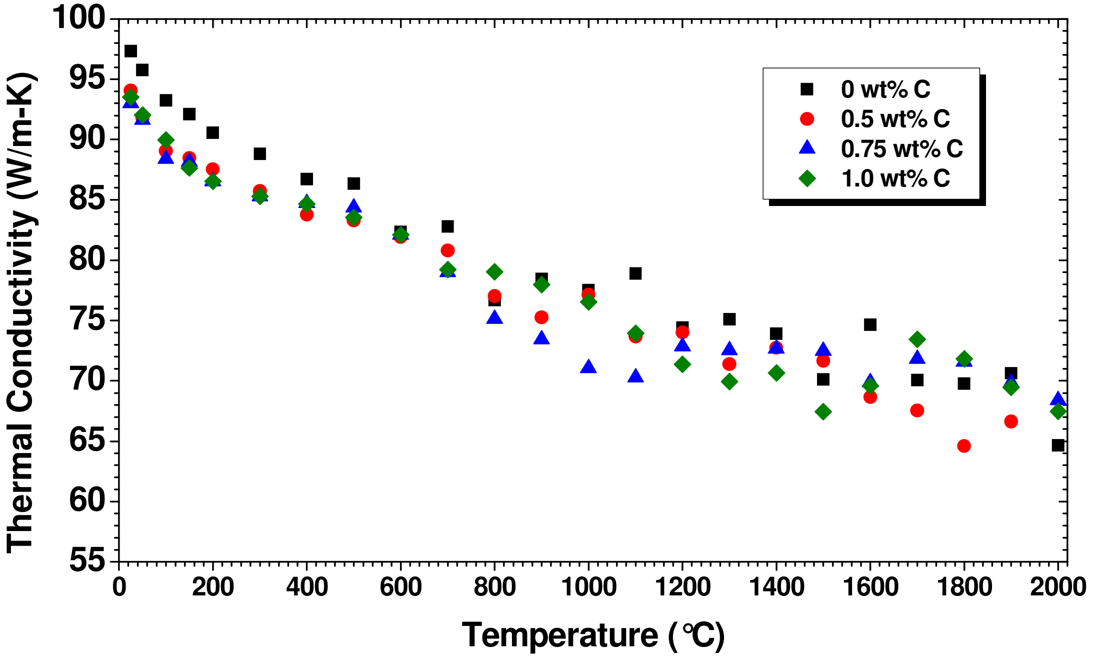
λ vs. Temperature – ZrB_2+C



- As-received ZrB_2 hot pressed w/varying carbon additions
  - Not milled in order to avoid contamination (i.e., WC)
  - 1 wt% ZrH_2 added to eliminate B_4C formation
- 0 through 0.375 wt% C
  - Carbon in SS
  - Decrease in λ with increasing C additions

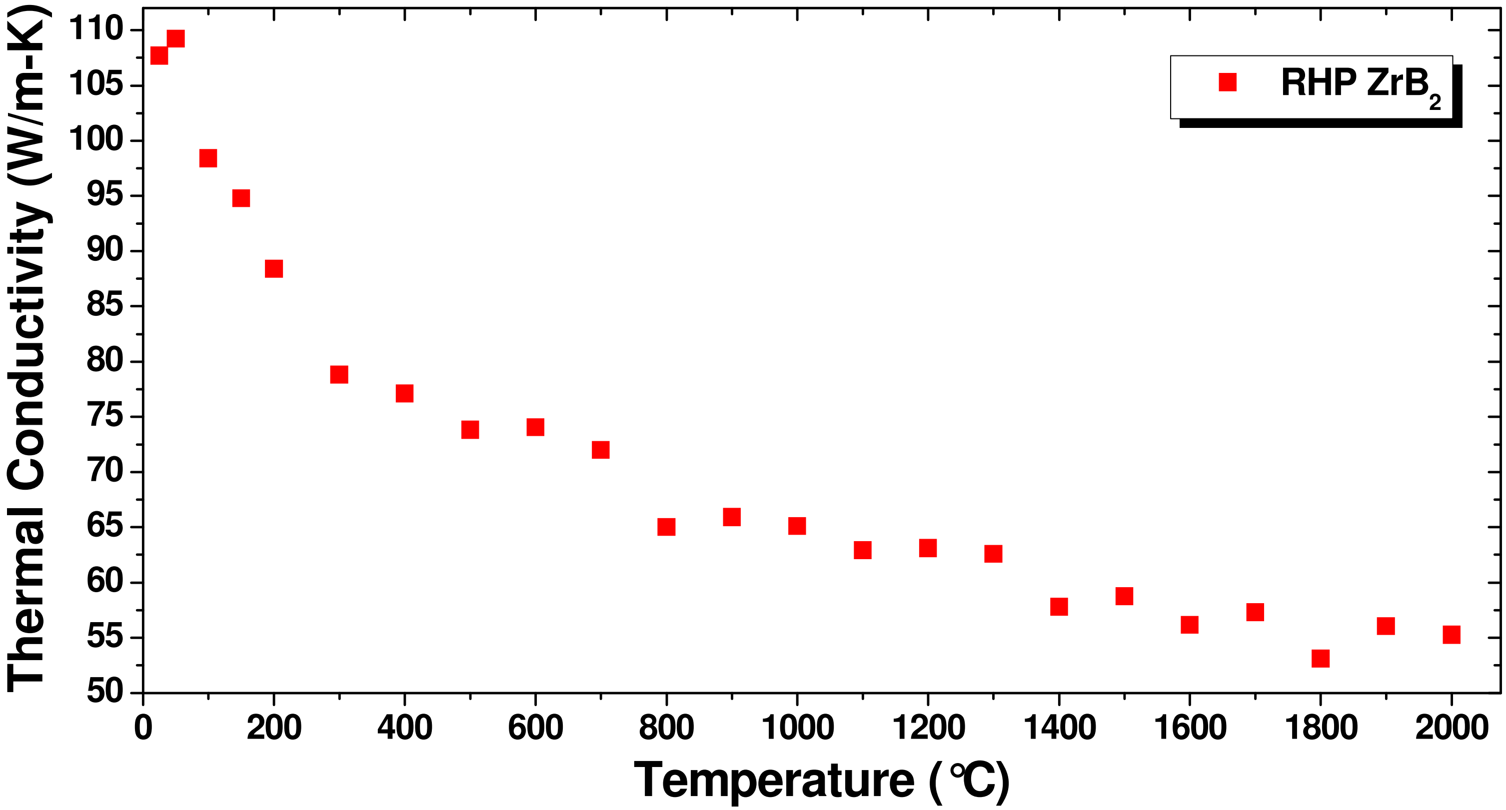
- >0.375 wt% C produces material w/carbon as a stable second phase
  - Little change in λ with increasing carbon

- λ of 0 wt% C still higher than compositions with 0.5 to 1 wt% C additions



High Purity Reaction Hot Pressed ZrB_2

$ZrH_2 + B \rightarrow ZrB_2 + H_2$ (2100° C)



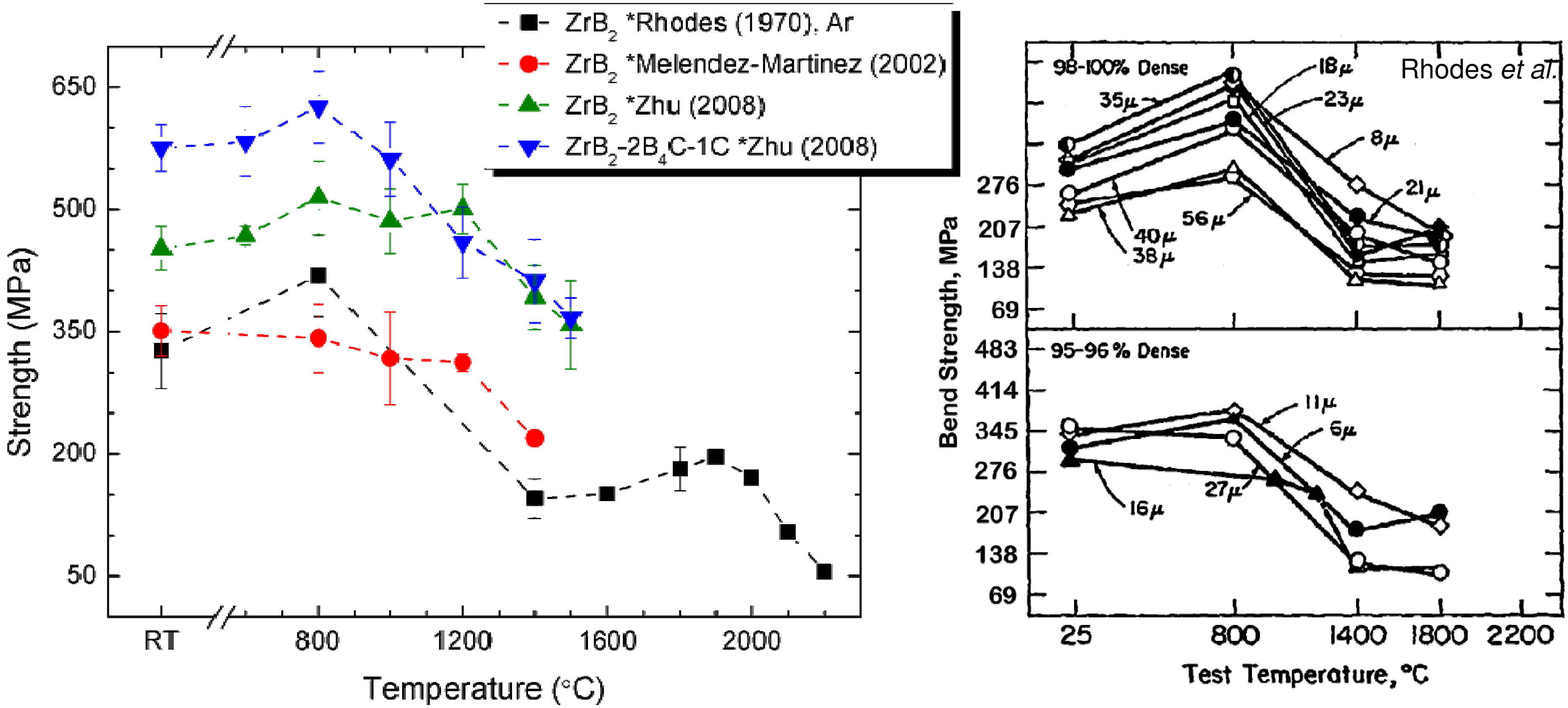
- **ZrB_2 reactively hot pressed from ZrH_2 and B powders to 98.8% density of theoretical**
- **High conductivity achieved because of the high density and low impurity content**

Summary – Thermal Conductivity

- λ strongly affected by impurities and second phases
- λ dominated by the electron contribution
- High λ material
  - Few ways to increase λ
    - Produce fully dense material
    - Decrease impurities (reaction process)
    - Increase grain size
  - Possibilities for the future
    - Improve phonon conduction
      - Study isotope affects
    - Increase electron conduction
      - Increase carrier concentration
      - Increase mean free path
- Low λ material
  - Many ways to lower λ
    - SS additions (C, WC, TiB_2)
    - Second phases (SiC)
    - Increasing porosity
  - Phonon modes are easiest to disrupt
  - Research required to understand role of electron conduction

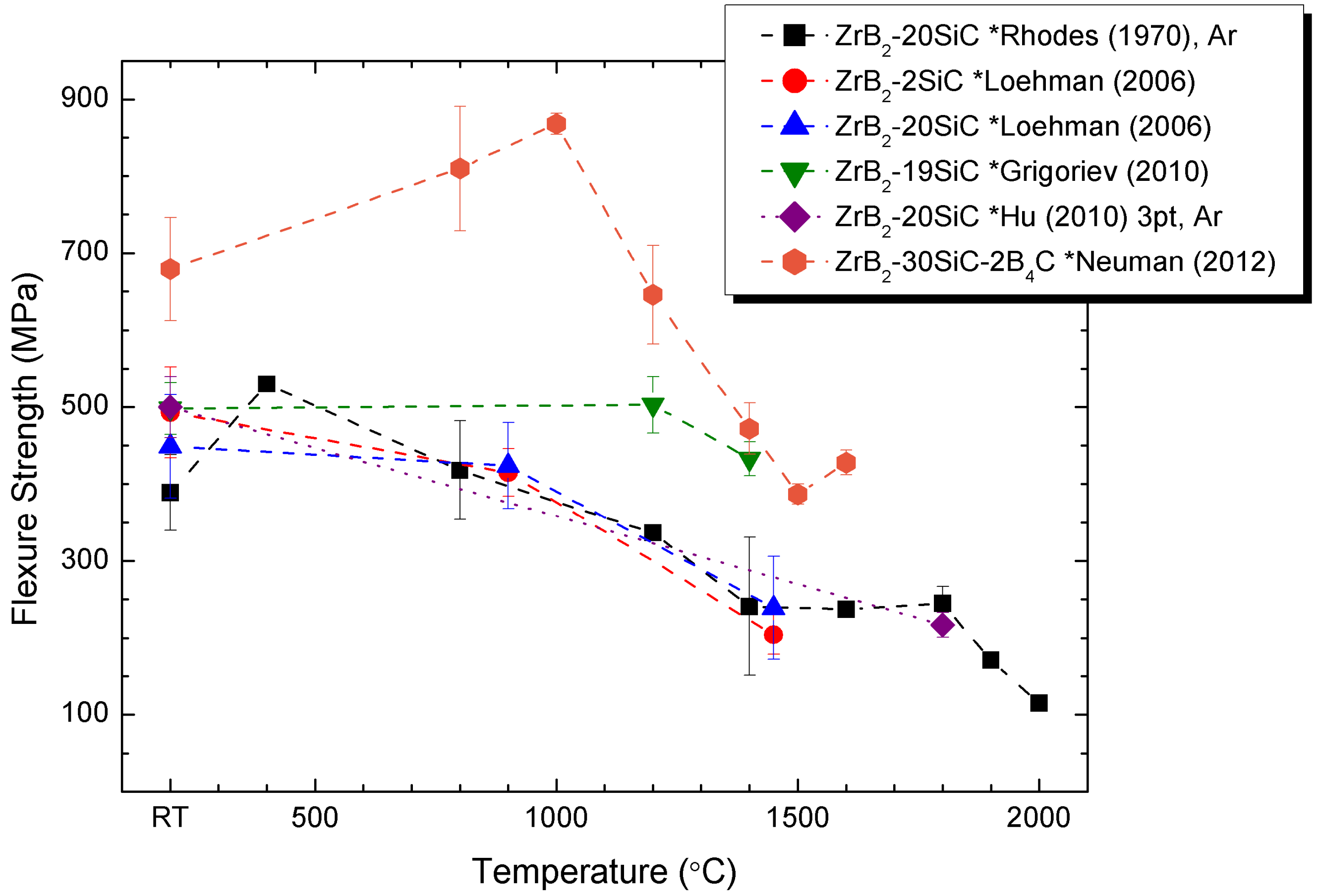
Flexure Strength
of ZrB_2-Based UHTCs

ZrB_2 Strength vs. Temperature



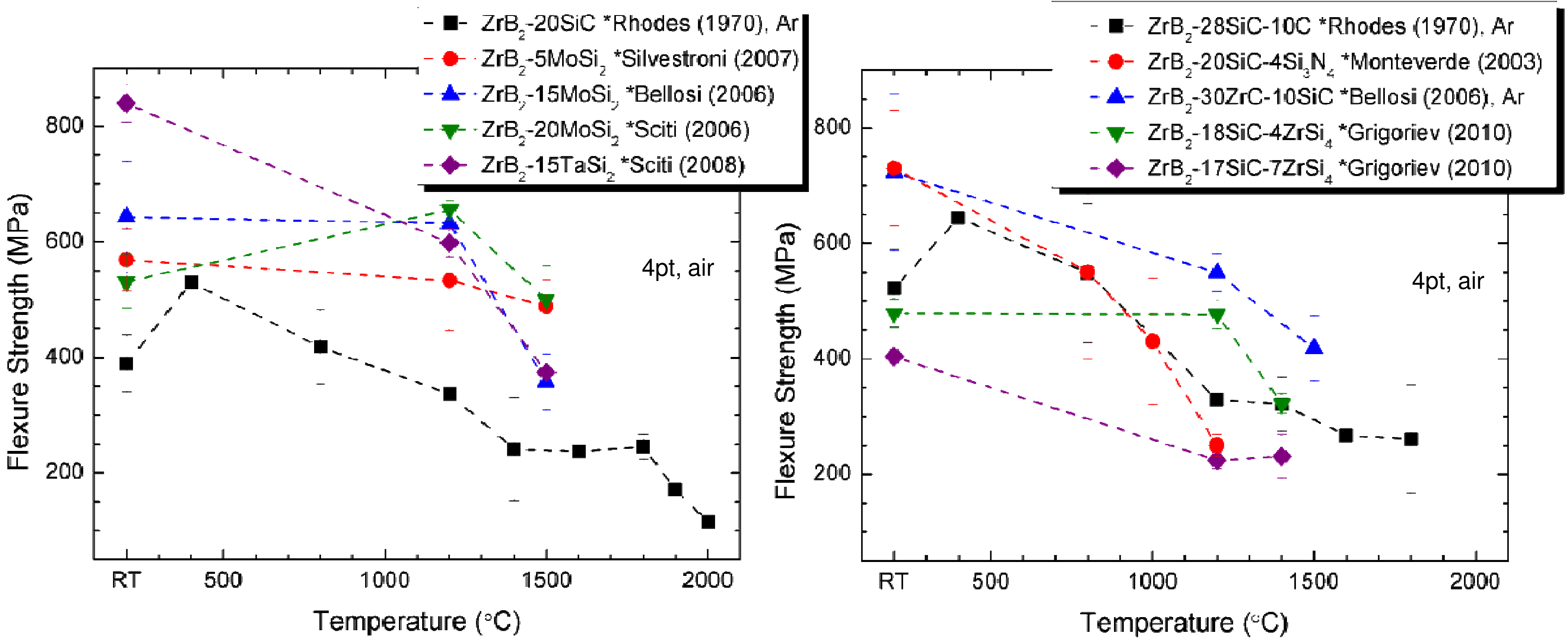
- Limited studies of ZrB_2 at elevated temperatures
  - Rhodes: various densities and grain sizes – 4 pt, Ar
  - Melendez-Martinez: 87% dense, GS ~20μm – 4 pt, air
  - Zhu: >97% dense, GS ~ 10μm – 4pt, air, TEOS coated
- Strength of ZrB_2 decreases for increasing grain size for all temperatures

ZrB_2-SiC Strength vs. Temperature



- **SiC additions to ZrB_2 increase strength at all temperatures**
  - **Grain size and residual stress effect**
- **Currently no strength data for ZrB_2-SiC system above 2000ºC**
- **Effect of grain size on high temp strength has not been investigated**

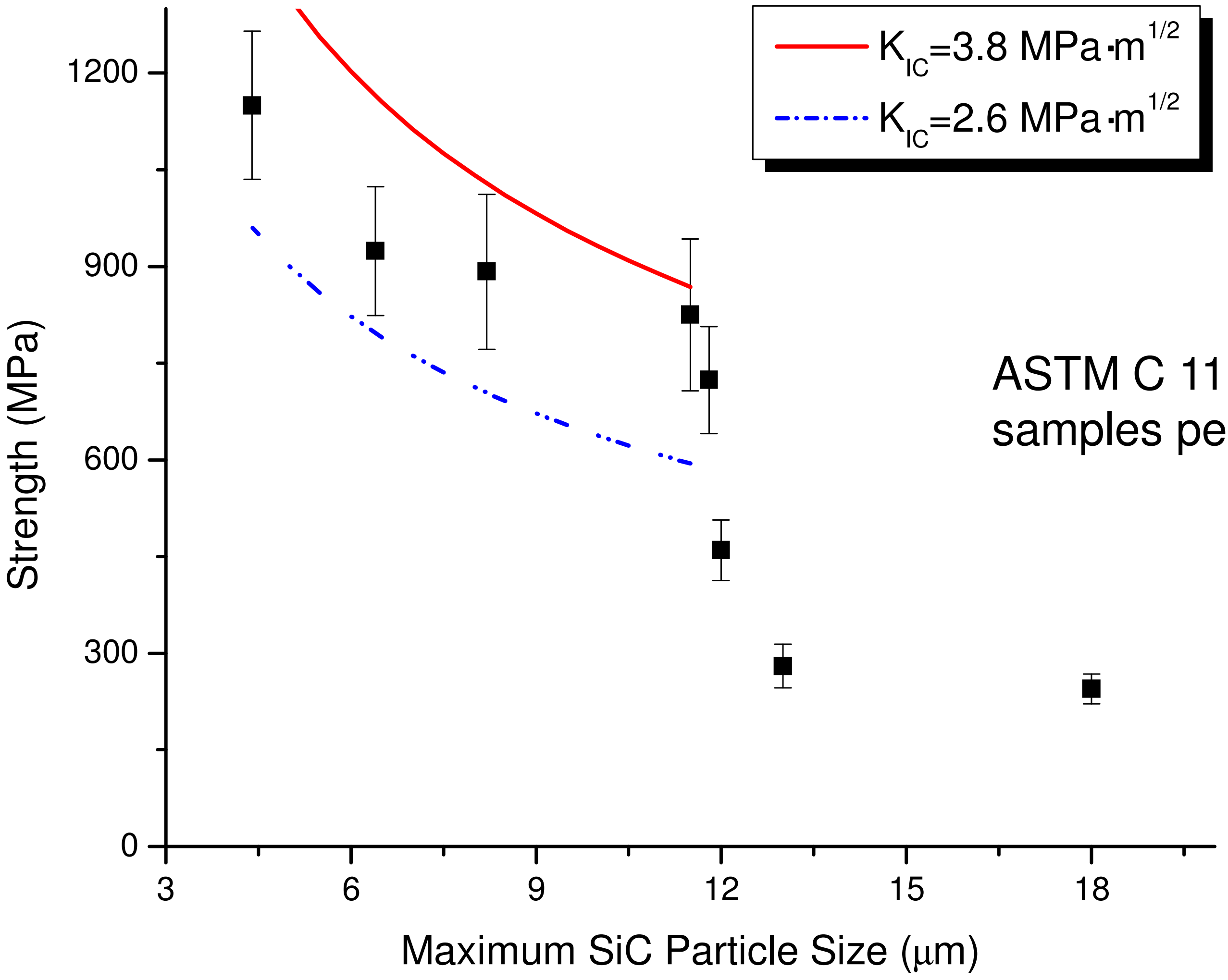
Other Additions to ZrB_2



- **Silicide additions can offer improved strength over SiC additions**
- **Lower melting point than ZrB_2-SiC eutectic (2270ºC)**
  - **$MoSi_2$ - 2030ºC; $TaSi_2$- ~2200ºC**
- **Mechanical behavior of ZrB_2 with silicide additions above 1500ºC is unkown**

SiC Particle Size/Shape Controls Strength

- **SiC particulate phase fit as an ellipse**

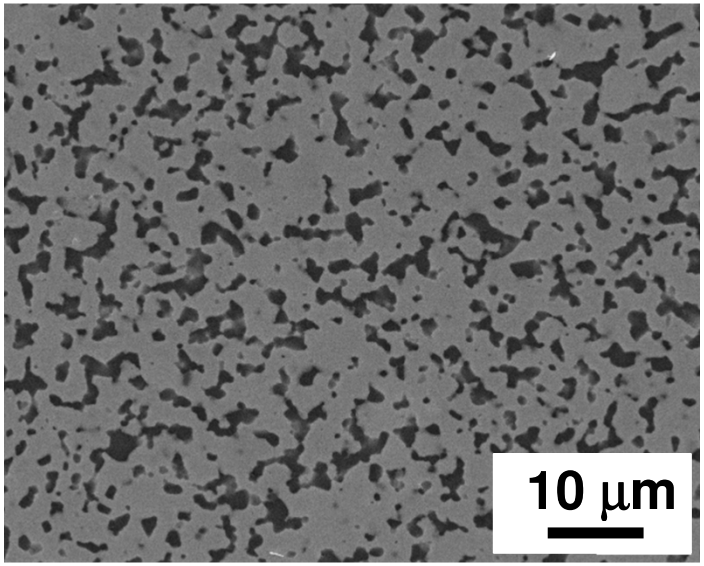


ASTM C 1161-2b, 10 samples per data point

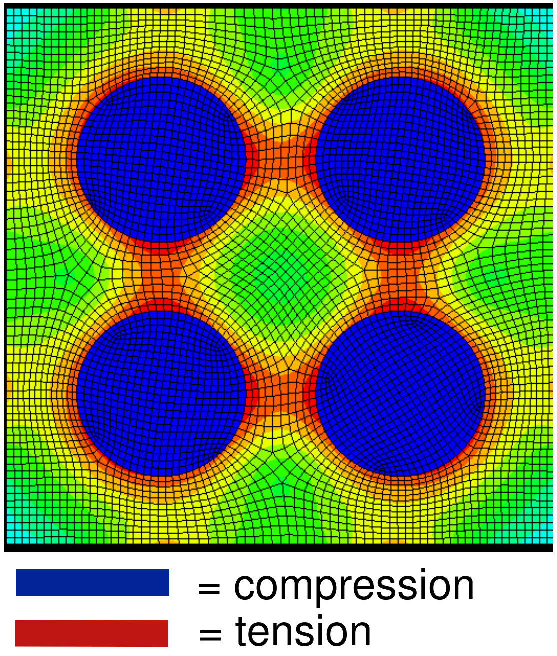
Watts, Hilmas, and Fahrenholtz, J. Am. Ceram. Soc., 94(12) 4410-4418 (2011).

Residual Stresses in ZrB_2-SiC

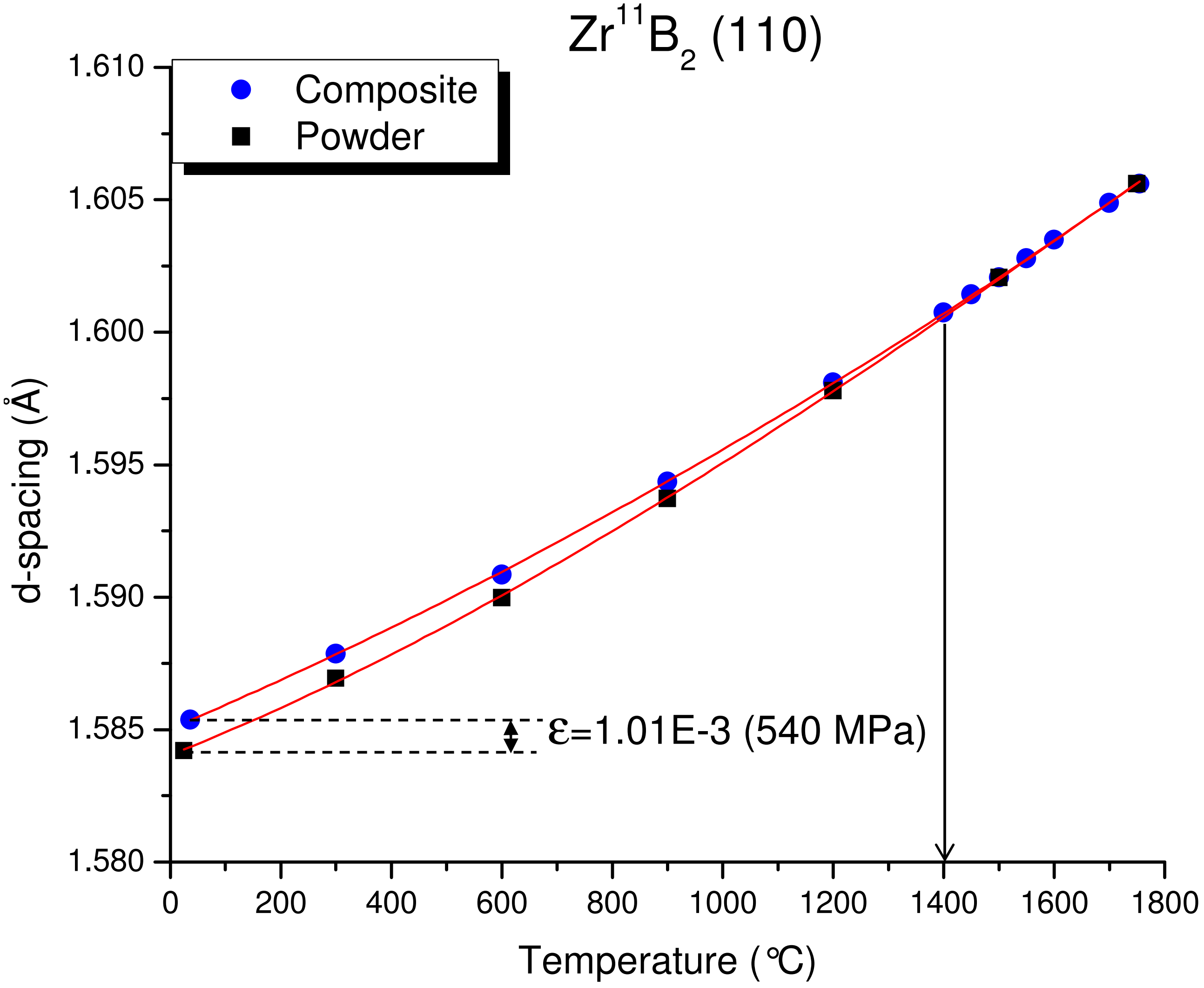
- ZrB_2-30 vol% SiC(6H)
  - Advantageous properties (high RT σ)
  - ~2 ppm/ºC difference in CTE
    - Thermal residual stresses upon cooling after hot pressing or sintering
    - SiC in compression
    - ZrB_2 in tension



- Residual stresses
  - Neutron diffraction using $Zr^{11}B_2$-30%SiC
    - Milled with SiC milling media
  - ZrB_2 is in tension (455 MPa)
  - SiC in compression (-878 MPa)
  - Stresses accumulate below 1400ºC
  - Can the stresses be manipulated to improve thermomechanical properties?



Neutron Diffraction – ZrB_2 Phase



Calculated Stresses

- **Calculated stresses vs. crystallographic directions**
  - **Stiffness coefficients from Okamoto (ZrB_2) and Yao (α-SiC)**

    Okamoto, *Journal of Applied Physics*, 93 (1), 2003

    Yao, *Journal of the American Ceramic Society*, 90 (10), 2007

$Zr^{11}B_2$

(h	k	l)	E_{hkl} (GPa)	ε	Calculated σ (MPa)
1	0	1	553	9.00E-04	498
0	0	2	390	7.18E-04	280
1	1	0	533	1.01E-03	540
1	1	1	557	9.61E-04	535
1	1	2	544	8.80E-04	478
3	0	0	533	1.01E-03	539
1	0	4	419	7.45E-04	313

Average **455**

Tensile

SiC

(h	k	l)	E_{hkl} (GPa)	ε	Calculated σ (MPa)
1	0	0	484	-1.94E-03	-937
1	0	1	474	-1.94E-03	-918
0	0	6	556	-1.51E-03	-842
1	0	2	452	-1.93E-03	-872
1	0	8	437	-1.87E-03	-820
1	1	0	484	-1.94E-03	-939
1	1	6	426	-1.92E-03	-815

Average **-878**

Compressive

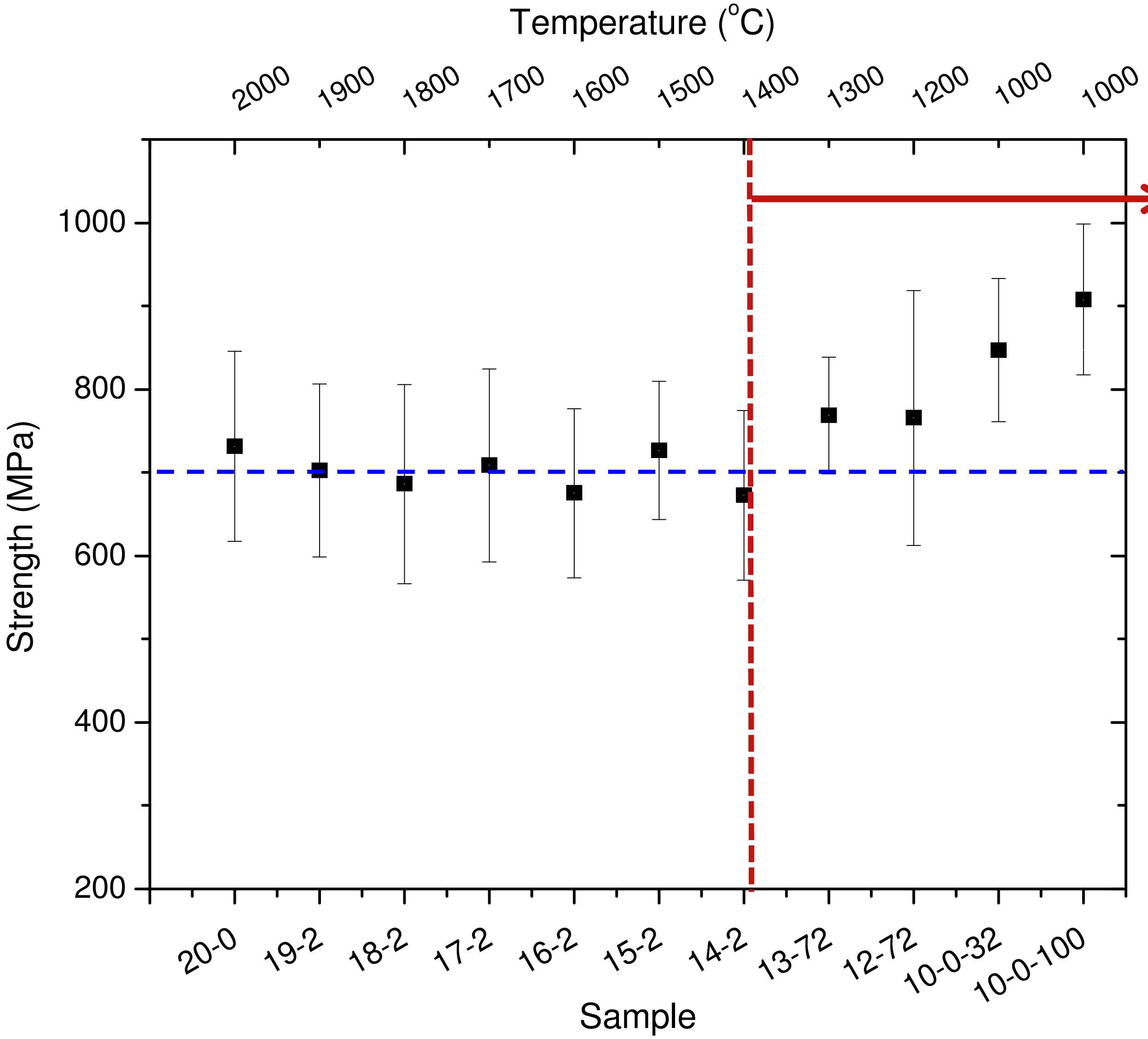
J. Watts, G. Hilmas, W. Fahrenholtz, D. Brown, B. Clausen,
Journal of the European Ceramic Society, **31**, 2011

Annealing Study

ZrB_2-30vol% SiC (milled using SiC media)

Sample Designation	Annealing Temperature (ºC)	Time at Temperature (Hrs)	Cooling Rate (ºC/min)	Applied Pressure (MPa)
20-0	2000	0	30	0
19-2	1900	2	30	0
18-2	1800	2	30	0
17-2	1700	2	30	0
16-2	1600	2	30	0
15-2	1500	2	30	0
14-2	1400	2	30	0
13-72	1300	72	30	0
12-72	1200	72	30	0
10-0-32	1000	0	2 (below 1500 ºC)	32
10-0-100	1000	0	2 (below 1500 ºC)	100

RT Flexure Strength after Annealing



All samples annealed below 1400ºC had a higher strength at room temperature

Baseline is ~700 MPa

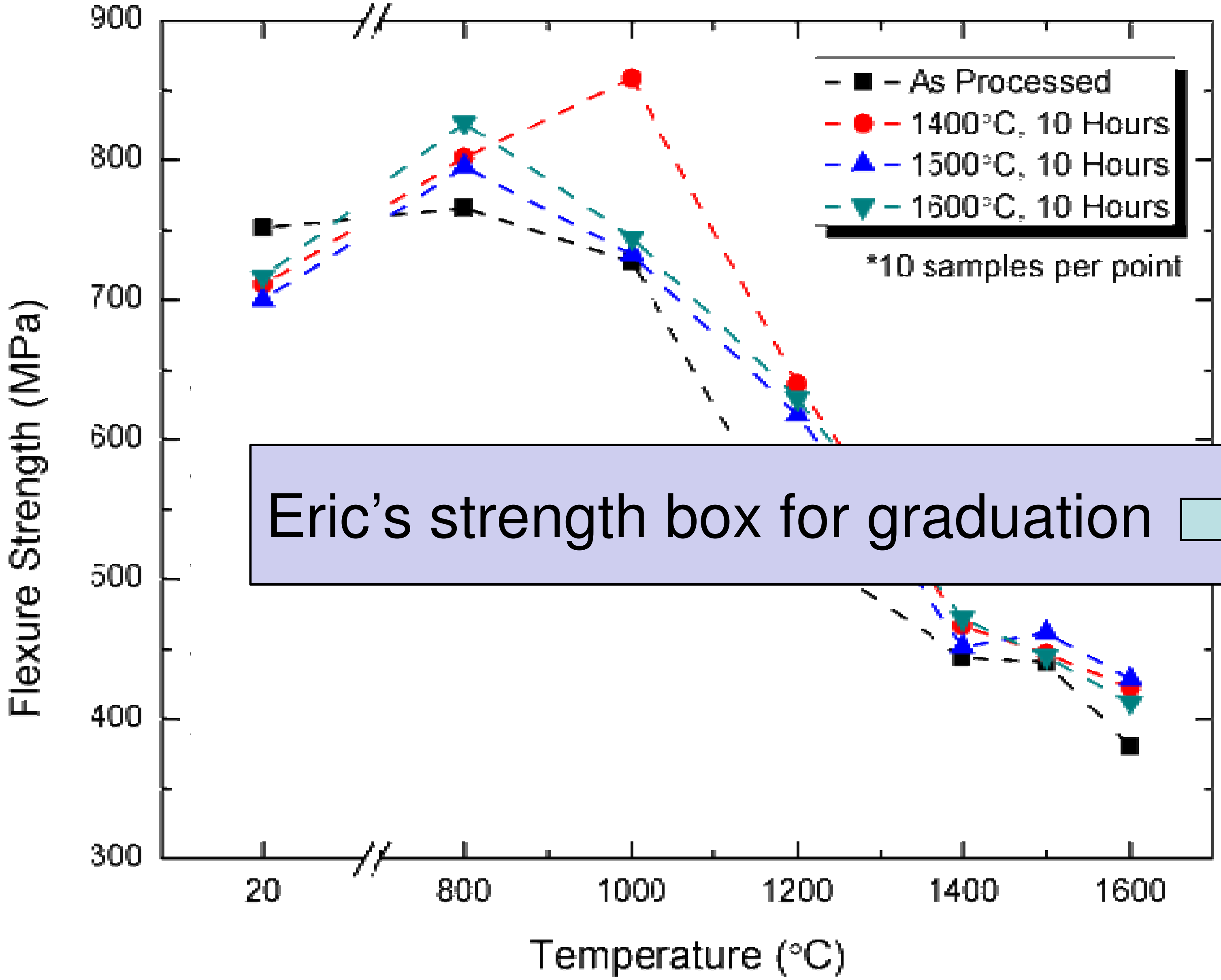
ASTM C 1161-02b, 4-point bending, 10 samples per data point

Annealing Study – Different Composition

- **Sample preparation**
  - ZrB_2 (H.C. Starck, Grade B)
  - 30 vol% α-SiC powder (H.C. Starck, UF-10)
  - 2 wt% B_4C (H.C. Starck, HD-20)
  - Milled using WC-6%Co milling media (0.24 wt% WC)
  - Hot pressed at 1950ºC/32 MPa

- **Annealing**
  - Temperatures from 1300 to 1600ºC
  - Times of 10 to 50 hours
  - Ar overpressure (1 atm)

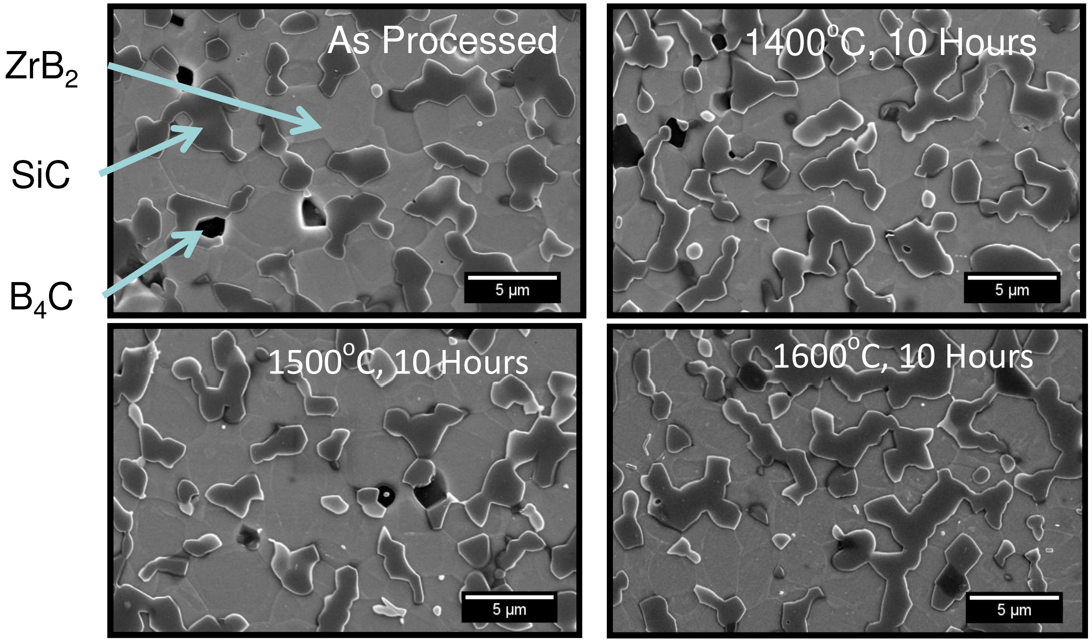
σ_f vs. Temperature after Heat Treatment



Eric’s strength box for graduation

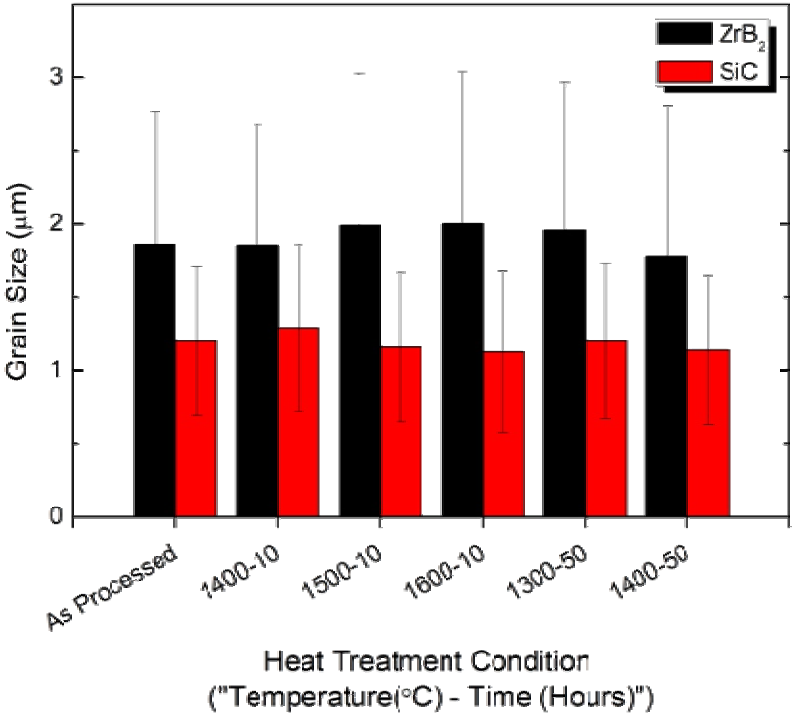
Heat Treatment Microstructure

Microstructures



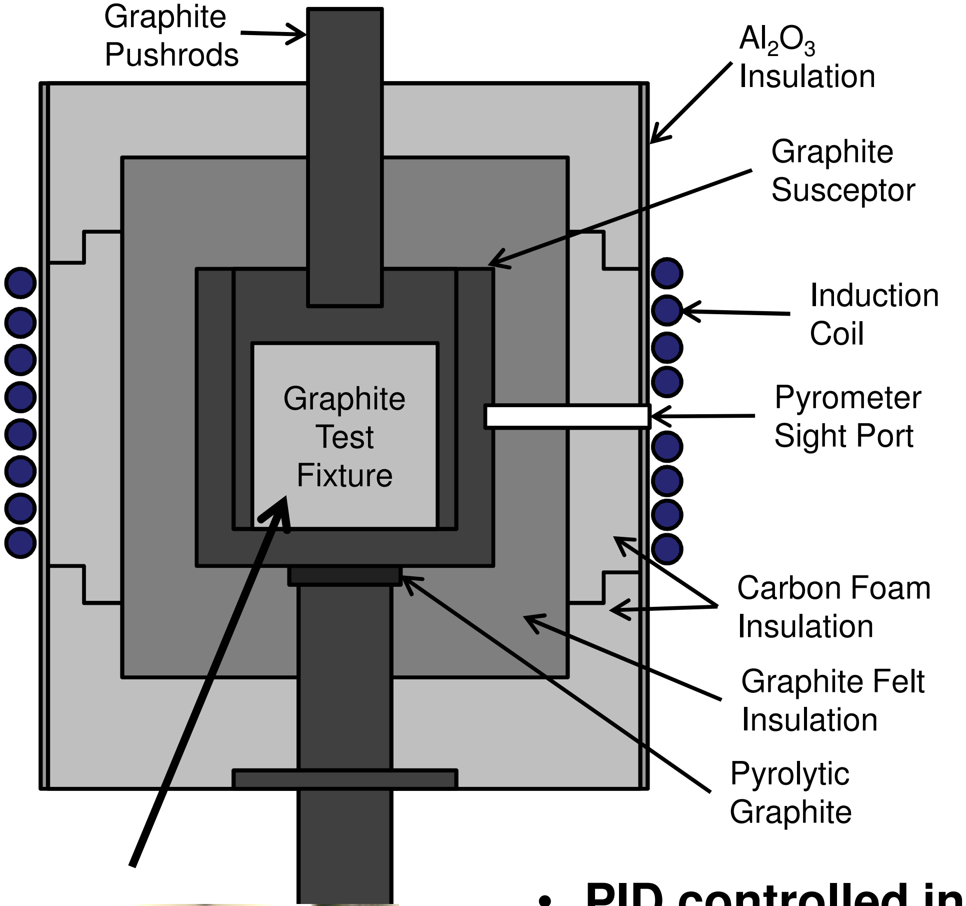
- No additional phases identified by XRD
- EDS shows no additional discreet phases present
    - i.e. no W-rich phase typical of ZrB_2-SiC ceramics produced by milling with WC media

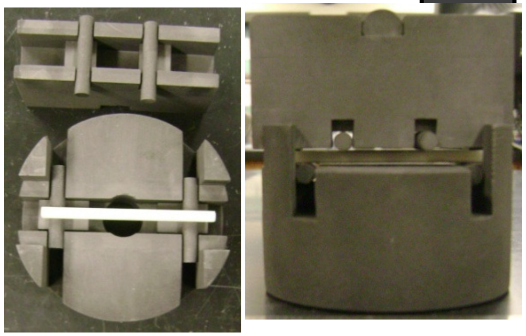
Grain Size



- No variation in grain size
    - ~1.9±1.0 µm for ZrB_2
    - ~1.2±0.5 µm for SiC

2500° C+ Environmental Chamber

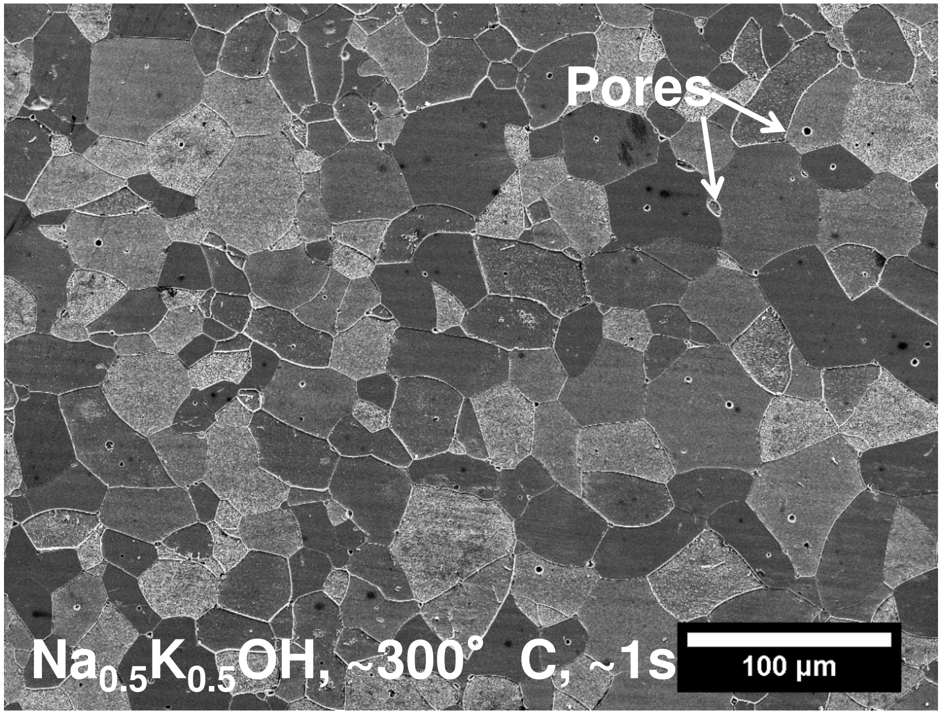




- **PID controlled induction heater**
- **2-color optical pyrometer (1500-3000ºC)**
- **Instron 4204 universal test frame**
- **Vacuum/gas flow control**
- **Fully articulated 4-pt fixture**
- **Capable of >2500ºC**

ZrB_2 Microstructure

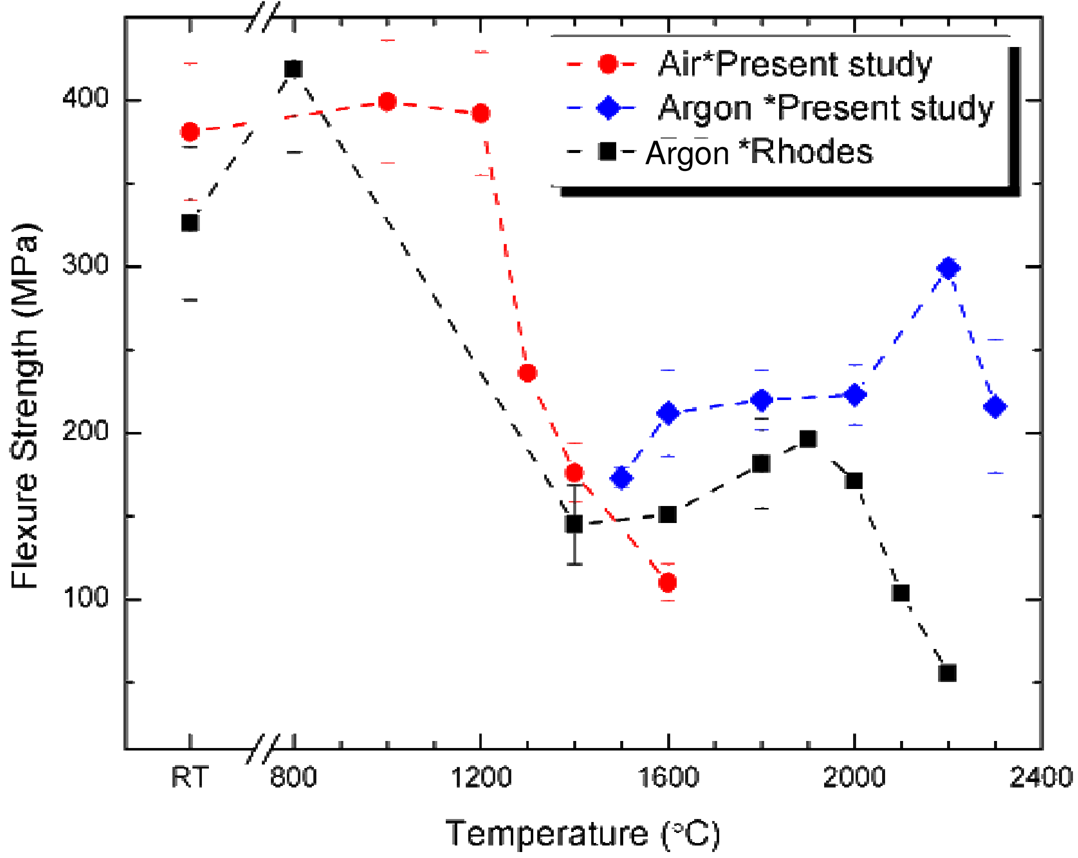
ZrB_2 + 0.5 wt% C, hot pressed at 2150ºC/1 hour, 32 MPa, He



- Held for extended time at 2150ºC to grow grains and reduce tendency for creep at temperatures over 1800ºC (as observed by Rhodes *et al.*)

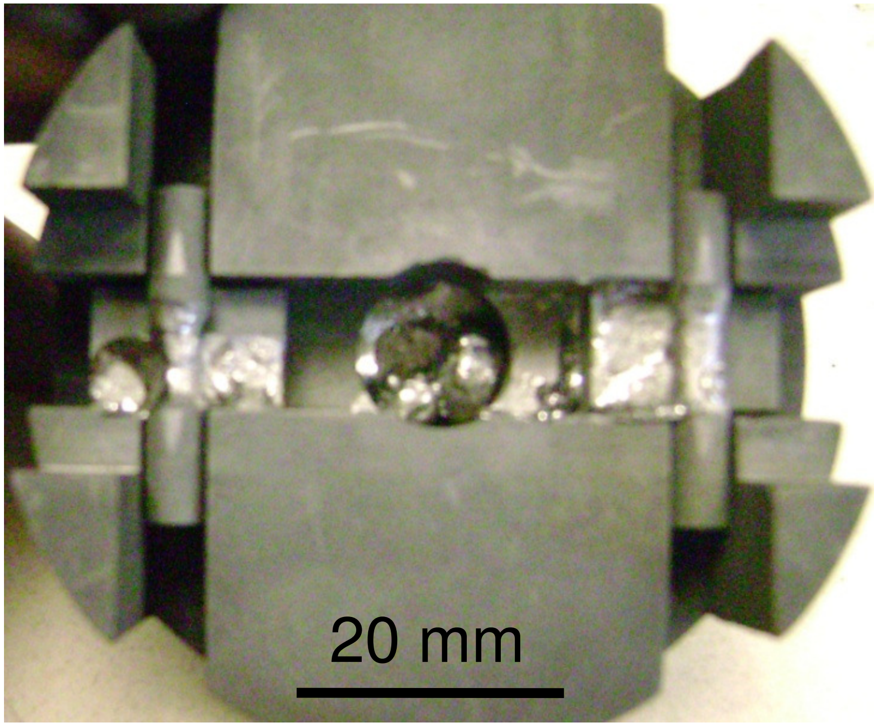
- **Density**
  - 6.04 g/cc, >99.2% RD
- **Grain Size**
  - 19.7 ± 13.0 µm (>2000 grains)
- **Strength in 4-point bending**
  - Room temp (ASTM C1161-02c)
  - Elevated temp (ASTM C1211-02c)
    - Air
      - TEOS sol coated, heat treated to 700ºC/1hour in air, repeated 4x
    - Argon
      - 100ºC/min to 200ºC below temperature, then 50ºC/ min to temperature, hold for 5 min
  - Variable crosshead speed

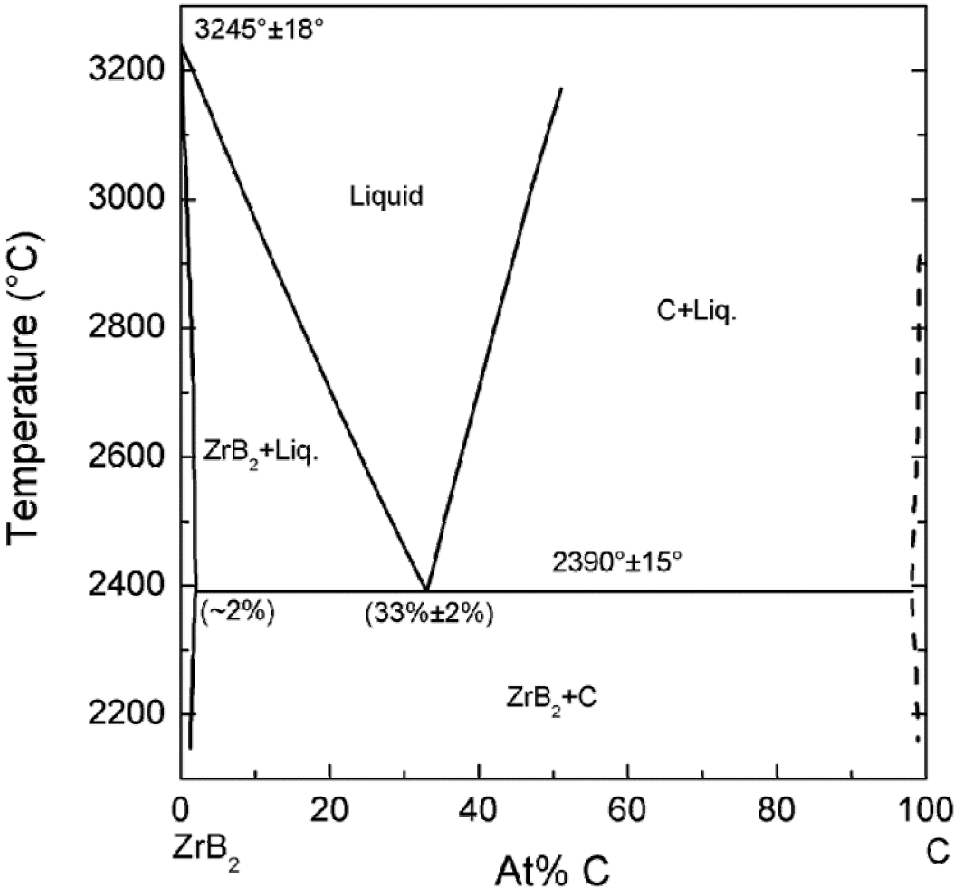
ZrB$_2$ Strength vs. Temperature



- Strength in air: ~380 MPa at RT, ~400 MPa at 1200ºC, ~110 MPa at 1600ºC
  - Oxidation affects strength above 1300˚ C
- Strength in Ar: ~170 MPa at 1500ºC, ~300 MPa at 2200ºC, ~220 MPa at 2300ºC
- Strength of material in present study is greater than historical material, particularly above 2000ºC, with similar grain size and density

Testing Limits





- **2400° C test resulted in a melted flexure bar**
- **ZrB_2 – C eutectic at 2390ºC – Verified!**
- **The solution for higher temperature testing?:**
  - **Use ZrB_2-ZrC (2660ºC eutectic) or ZrB_2-$ZrC_{0.88}$ (2830ºC eutectic)**

Summary – Mechanical Properties

- Strength of ZrB_2-30% SiC improved by annealing
  - Can be annealed to affect the stress state
    - Appropriate annealing temperature affected by impurities
  - Increased to >900 MPa from ~700 MPa after annealing at 1000ºC under a 100 MPa applied load
    - Milled using SiC media
  - At a test temperature of 1600ºC: ~375 MPa (as-processed) and ~440 MPa (annealed for 10 hours at 1500ºC)
    - Milled using WC media
- Strength of ZrB_2 (~20 µm grain size)
  - ~380 MPa at RT
  - Strength decreased rapidly in air above 1200° C due to oxidation despite protective silica coating…need testing in Ar to verify behavior in this region (near stress relaxation temp.!)
  - ~170 MPa at 1500ºC & increased to ~300 MPa at 2200ºC (Ar)

Acknowledgements

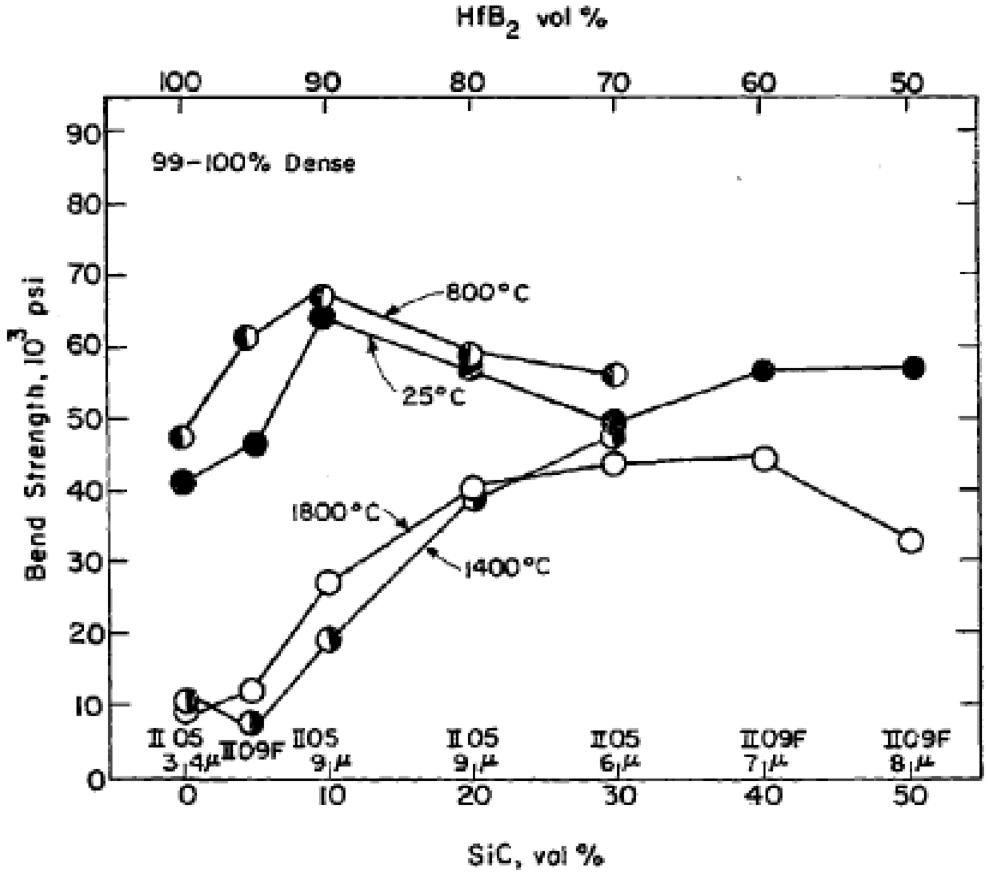
- **Thermal property studies**
  - Dr. Matt Thompson, now at St. Gobain-Norpro
  - Greg Harrington, PhD candidate
  - Jason Lonergan, PhD student
- **Mechanical property studies**
  - Prof. Jeremy Watts, now a Research Professor at Missouri S&T
  - Eric Neuman, PhD candidate

Conclusions

- UHTC community needs to be testing properties to "ultra-high" temperatures
  - We must report processing procedures, grain size(s), impurities, other microstructural effects
- UHT test capabilities at Missouri S&T
  - Thermal diffusivity to 2800° C
    - well, perhaps to 2500° C
  - Electrical resistivity to 1200° C
    - Concept for increasing capability to 2000° C
  - Four-point bending to 2800° C
    - well, perhaps to 2600° C
  - Testing in a simulated hypersonic environment to 2800° C
    - well, perhaps we don't have this capability…or do we?

Mechanical Properties

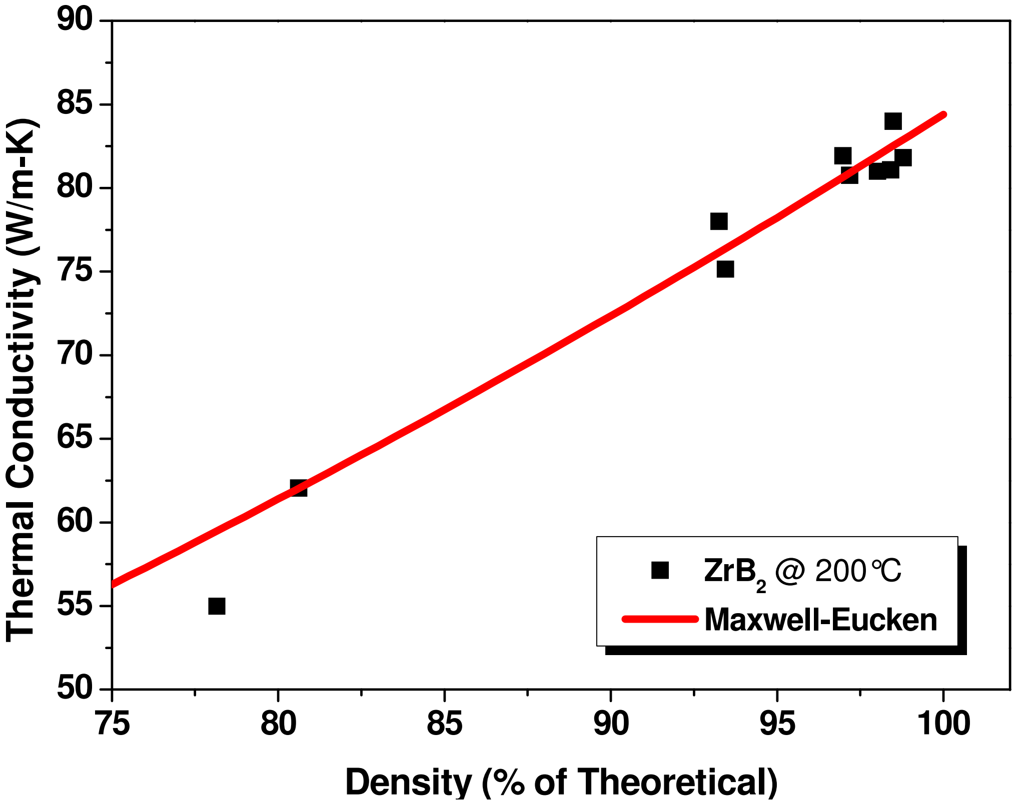
- Strength tested up to 1800° C
- Range of relative density values
- ZrB_2 and HfB_2
  - Nominally pure
  - SiC additions
  - Carbon additions
- Porosity reduces strength despite a decrease in grain size
- SiC reduces grain growth
- Carbon improves resistance to crack propagation and reduces elastic modulus



50 ksi ≈ 350 MPa

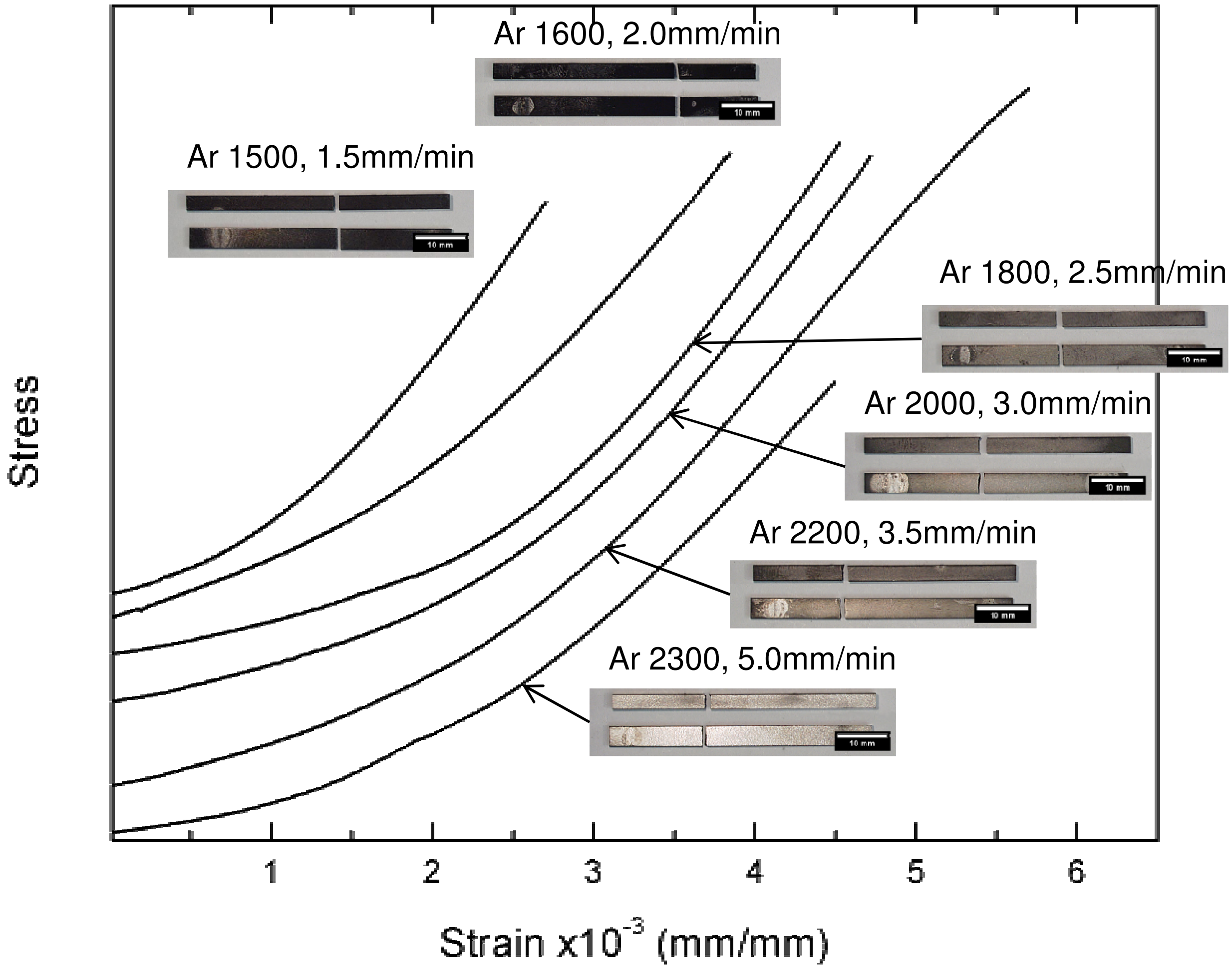
W.H. Rhodes, E.V. Clougherty, and D. Kalish "Research and Development of Oxidation-Resistant Diborides: Mechanical Properties" AFML-TR-68-190 Part II, Vol IV.

λ vs. Density



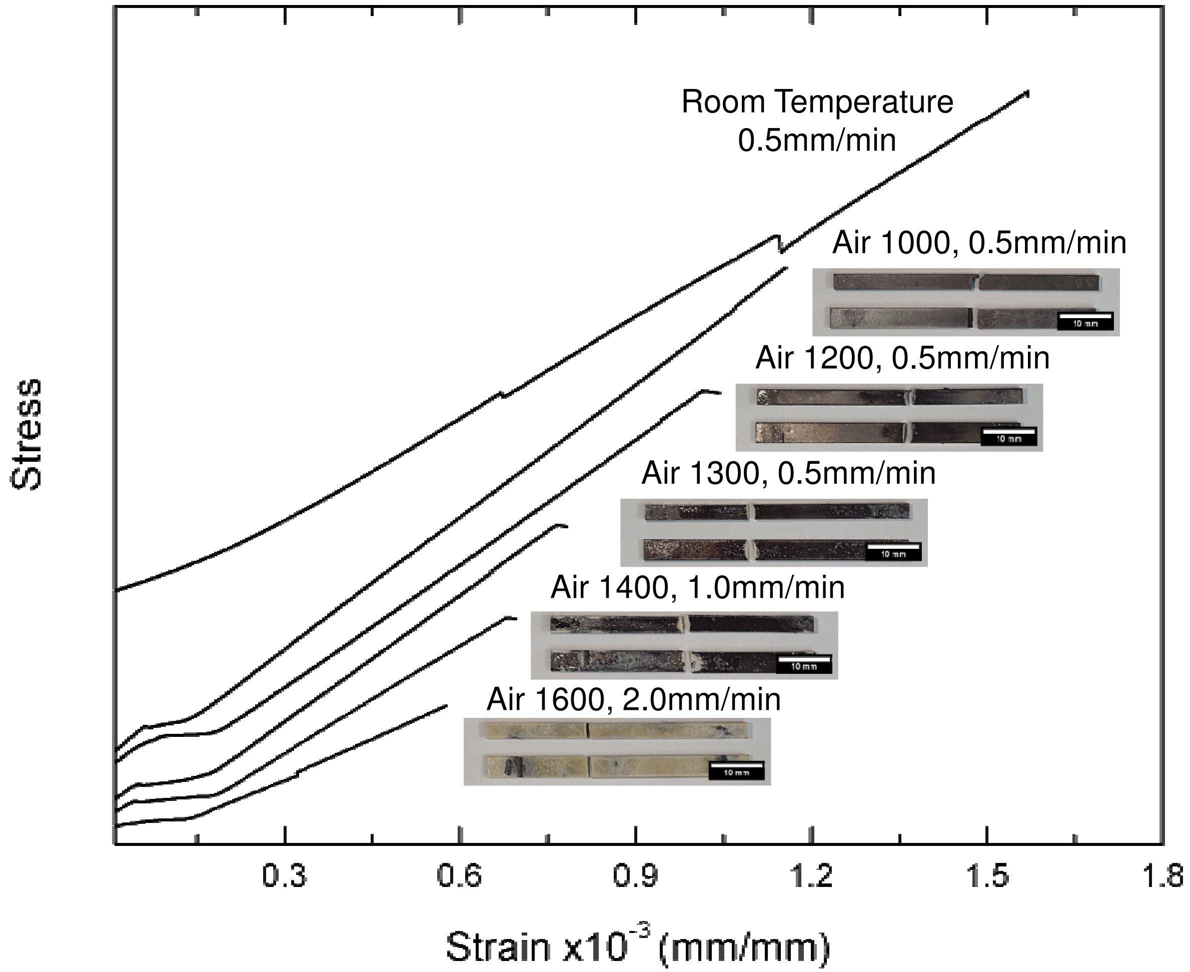
- Density a large factor in thermal conductivity
  - Has to be accounted for when researching affects of other variables
  - Can be corrected using Maxwell-Eucken equation
- Maximizing density is crucial for obtaining highest conductivity
- Depending on mechanical requirements density can be used to lower conductivity for specific applications

Argon Stress-Strain Curves



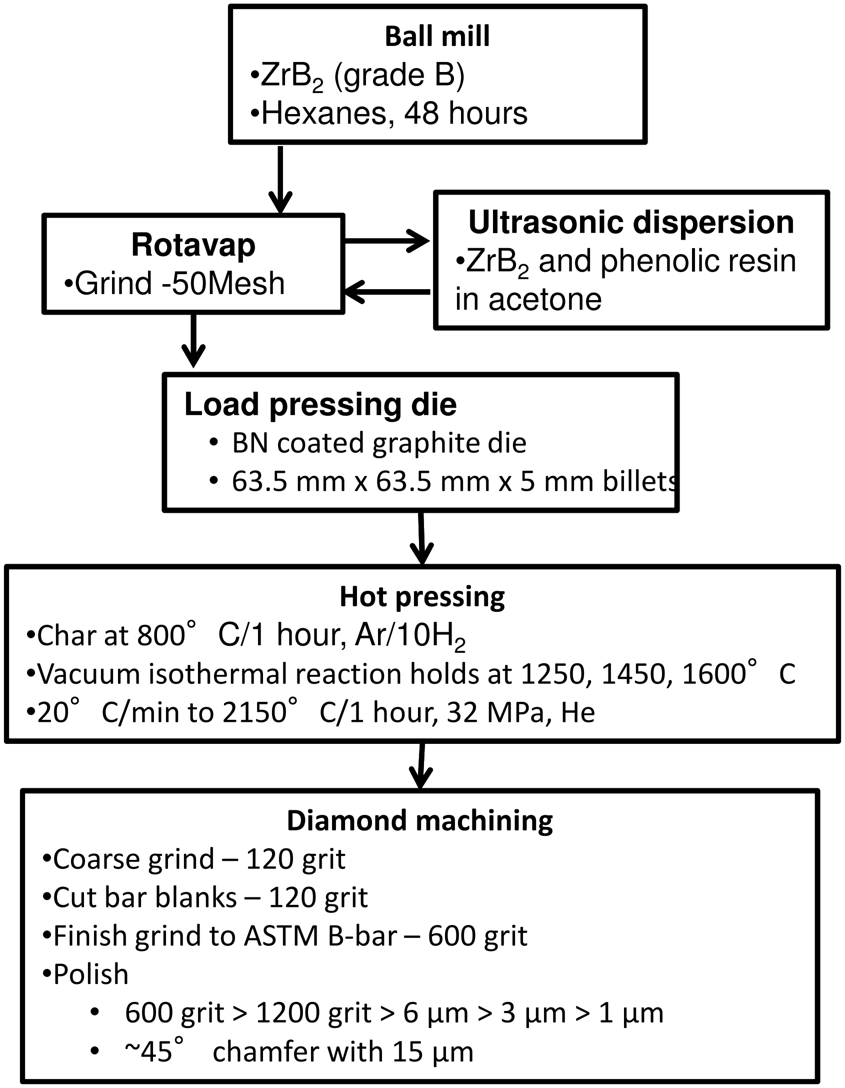
- **No visible oxidation scale**
- **Linear elastic failure**
  - **Test curves for samples tested in argon are not compliance corrected**

Stress-Strain Curves



- **Linear elastic failure for all temperatures**
  - **No bending observed in bars after testing**
- **Significant oxidation damage visible at 1400 and 1600° C**

ZrB$_2$ + 0.5 wt% C Processing



Ball mill
- ZrB$_2$ (grade B)
- Hexanes, 48 hours

Rotavap
- Grind -50Mesh

Ultrasonic dispersion
- ZrB$_2$ and phenolic resin in acetone

Load pressing die
- BN coated graphite die
- 63.5 mm x 63.5 mm x 5 mm billets

Hot pressing
- Char at 800° C/1 hour, Ar/10H$_2$
- Vacuum isothermal reaction holds at 1250, 1450, 1600° C
- 20° C/min to 2150° C/1 hour, 32 MPa, He

Diamond machining
- Coarse grind – 120 grit
- Cut bar blanks – 120 grit
- Finish grind to ASTM B-bar – 600 grit
- Polish
  - 600 grit > 1200 grit > 6 µm > 3 µm > 1 µm
  - ~45° chamfer with 15 µm

- Density
  - Archimedes method (ASTM C373-88)
- Grain Size
  - Etched Na$_{0.5}$K$_{0.5}$OH, ~300° C, ~1s
  - Image analysis, >2000 grains
- Flexural Strength
  - Ambient (ASTM C1161-02c)
  - Elevated temperature (ASTM C1211-02c)
    - Air
      - TEOS sol coated, heat treated to 700° C/1hour in air, repeated 4x
      - 10° C/min to temperature, hold for 10 min
    - Argon
      - 100° C/min to 200° C below temperature, then 50° C/ min to temperature, hold for 5 min
  - ASTM B-bar configuration, 4-point bend, fully articulated fixture
  - Variable crosshead speed

Conclusions

- **Thermal Properties**
  - Thermal conductivity of “phase-pure”, dense ZrB_2 is:
    - 110 W/m•K at RT and 55 W/m•K at 2000° C
  - SiC additions decrease thermal conductivity ZrB_2 is:
    - 110 W/m•K at RT and 55 W/m•K at 2000° C

- **Mechanical Properties**
  - Flexure strength of ZrB2-30%SiC: