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Ultra-High Temperature Mechanical Properties of Zirconium Diboride-Based Ceramics

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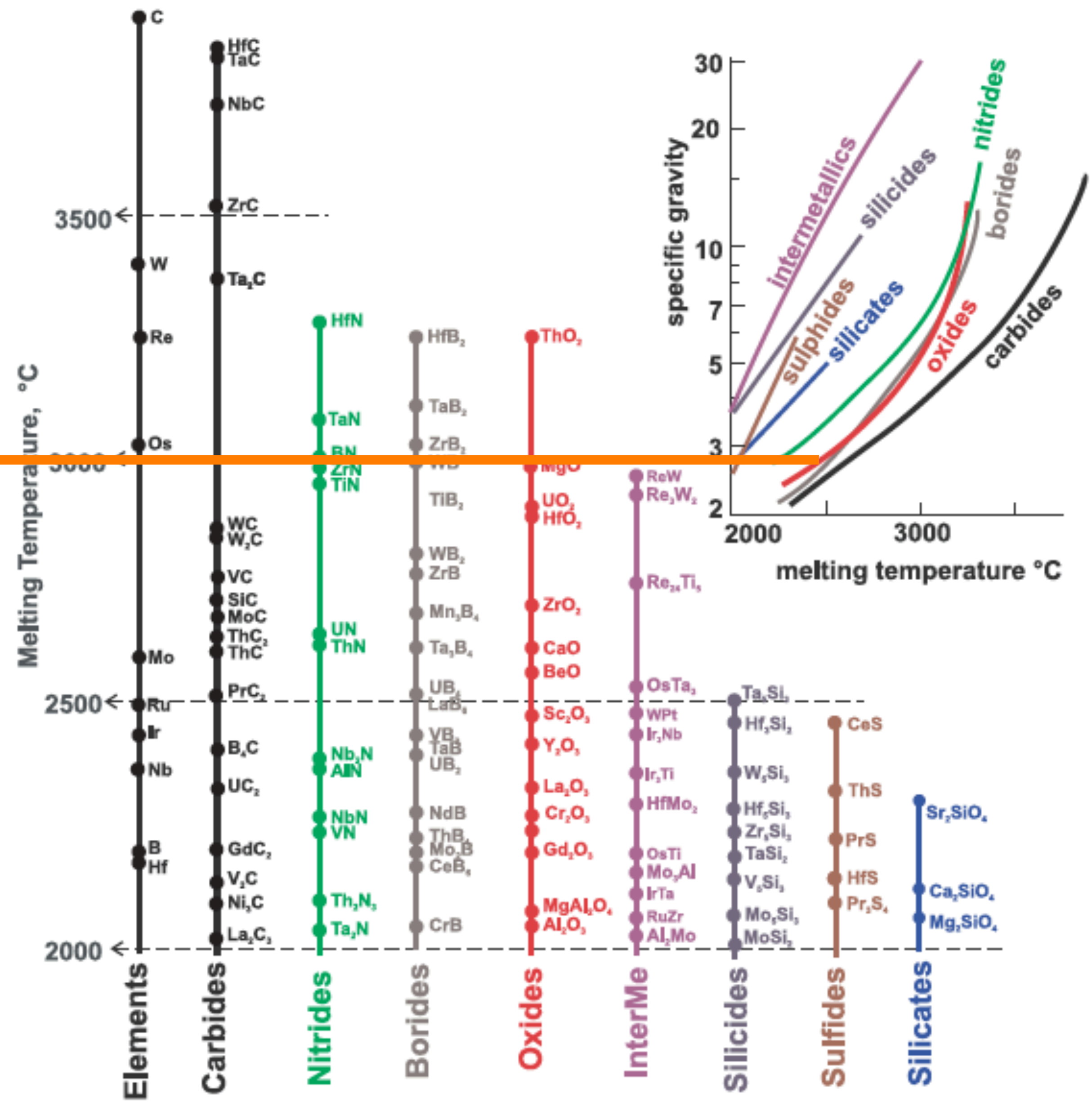
Acknowledgement

- Dr. Eric Neuman
    - Dissertation research
- – Drs. Jeremy Watts, Harlan Brown-Shaklee, and Eric Neuman
    - Building UHT mechanical testing system
- This project was funded by the U.S. Air Force Office of Scientific Research Aerospace Materials for Extreme Environments Program Grant number FA9550-09-1-0168

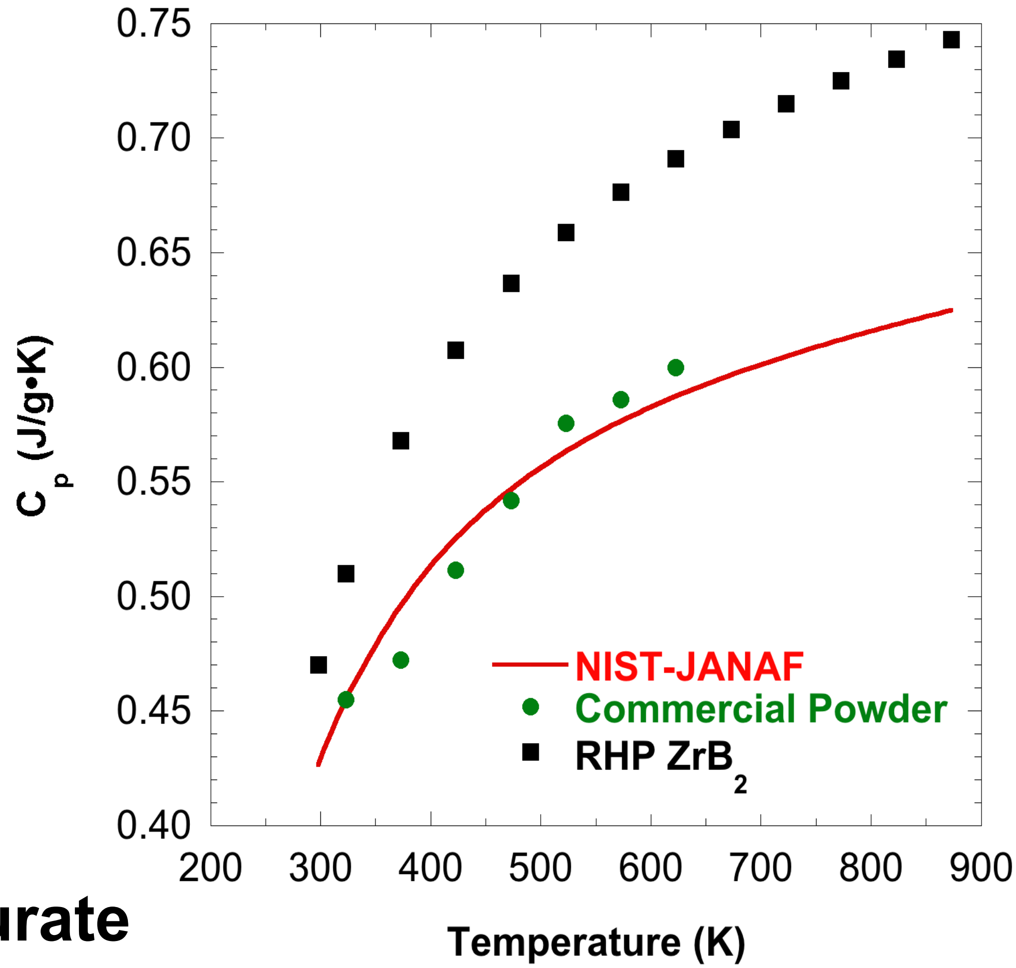
High Melting Temperature Materials



S.V. Ushakov and A. Navrotsky, “Experimental Approaches to Thermodynamics above 1500°C,” Journal of the American Ceramic Society, 95(5) 1463-1482 (2012).

Motivation and Purpose

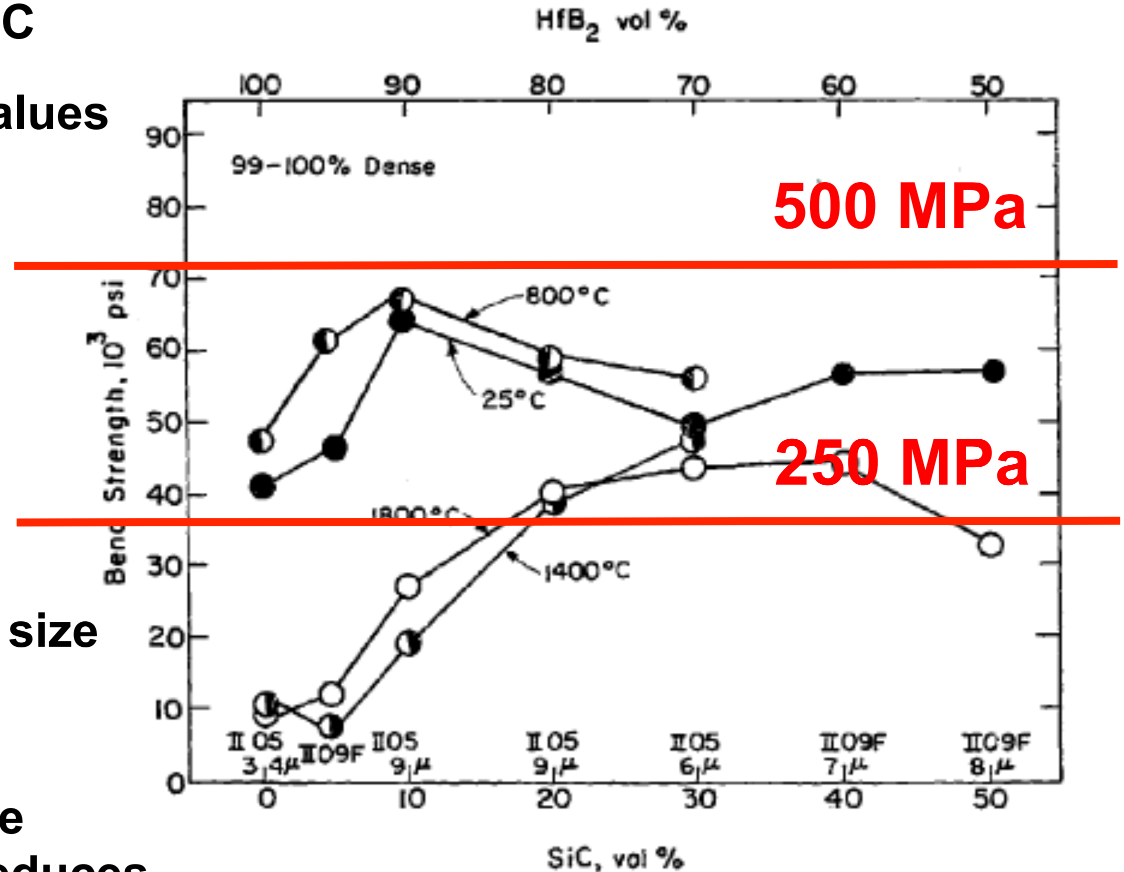
- Intrinsic properties
  - Measuring is simple conceptually, but difficult in practice
- Thermal conductivity
  - Impurity effects
  - Lack of single crystals
- Heat capacity
  - Historic data are inaccurate



Systematically study the mechanical behavior of ZrB_2-based ceramics at ultra-high temperatures

Historic Strength Studies

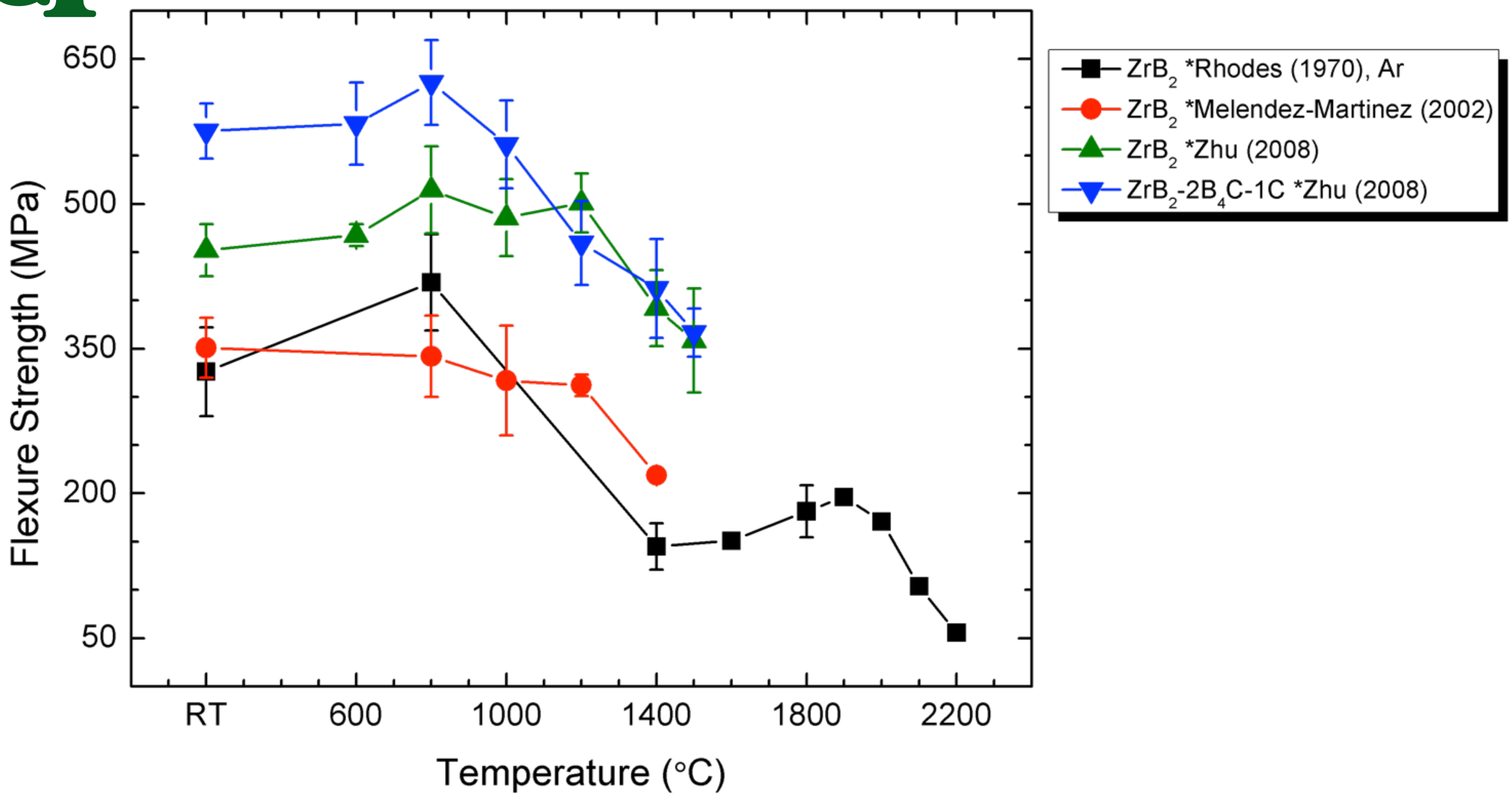
- Strength tested up to 2200°C
- Range of relative density values
- ZrB_2 and HfB_2
  - Nominally pure
  - SiC additions
  - Carbon additions
- Porosity reduces strength despite a decrease in grain size
- SiC reduces grain growth
- Carbon improves resistance to crack propagation and reduces elastic modulus



50 ksi ≈ 350 MPa

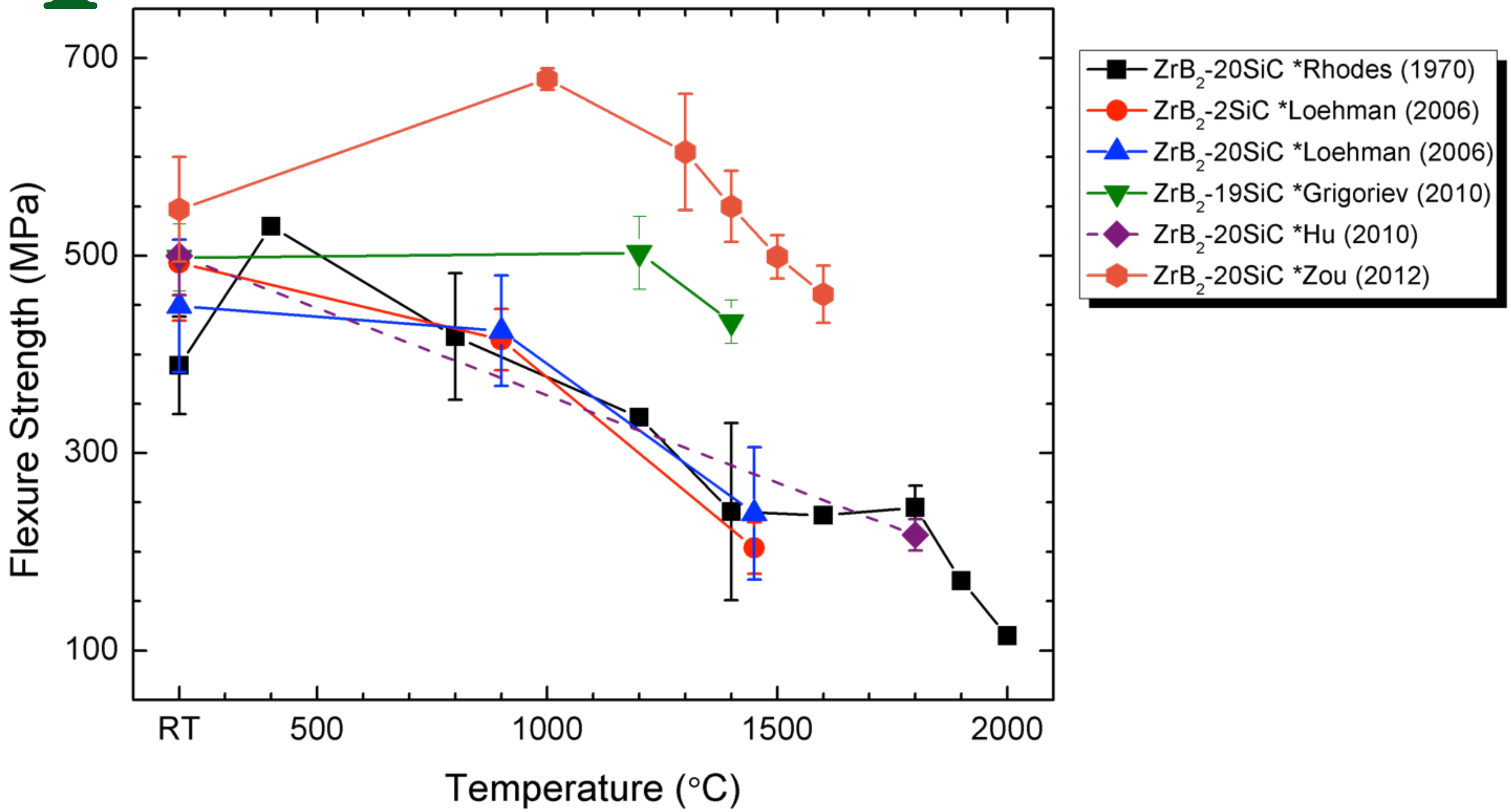
W.H. Rhodes, E.V. Clougherty, and D. Kalish "Research and Development of Oxidation-Resistant Diborides: Mechanical Properties" AFML-TR-68-190 Part II, Vol IV.

ZrB_2 Strength vs. Temperature



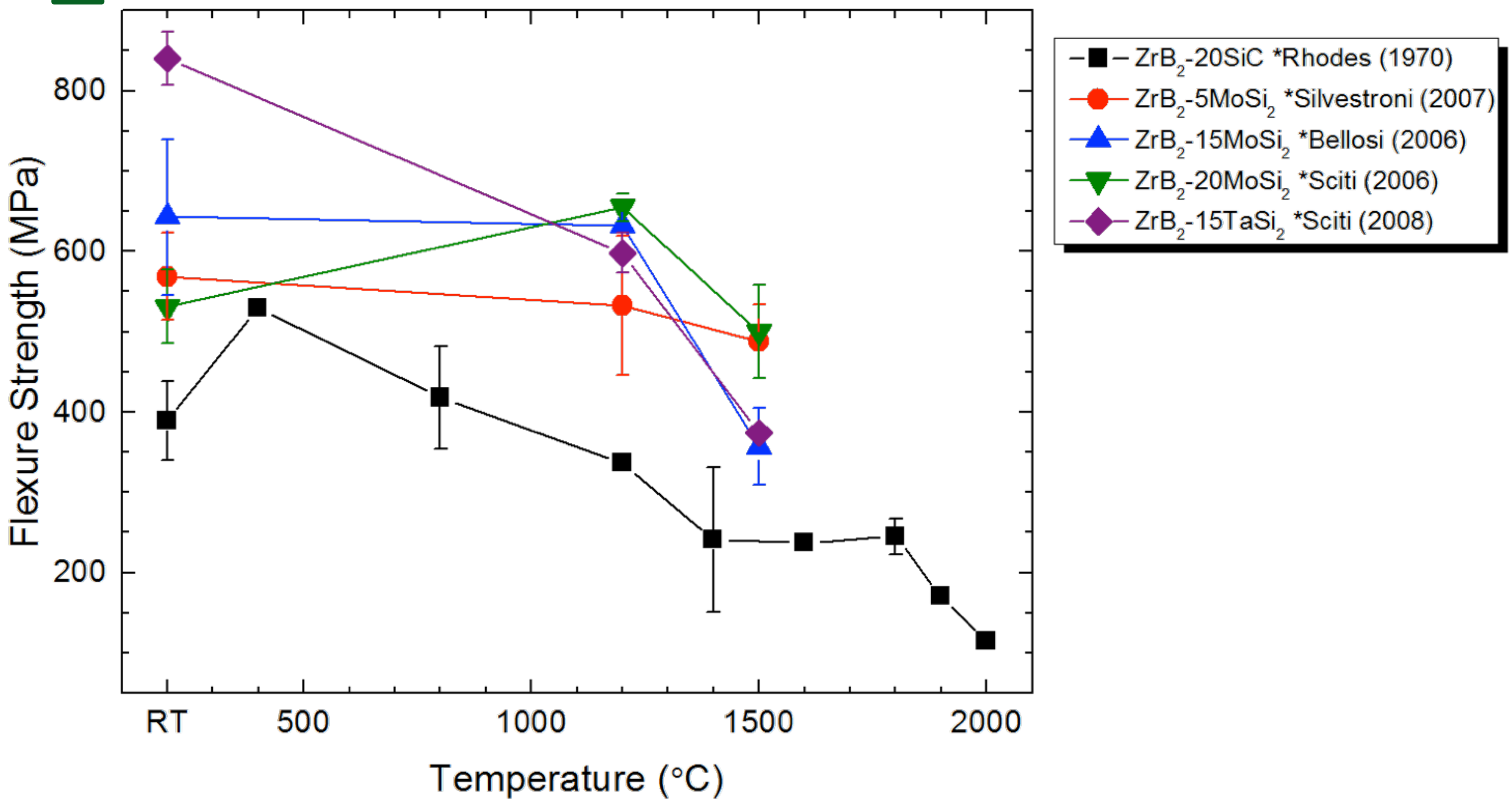
- **Limited studies of ZrB_2 at elevated temperatures**
- **ZrB_2 strength decreases as grain size increases**
- **Diffusional creep limits strength at the highest temps**

ZrB_2-SiC vs. Temperature



- More studies than pure ZrB_2, but few over 1600°C
- ZrB_2-SiC eutectic at 2270°C limits upper use temperature

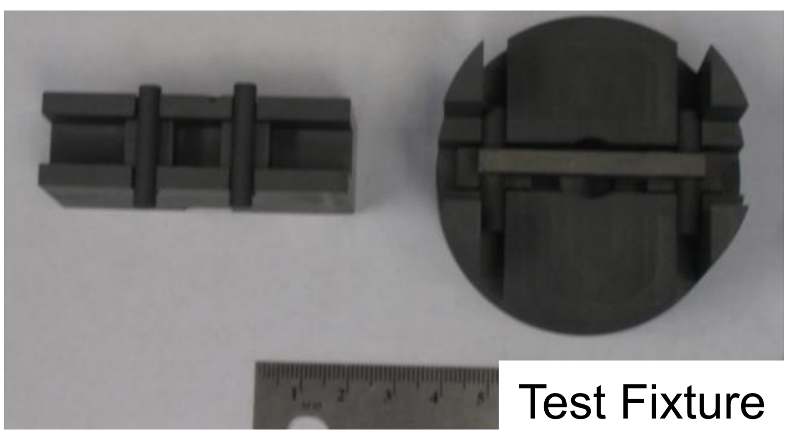
ZrB_2-Disilicide vs Temperature



- **Disilicide additions can improve strength compared to SiC**
- **No studies of ZrB_2 with silicides above 1500°C**
- **Use limited by T_{melt} ($MoSi_2$ - 2030°C; $TaSi_2$- ~2200°C)**

UHT Mechanical Test System

- Instron 33R4204 load frame
- Custom-built environmental chamber
  - Inert atm or mild vacuum
  - ~10^{-14} atm pO_2 using Ar
- Induction heating system
  - Capable of 2600°C
  - Heating rate of 100's°C/min
- Graphite load train and test fixture
- Testing limited by phase stability
  - Ex: ZrB_2-C eutectic at 2370°C



Test Fixture

*Neuman, et al., *Am. Ceram. Soc. Bull*., **92**[1] 36-38 (2013)

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Processing

ZrB_2

Ball mill
ZrB_2 (H.C. Starck, Grade B)
Hexanes, 48 hrs, WC media

Ultrasonic dispersion
0.5 wt% C (Phenolic resin)
Acetone

Hot pressing
Char at 800°C/1 hour, Ar/10H_2
Vacuum hold:1250, 1450, 1600°C
2150°C, 1 hr, 32 MPa, He

ZrB_2-30SiC

Ball mill
ZrB_2 (H.C. Starck, Grade B)
30 vol% SiC (H.C. Starck, UF-10)
2 wt% B_4C (H.C. Starck, HD-20)
Acetone, BYK-110, 48 hrs, WC media

Rotary evaporate
Grind -50 Mesh

Hot pressing
Vacuum holds: 1450, 1650°C
1950°C, 10 min, 32 MPa, Ar

Testing and Characterization
Microstructure (SEM)
Flexural Strength (ASTM C1161-02c, C1211-02c)
- B-bar, 4-pt-¼-pt

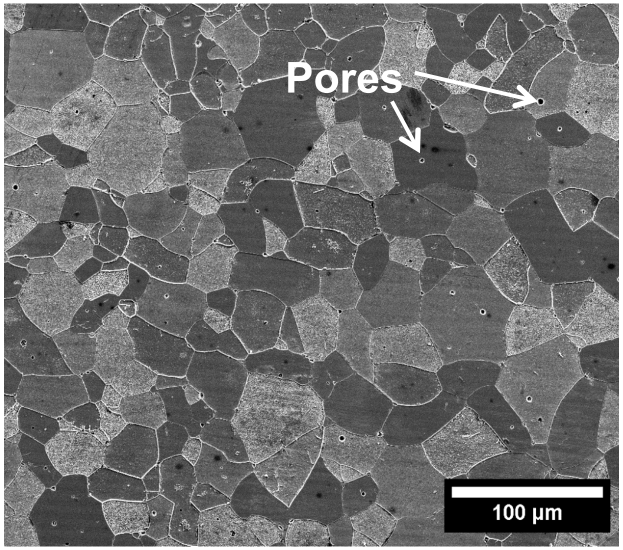
Fracture Toughness (ASTM C1421-01b)
- Chevron-notch A-bar

All elevated temperature testing performed in Ar

Room for improvement?

Microstructures

ZrB_2



99.2% dense

Grain size: 19.7 ± 13.0 µm

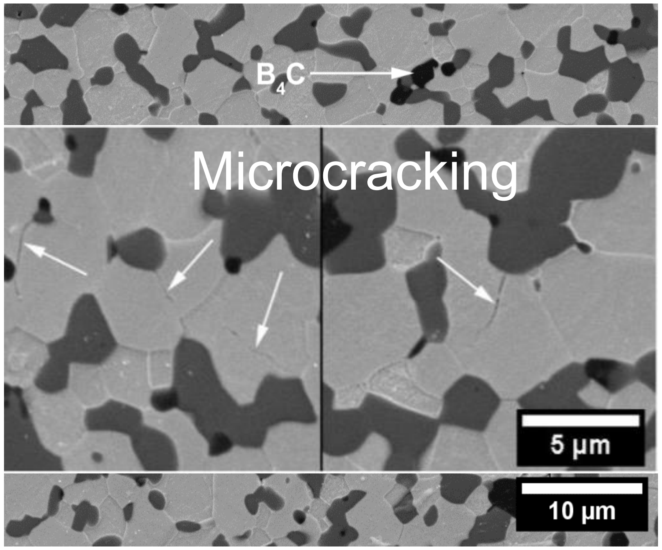
Held at 2150°C for 1 hr

– Grow grains and reduce creep above 1800°C

Minimal entrapped porosity

No residual carbon

ZrB_2-30SiC



>99.9% dense

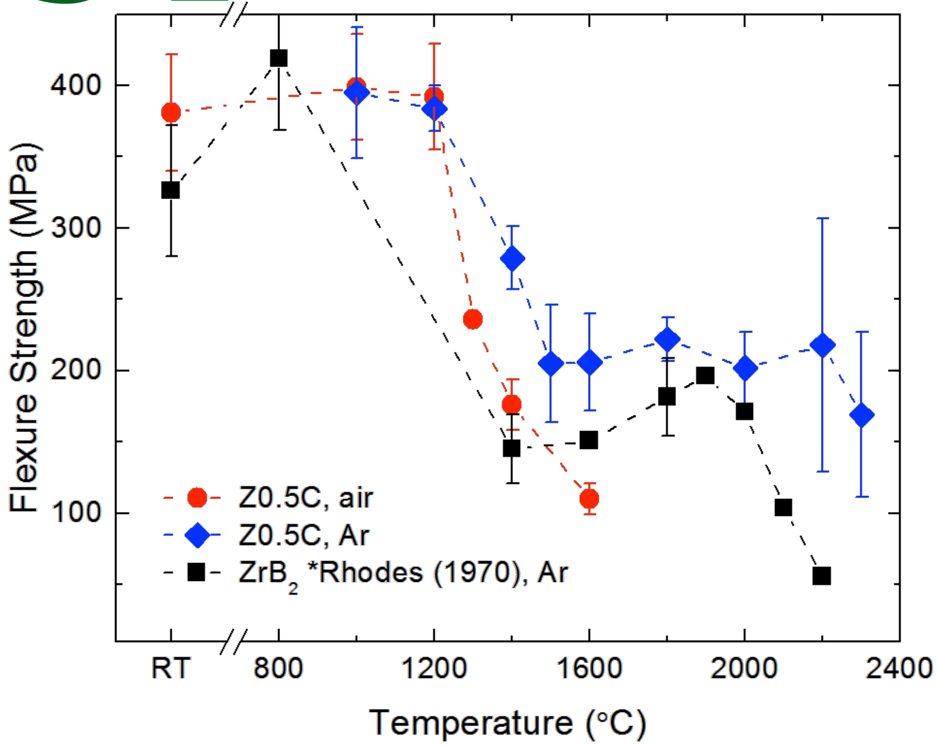
ZrB_2 grain size: 1.9 ± 0.9 µm

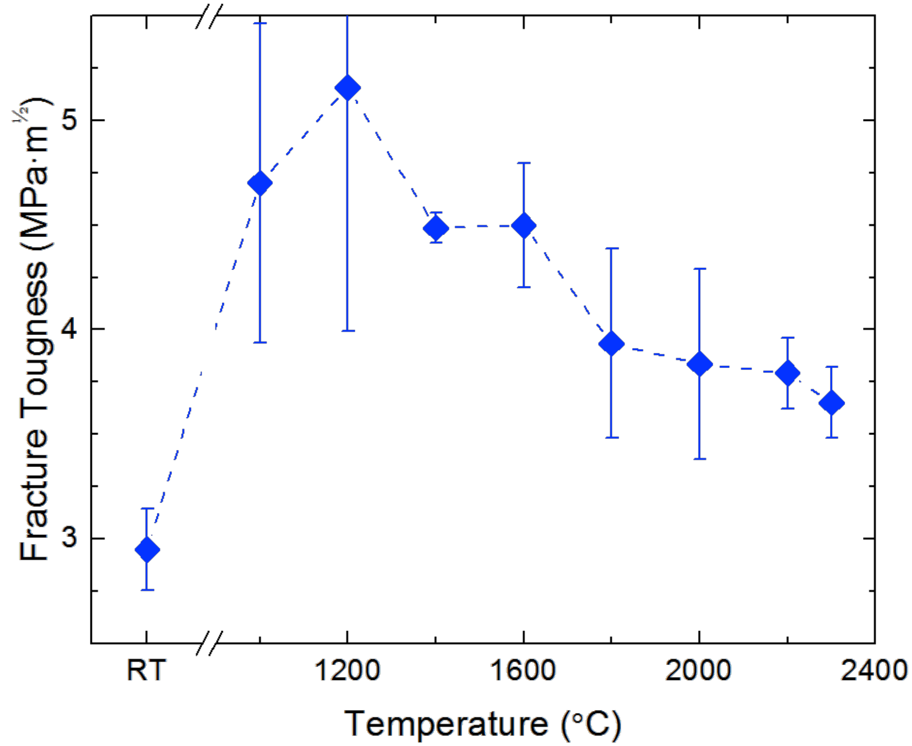
SiC cluster size: 6.1 ± 4.4 µm

Max SiC cluster size: 59.1 µm

Micrcracking threshold ~ 15 µm

ZrB_2 Strength and Toughness

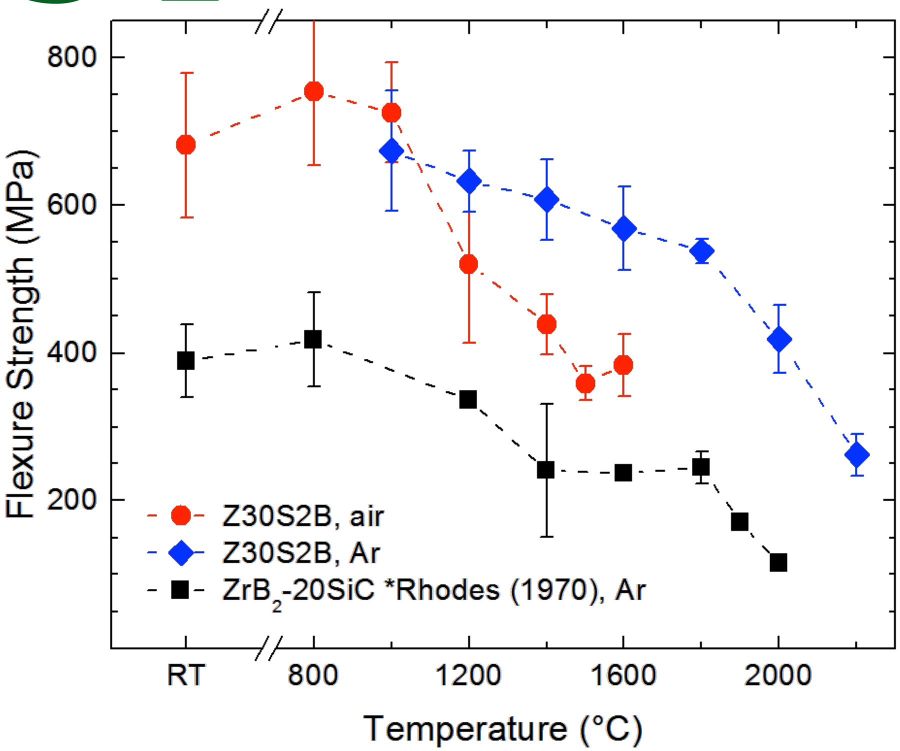


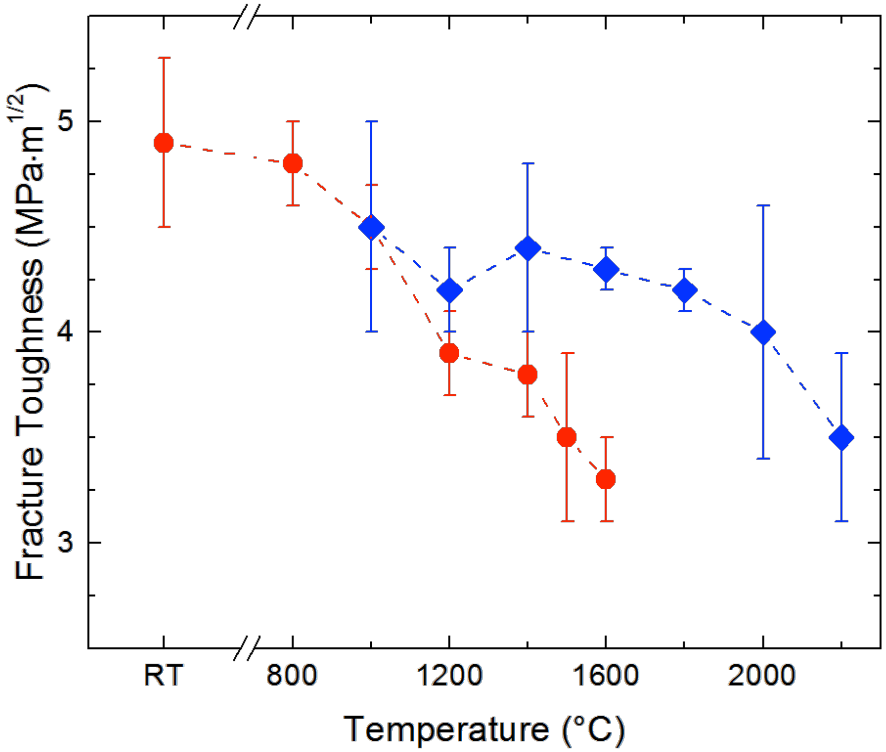


- **Air: Strength 300-400 MPa up to 1200°C, ~200 MPa above (oxidation)**
- **Inert: Strength stabilizes at ~200 MPa up to 2300°C (creep?)**
- **Critical flaw size consistent with grain size at elevated temperatures**
  - **Grain growth during tests at 2000°C and above**

Neuman, et al., *J. Am. Ceram. Soc.*, 96[1] 47-50 (2013)

ZrB_2-SiC Strength and Toughness

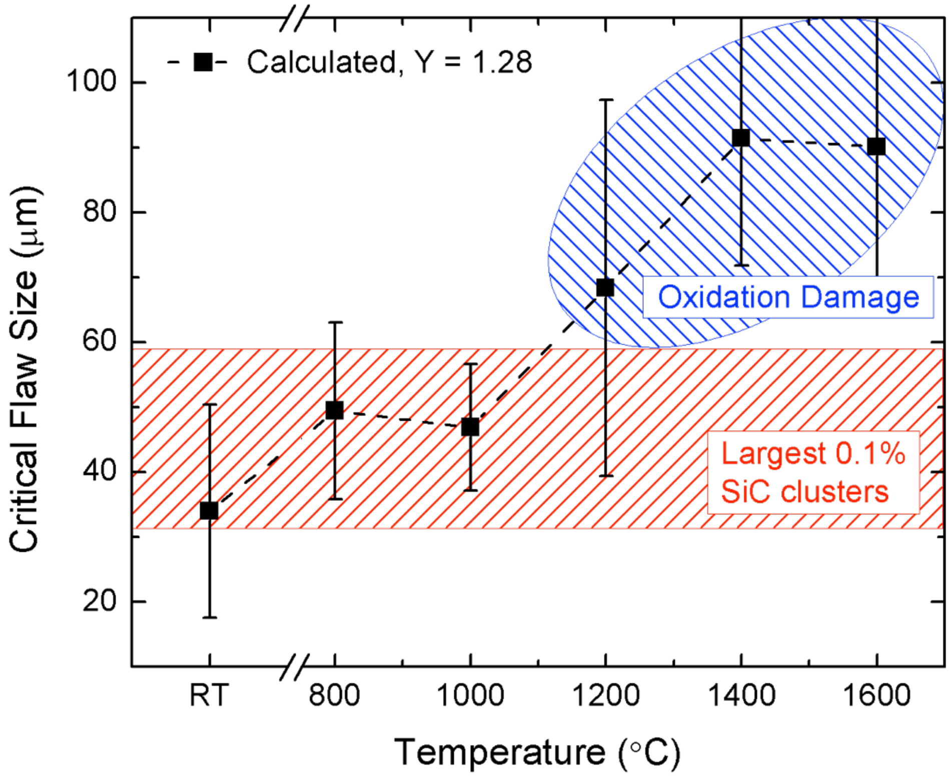


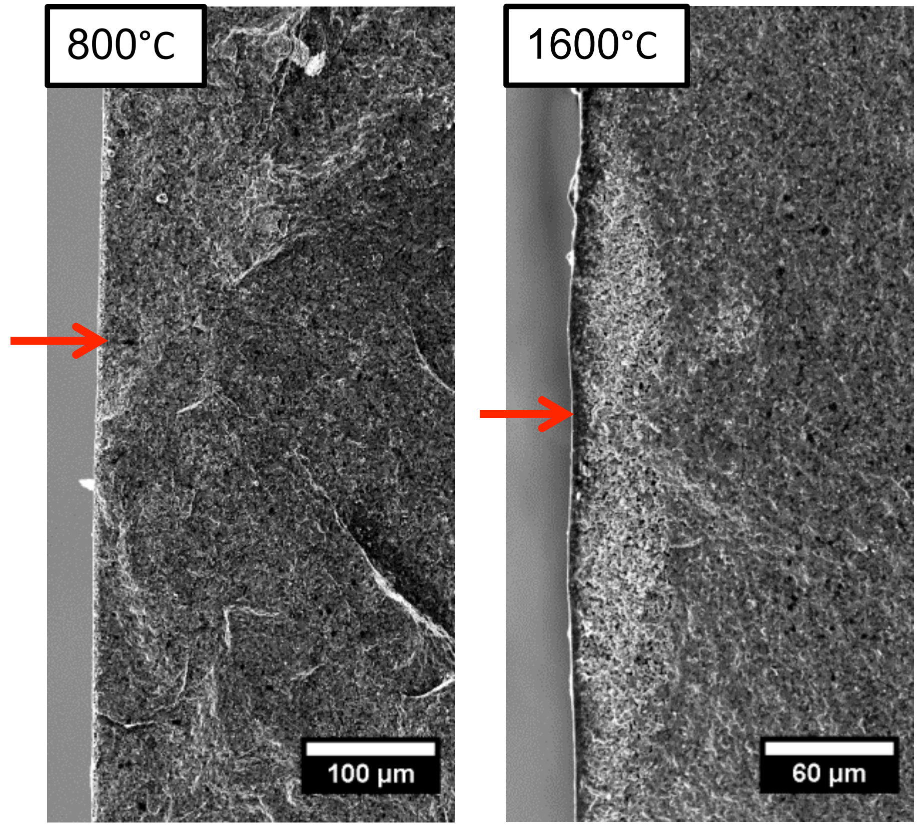


- **Air: σ increases ≤1000°C (flaw healing), decreases >1200°C (oxidation)**
- **Inert: σ >550 MPa up to 1800°C, decreases to 2200 MPa at 2200°C**
- **Both: K_{IC} decreases steadily from ~4 MPa•$m^{1/2}$ at RT to ~3.5 MPa•$m^{1/2}$**

Neuman, et al., *J. Euro. Ceram. Soc.*, 33[15-16] 2889-2899 (2013)
Neuman, et al., *J. Euro. Ceram. Soc.*, 35[2] 463-476 (2014)

ZrB_2-SiC Failure Analysis

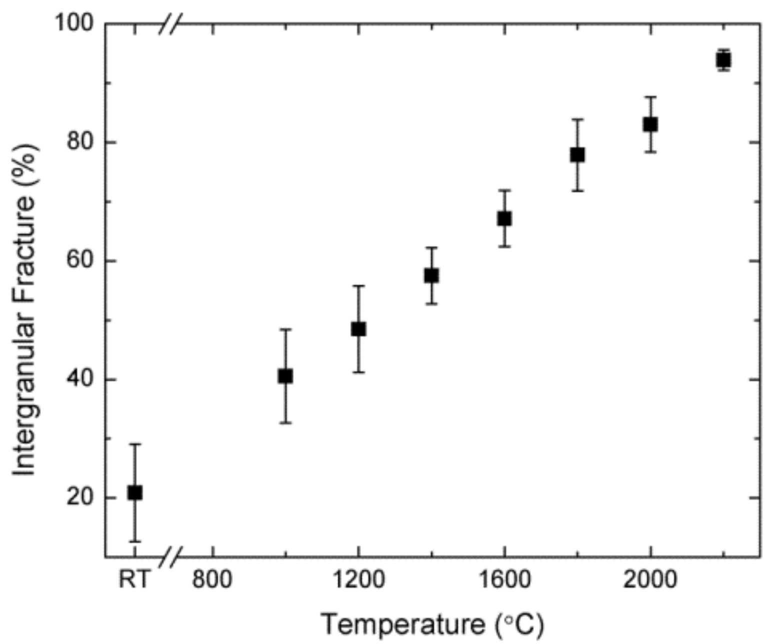


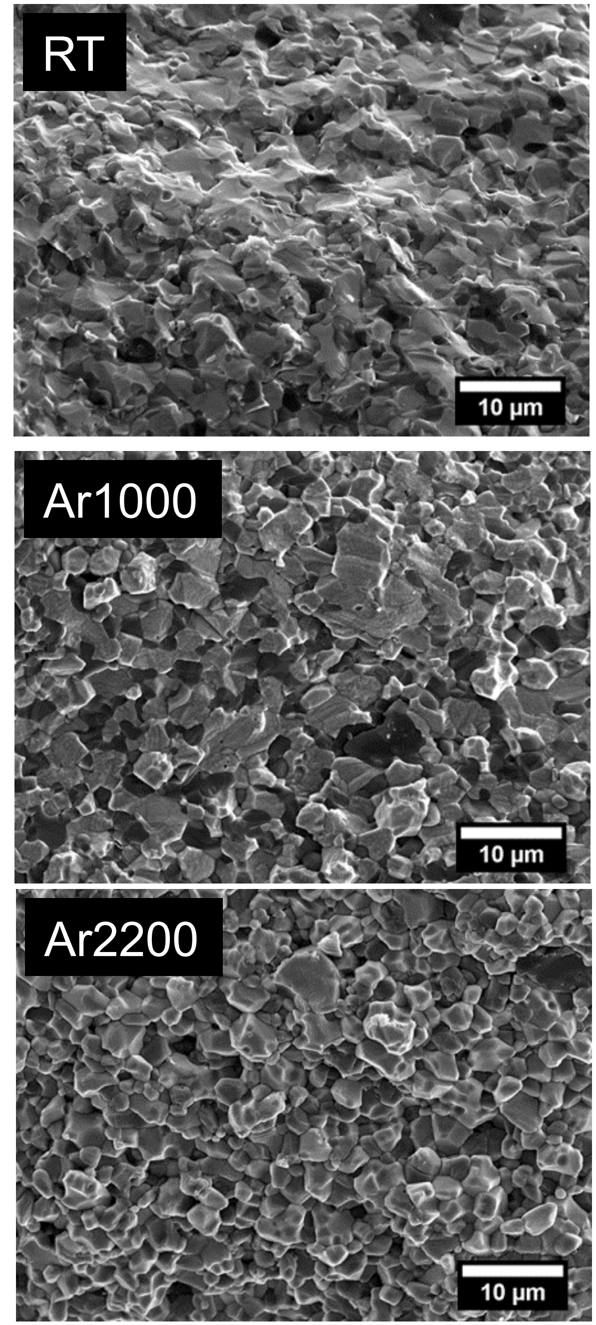


- **Below 1000°C, SiC clusters are the critical flaw**
- **Oxidation damage controls strength at ≥1200°C (3 pt. bending of bar halves)**
- **Observed fracture origins are consistent with size of calculated critical flaws**
- **Improve strength by reducing SiC cluster size or reducing oxidation damage**

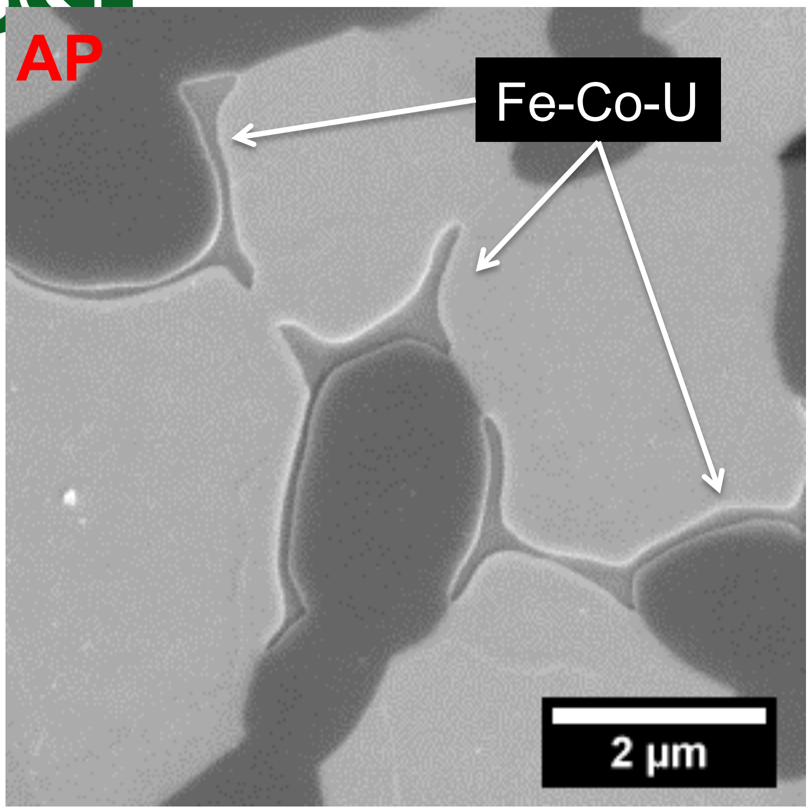
ZrB_2-SiC Fracture in Argon

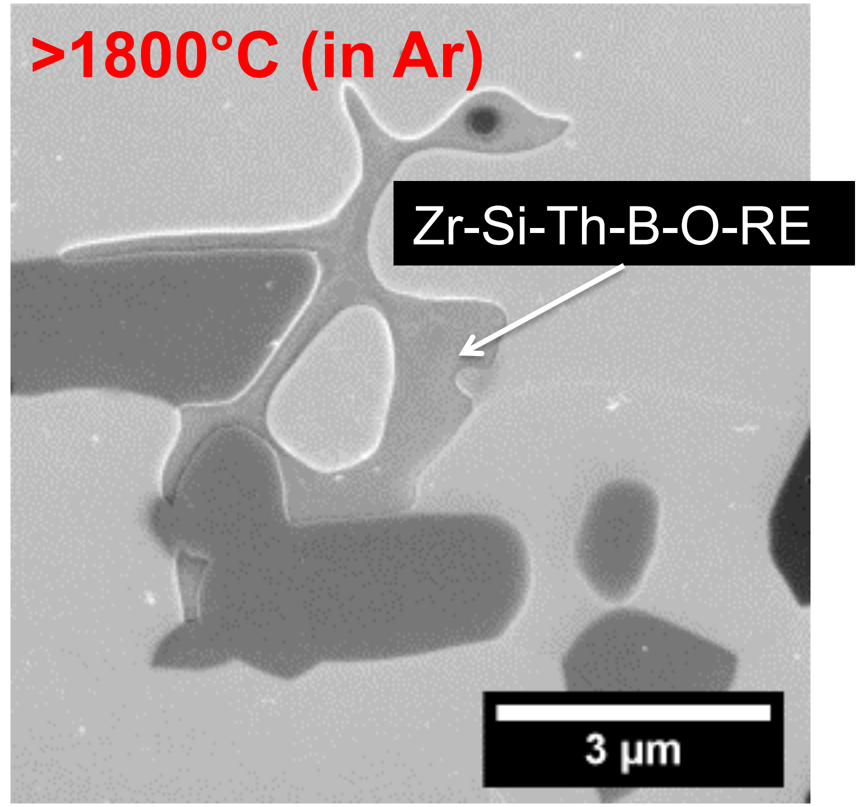
- ~20% intergranular fracture at RT
- Fraction steadily increases with temperature
  - Trend contrary to historic reports
  - SiC cluster size grows >1800°C
- Lower temp. tests do not predict UHT strength





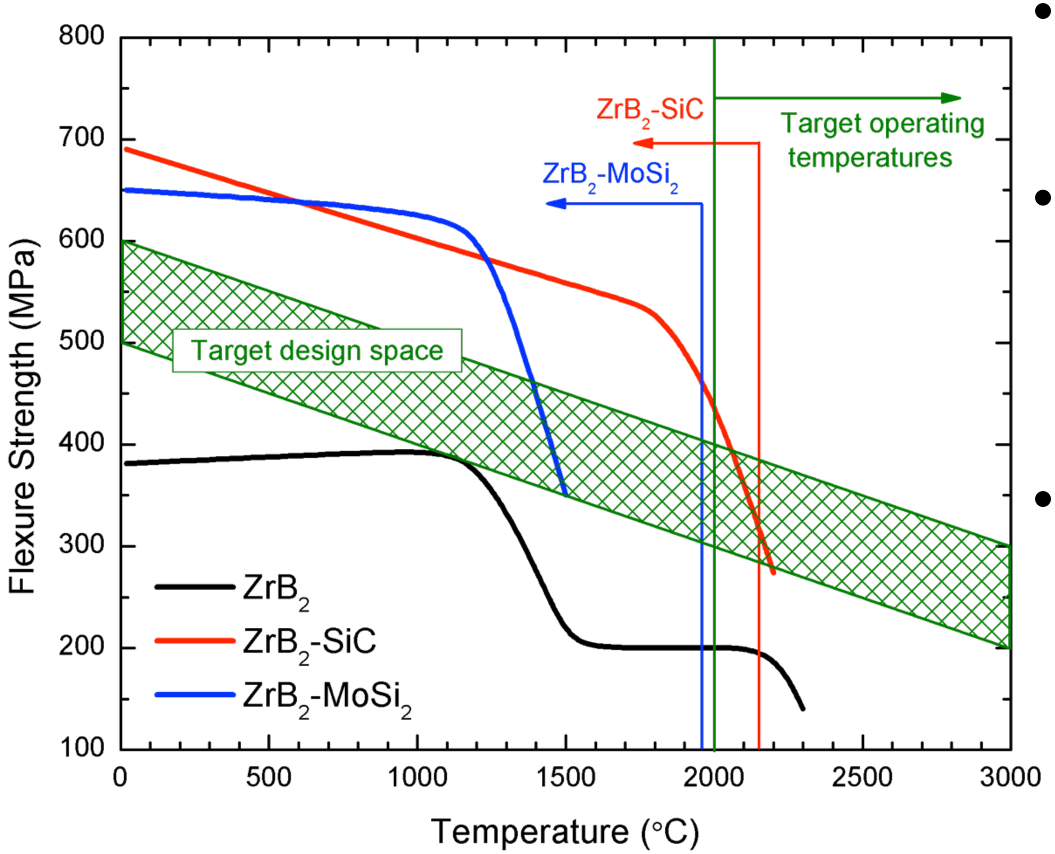
Oxide Impurity Phases





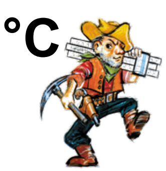
- Fe, Co, U containing phase present following hot pressing
  - Appears wetting to both ZrB_2 and SiC
  - Possibly a silicide phase – Reduction of SiC by Fe and Co

Can We Increase Use Temperature?



What are we looking for?

- **Chemical stability at 2000°C+**
- **Second phase additions**
  - **Improve properties**
  - **Enhance densification**
- **Higher eutectic temps**
  - **ZrB_2 – SiC at 2270°C**
  - **ZrB_2 – ZrC at 2660°C**
  - **ZrB_2 – $ZrC_{0.88}$ at 2830°C**
  - **HfB_2 – $HfC_{0.9}$ at 3140°C**



Processing

ZrB_2

Ball mill
ZrB_2 (H.C. Starck, Grade B)
Hexanes, 48 hrs, WC media

Ultrasonic dispersion
0.5 wt% C (Phenolic resin)
Acetone

Hot pressing
Char at 800°C/1 hour, Ar/10H_2
Vacuum hold:1250, 1450, 1600°C
2150°C, 1 hr, 32 MPa, He

ZrB_2-30SiC

Ball mill
ZrB_2 (H.C. Starck, Grade B)
30 vol% SiC (H.C. Starck, UF-10)
2 wt% B_4C (H.C. Starck, HD-20)
Acetone, BYK-110, 48 hrs, WC media

Hot pressing
Vacuum holds: 1450, 1650°C
1950°C, 10 min, 32 MPa, Ar

ZrB_2-10ZrC

Ball mill
ZrB_2 (H.C. Starck, Grade B)
9.5 vol% ZrC (H.C. Starck, B)
0.1 wt% C (Phenolic resin)
1.2 mol% ZrH_2 (Chemetall, S)
MEK, BYK-110, 24 hrs, ZrB_2 media

Hot pressing
Char at 800°C/1 hour, Ar/10H_2
Vacuum hold: 1250, 1450, 1600°C
1900°C, 45 min, 32 MPa, Ar/10H_2

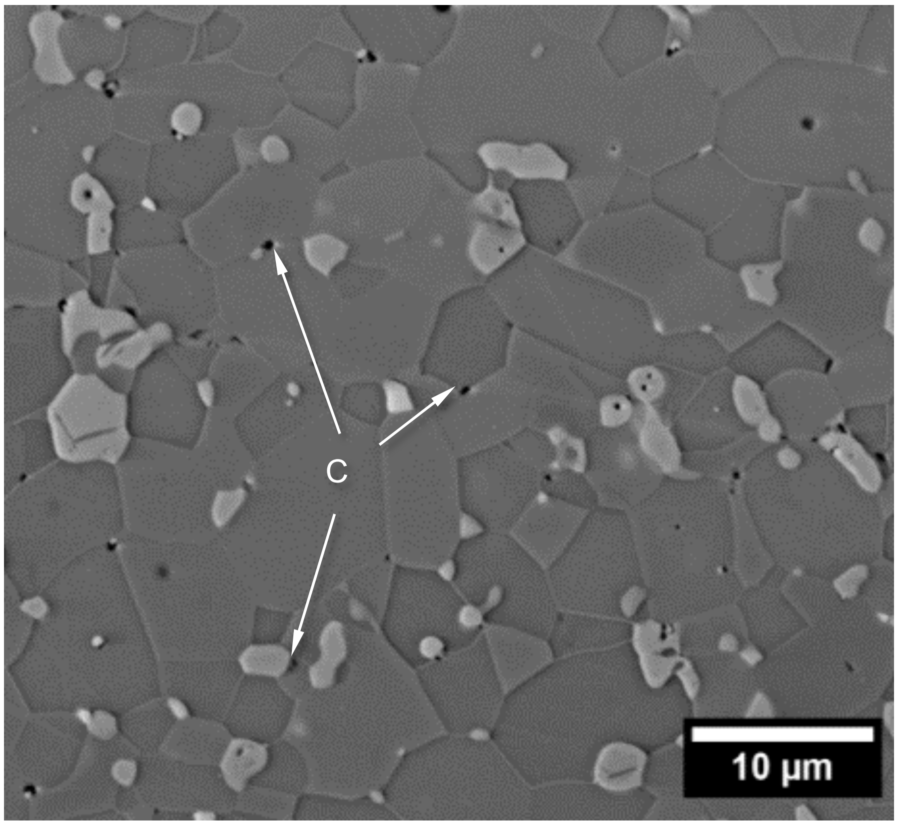
Rotary evaporate
Grind -50 Mesh

Testing and Characterization
Microstructure (SEM)
Flexural Strength (ASTM C1161-02c, C1211-02c)
- B-bar, 4-pt-¼-pt

Fracture Toughness (ASTM C1421-01b)
- Chevron-notch A-bar

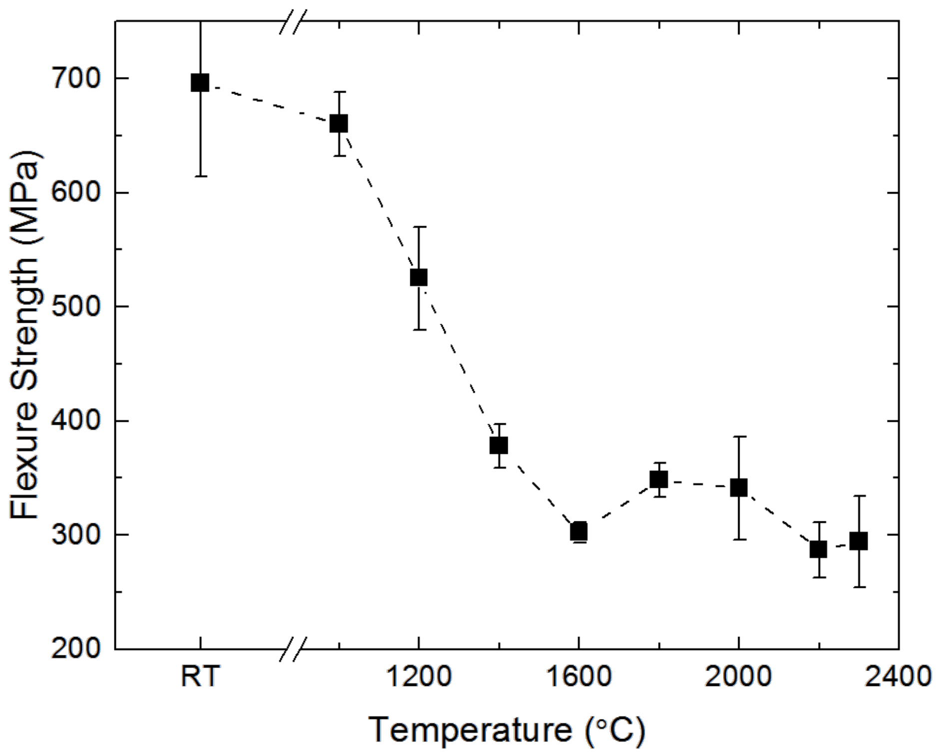
All elevated temperature testing performed in Ar

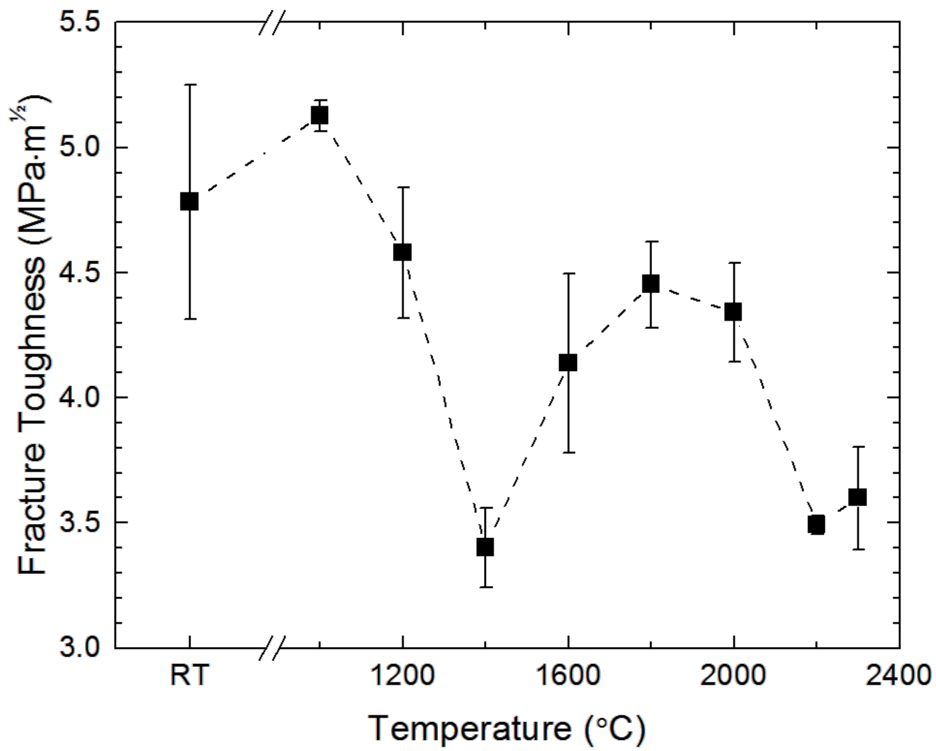
ZrB_2-10ZrC Microstructure



- >99% dense
- ZrB_2 grain size 4.9 ± 3.0 µm
- ZrC cluster size 1.8 ± 1.5 µm
- Max ZrC cluster 9.8 µm
- 9.5 ± 0.4 vol% ZrC
- 0.10 ± 0.02 vol% C
- 0.05 ± 0.02 vol% porosity

ZrB_2-ZrC Strength and Toughness

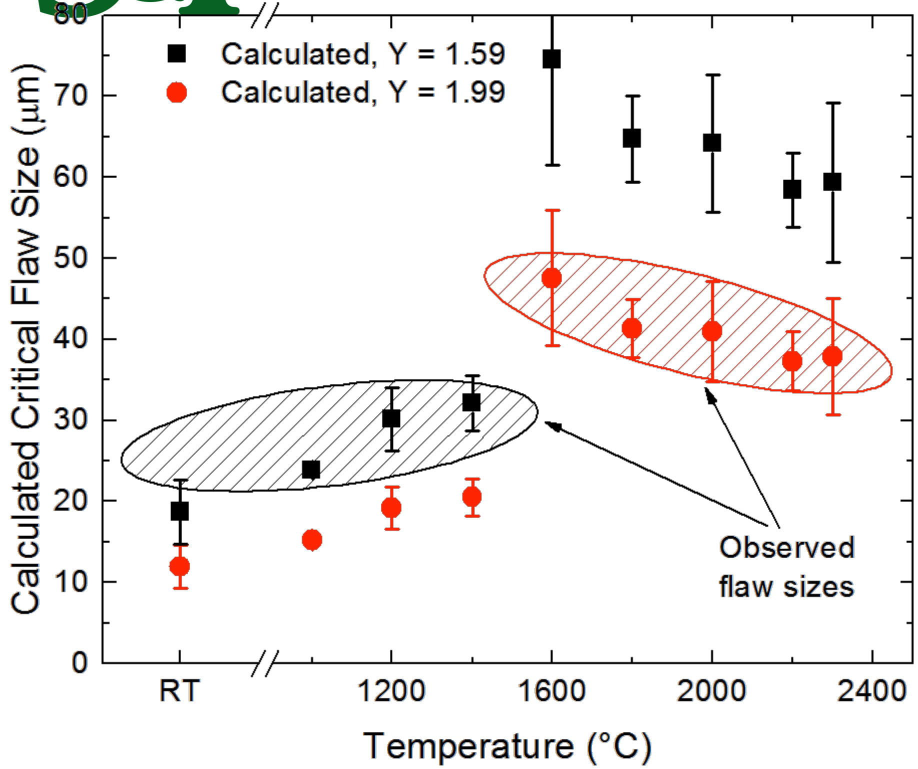


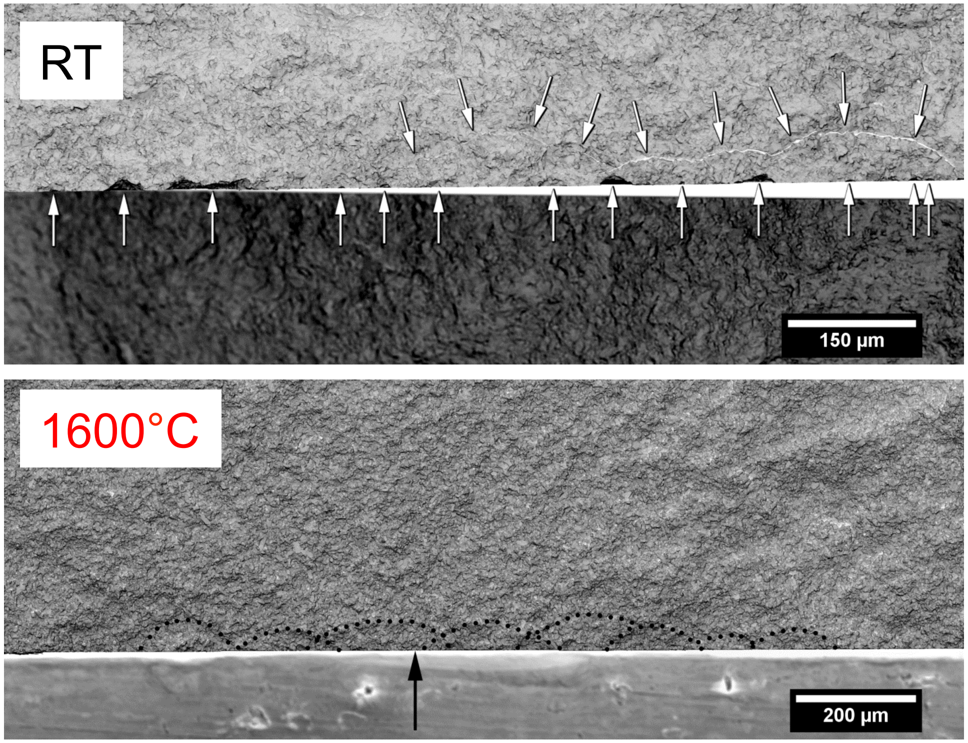


- **Strength decreases from ~700 MPa at 800°C to ~300 MPa at 1600°C**
  - **Maintains ~300 MPa up to 2300°C**
- **~4.5 MPam$^{1/2}$ at RT with no discernible trend**
  - **Minimum about temperature for relaxation of residual stresses**

Neuman, et al., *submitted*

ZrB_2-ZrC Failure Analysis

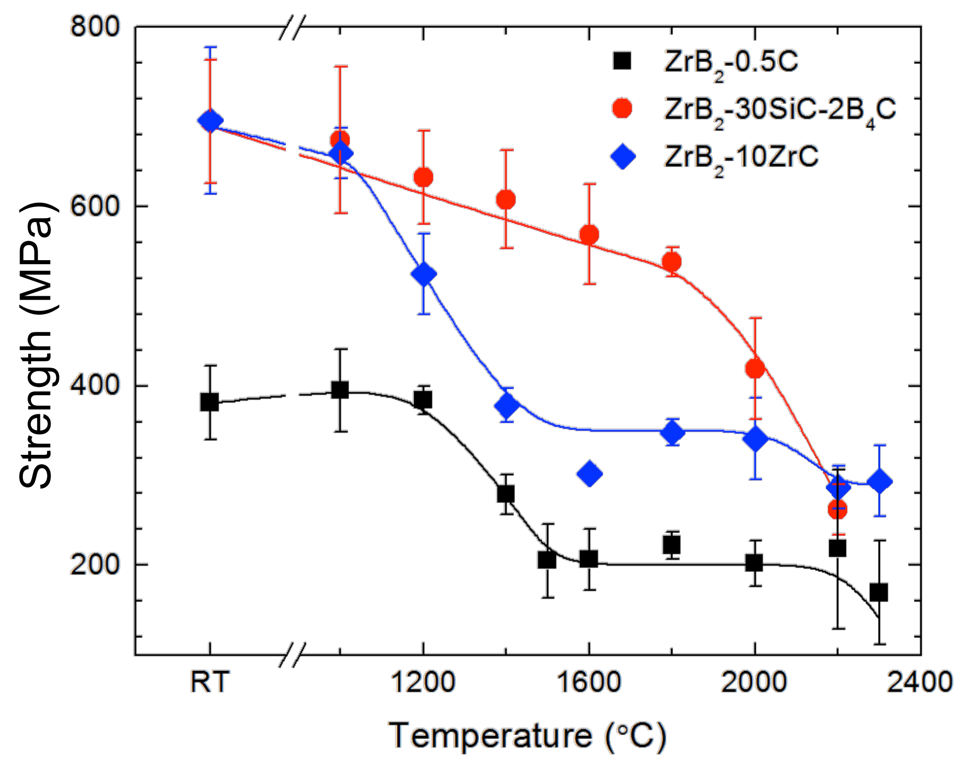




- **Two regimes of failure behavior**
  - **1400°C and below strength limited by machining damage**
  - **1600°C and above controlled by subcritical crack growth**
- **Both related to original flaw population induced by machining**

Can We Get Higher Strengths?

- **Materials**
  - Higher eutectic temperatures
  - HfB_2-HfC, (Hf,Ta)C, others?
- **Microstructures**
  - Fully dense, no microcracks
  - Grain size?? (creep vs σ)
  - No grain growth at UHT??
- **Impurities**
  - Eliminate undesired impurities (transition metals, oxides, etc.)
  - Effects of doping or pinning??



We have only scratched the surface for UHT structure-property relationship studies