Ultra-High Temperature Thermal and Mechanical Properties of Boride Ceramics

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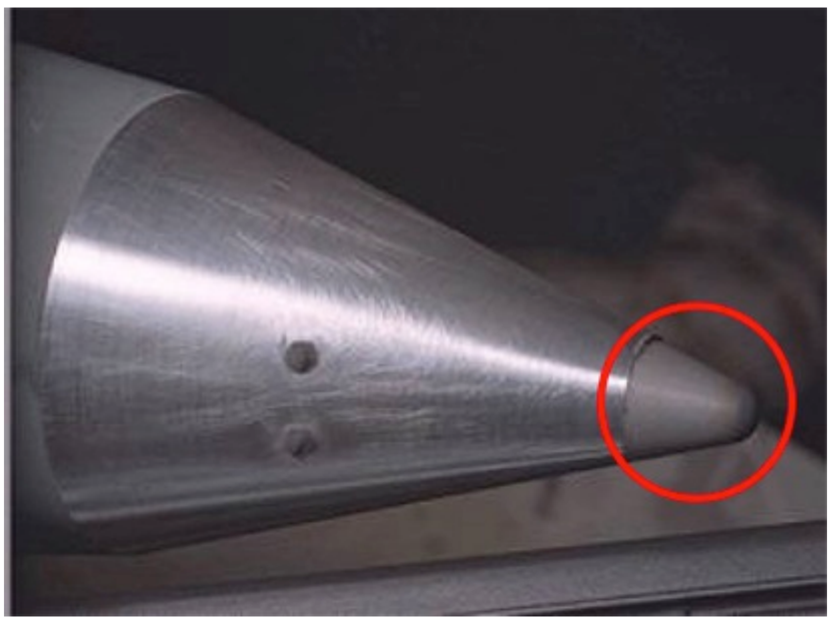
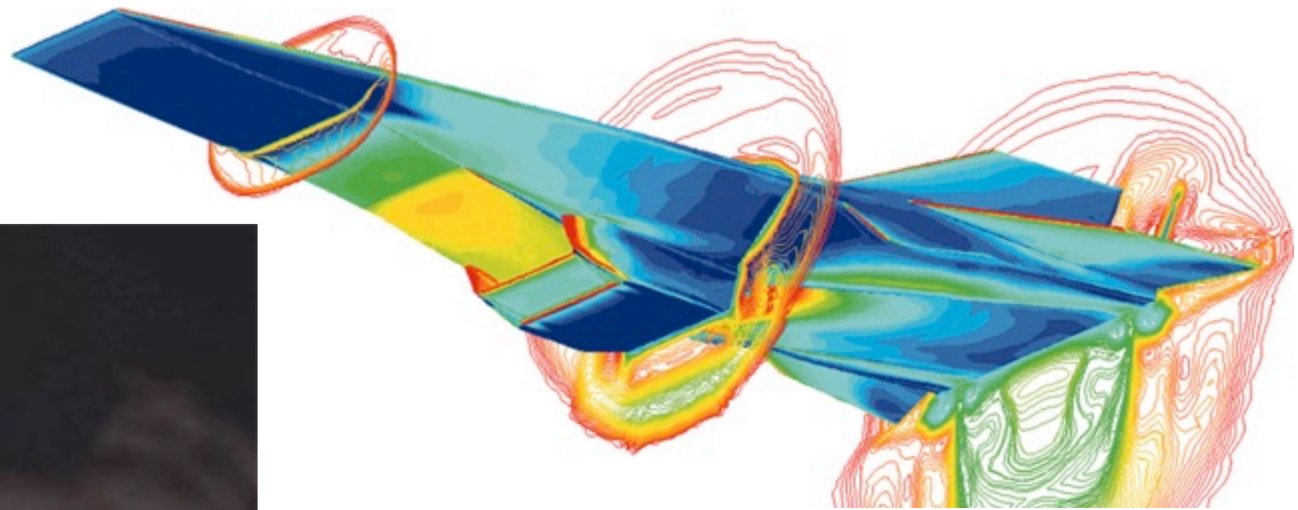
Objective

- **Investigate the effects of microstructure and composition on thermal and mechanical properties**





Dryden Flight Research Center ED97 43968-01
Hyper-X at Mach 7: This computational fluid dynamic (CFD) image is of
The Hyper-X vehicle at the Mach 7 test condition with the engine operating.

Temperature-dependent property information is needed to more accurately predict material response in operating environments

Approach

- Characterize mechanical and thermal properties of boride ceramics
  - Extend temperature range for measurements to at least 2000°C
  - Determine effects of solid solution on thermal properties
    - Why does W have a more drastic affect on thermal conductivity than other transition metal additives?
  - Study mechanical behavior at ultra-high temperatures
    - No systematic studies of UHTC mechanical properties at temperatures above 1800°C since the 1970s
    - Separate effects of temperature from environmental damage

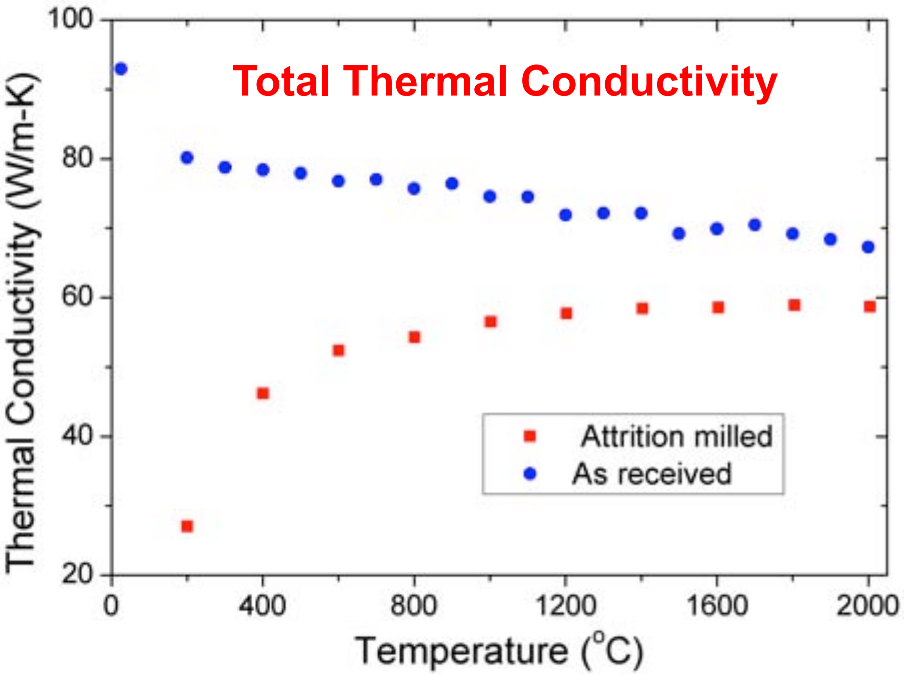
A ZrB_2-SiC wedge prepared by pressureless sintering was evaluated in the large core arc tunnel (LCAT) facility at Boeing-St. Louis

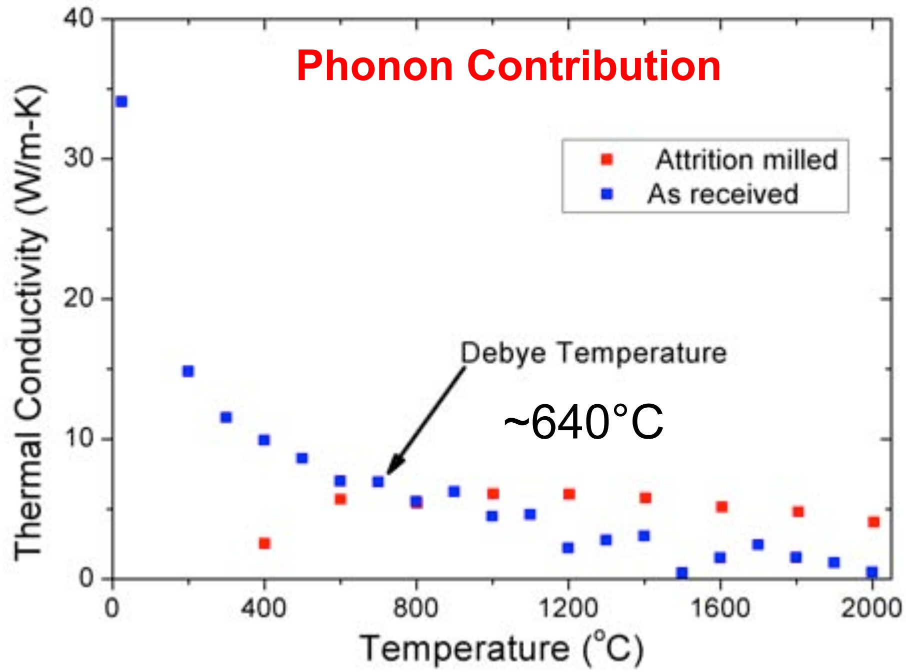
Thermal Properties

- **Goal: Determine inherent thermal properties of boride ceramics**
- **Key technical questions:**
  - **How does solid solution formation affect thermal conductivity?**
  - **Do additions impact the electron or phonon contributions or both?**
  - **What is the intrinsic thermal conductivity of ZrB_2?**
- **Graduate students**
  - **Devon McClane (current) and Matt Thompson (graduated)**

Room temperature thermal conductivities ranging from ~30 W/m•K to as high as ~120 W/m•K have been reported for ZrB_2 with no clear reasons for the differences

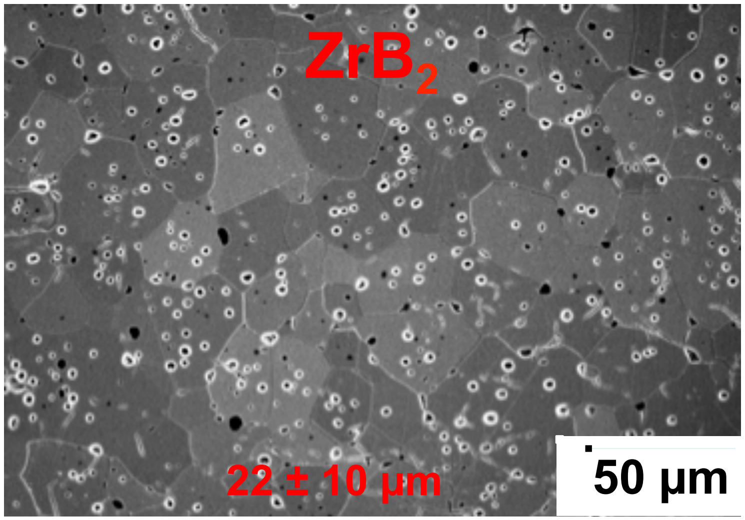
W Decreases Thermal Conductivity

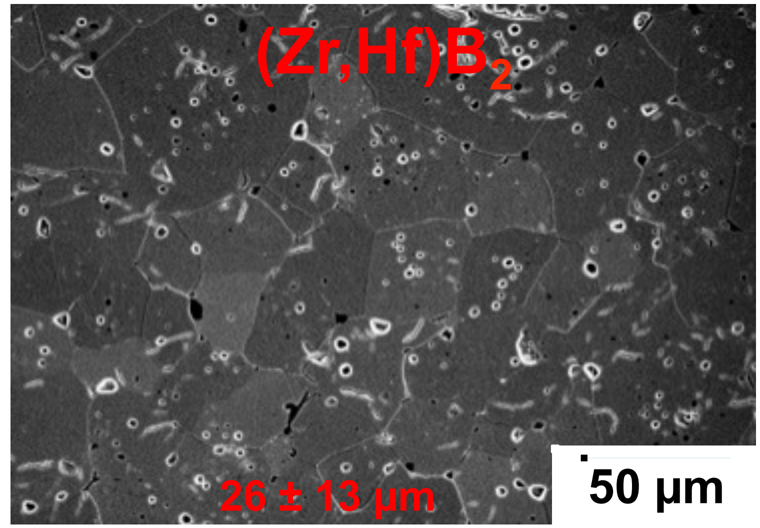


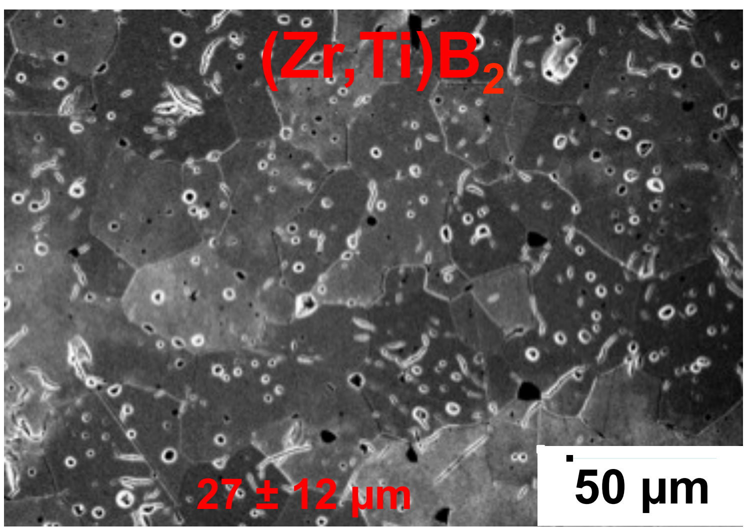


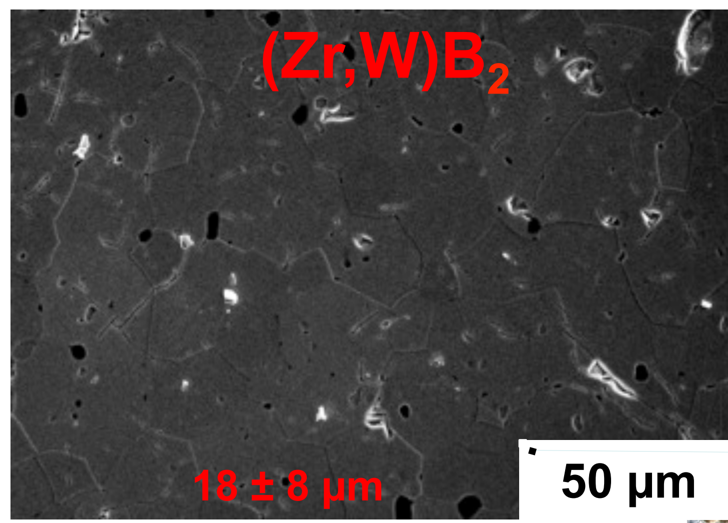
- Previous research showed that W decreases thermal conductivity
  - Impurity from reducing particle size by attrition milling with WC media
  - Promotes densification, but decreases phonon conductivity below T_{Debye}
- A detailed study of other transition metal additives is underway
  - 3 mol% additions of Y, Ti, Hf, Nb, or W

Microstructures





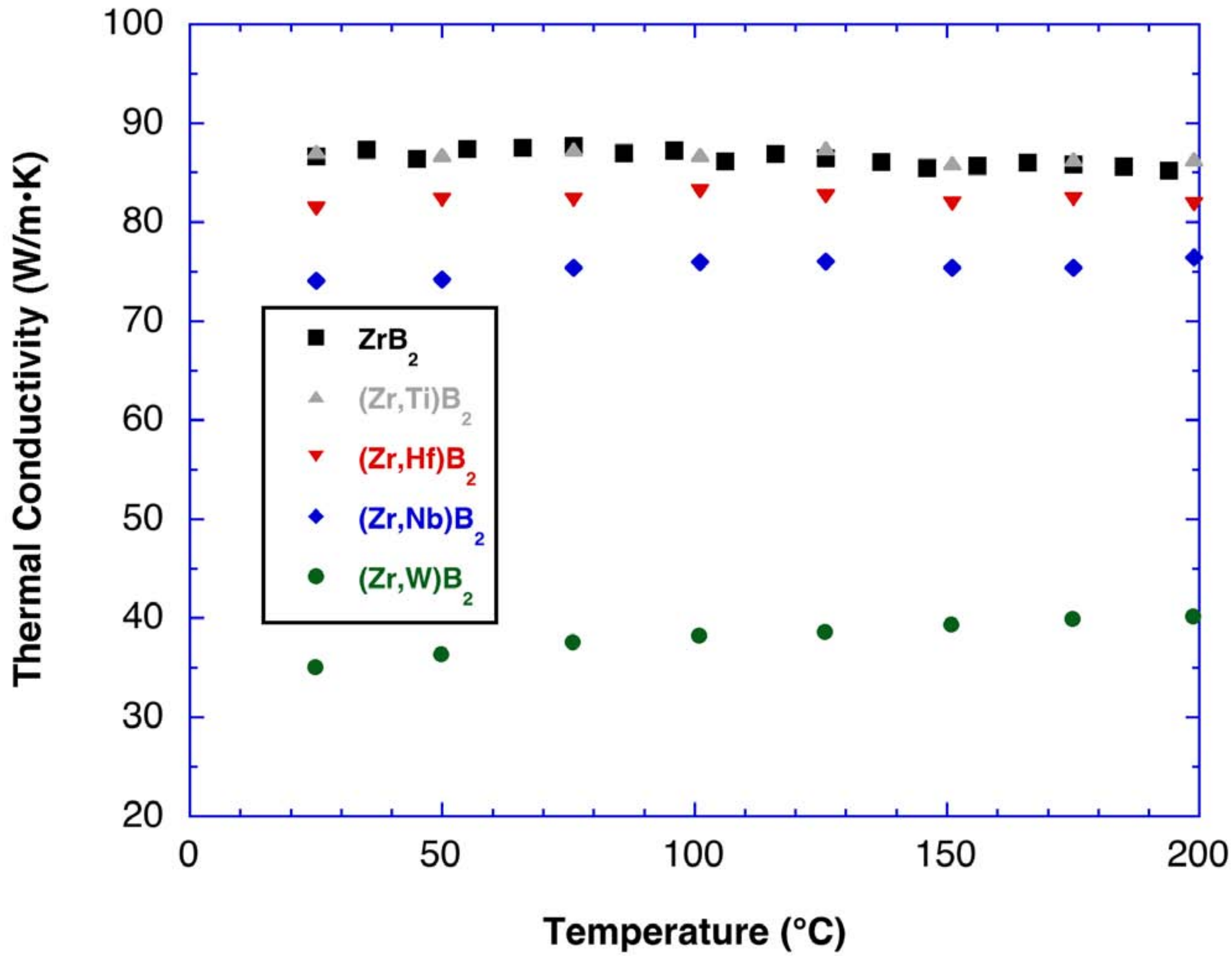




All Relative Densities >98%

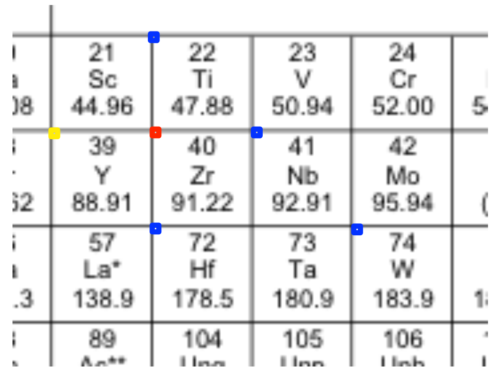
Note: chemical etching highlighted intragranular porosity

Thermal Properties



- 3 mol% of each transition metal compared to nominally pure ZrB_2
- Ti has minimal effect, W has the greatest effect on thermal conductivity

Future Work



- Complete compositional matrix
  - Y additions
- Examine microstructures
  - Grain size
  - Porosity
- Separate phonon and electron contributions
  - Measure electrical conductivity
  - Calculate electron contribution using Wiedemann-Franz law
  - Analyze effect of composition and grain size
- MS thesis for Devon McClane

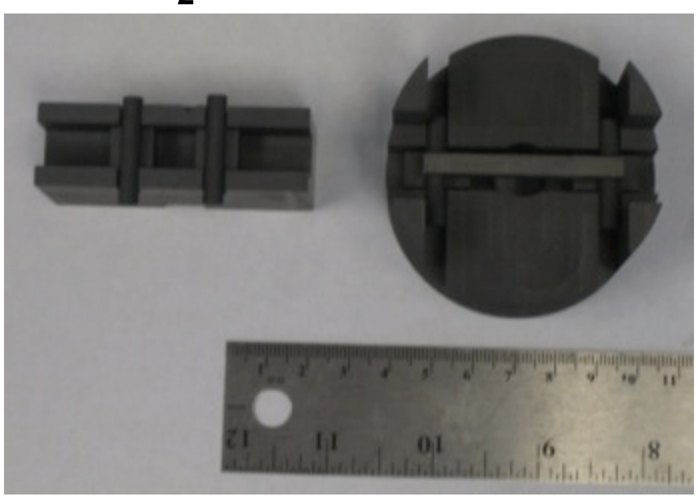
Mechanical Properties

- Goal: Characterize the mechanical properties of ZrB_2-based ceramics at ultra-high temperatures
- Key technical questions:
  - Does ZrB_2 retain strength above 1800°C?
  - How does the addition of SiC affect strength and modulus at ultra-high temperatures?
  - What controls the strength of ZrB_2-SiC at elevated temperatures?
- Students
  - Graduate student Eric Neuman
  - Undergrads Ryan Wilkerson, Lucas Showalter, John Tomaszewski

No reports published since the early 1970s have described the mechanical properties of UHTCs above 1800°C

UHT Mechanical Testing System

- **Instron 4204 load frame**
- **Custom-built environmental chamber**
  - **Inert atmosphere or mild vacuum**
- **Induction heating system**
  - **Has been heated to 2600°C**
- **Graphite load train and test fixture**
- **Testing of ZrB_2 limited to ~2300°C**
  - **ZrB_2-C eutectic**



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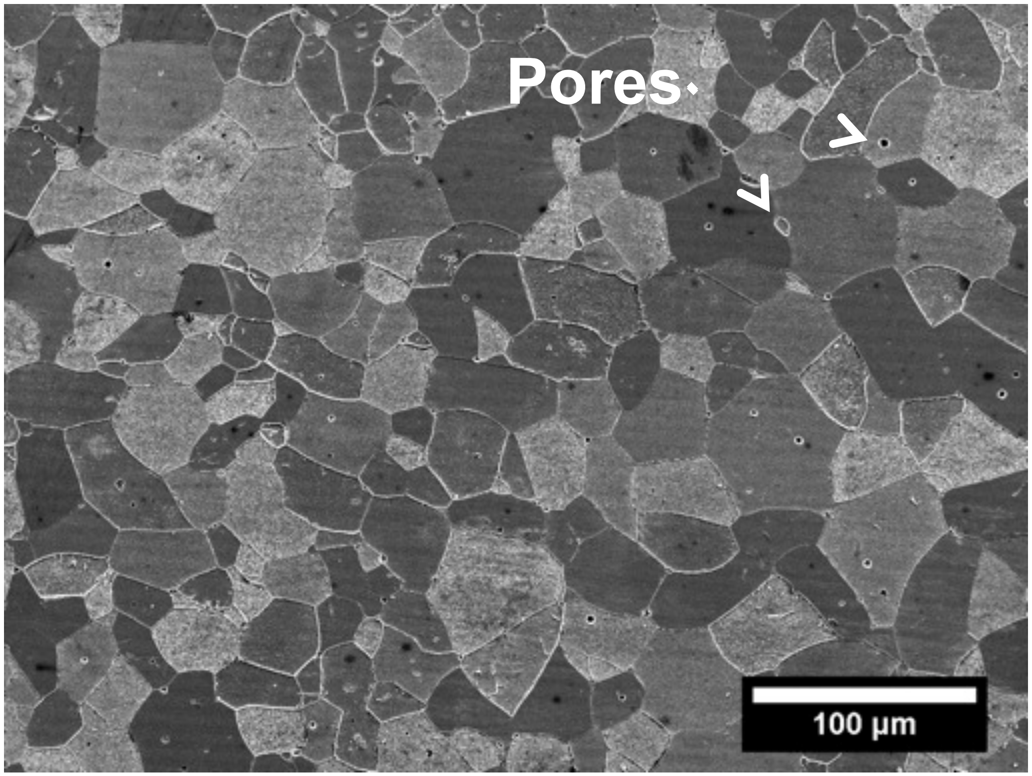
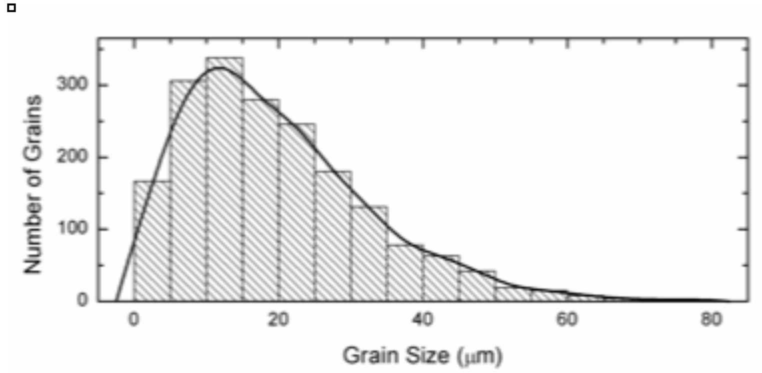
Zirconium Diboride

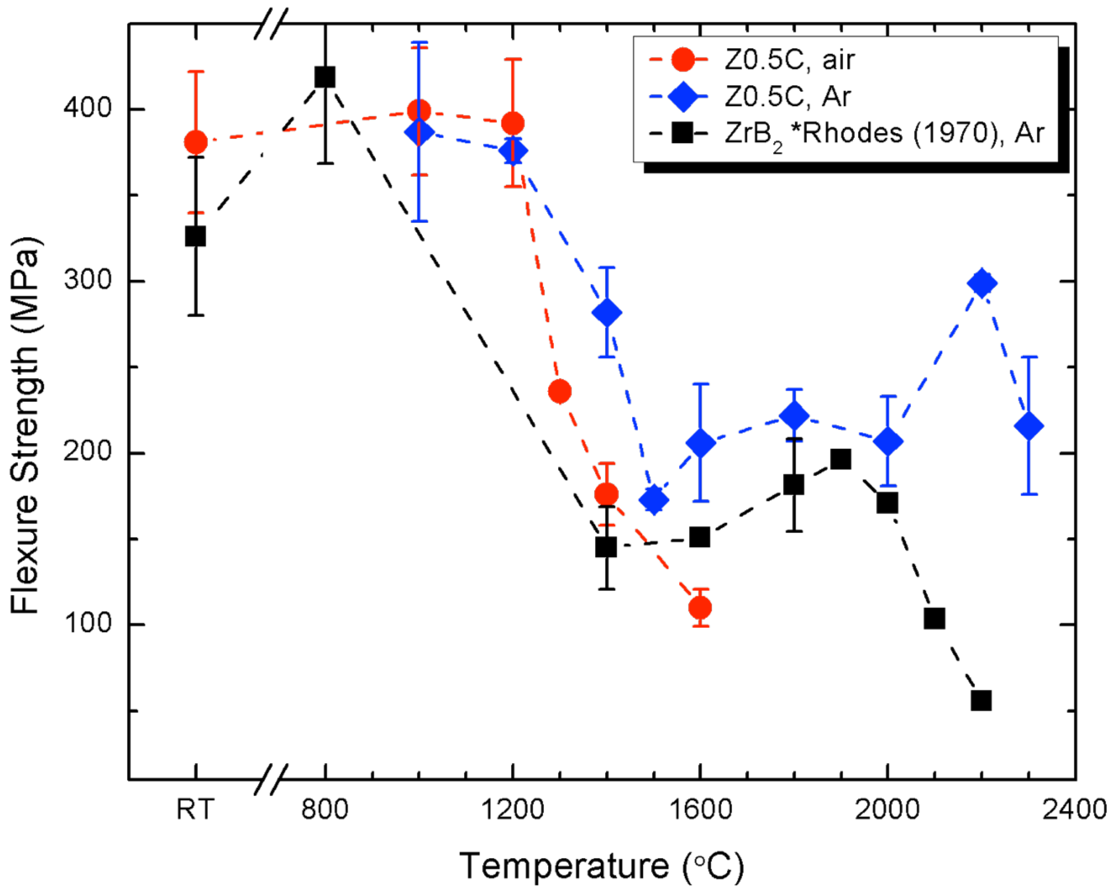




Hot pressed at 2150°C
ρ = 6.04 g/cc (99.2%)
GS = 19.7 ± 13.0 µm

- **Held at 2150°C for 1 hr to grow grains**
  - **Reduced tendency for creep at temperatures over 1800°C**
  - **Rhodes et al. observed significant creep**
- **Minimal entrapped porosity, no residual carbon observed**

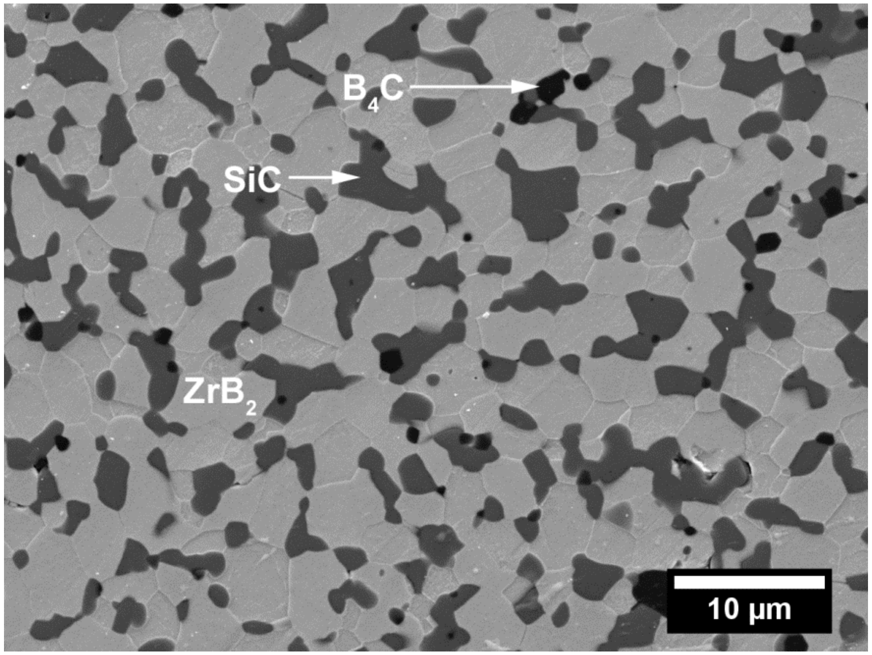
Ultra-High Temperature Strength

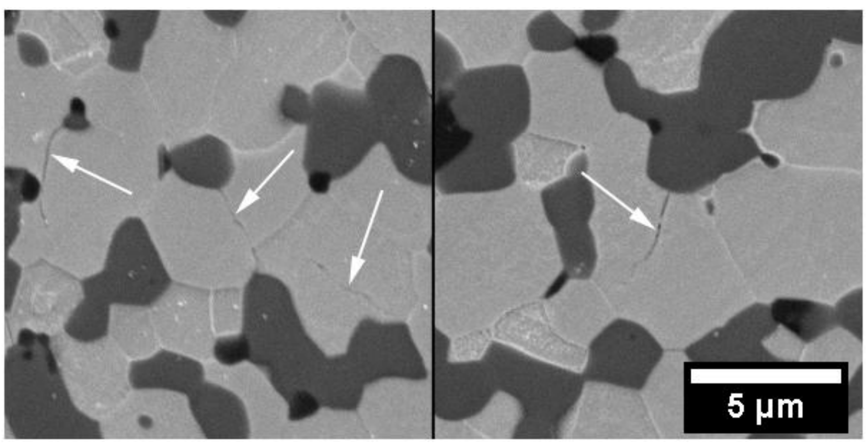


First systematic study of the strength of UHTCs at temperatures above 1800°C since the 1970s.

- **Strength was ~ 400 MPa up to ~1200°C**
- **Dropped to ~200 MPa between 1200°C and 1600°C (stress relaxation?)**
- **Stabilized at ~200 MPa up to 2300°C (plasticity?)**

ZrB_2-SiC Microstructure



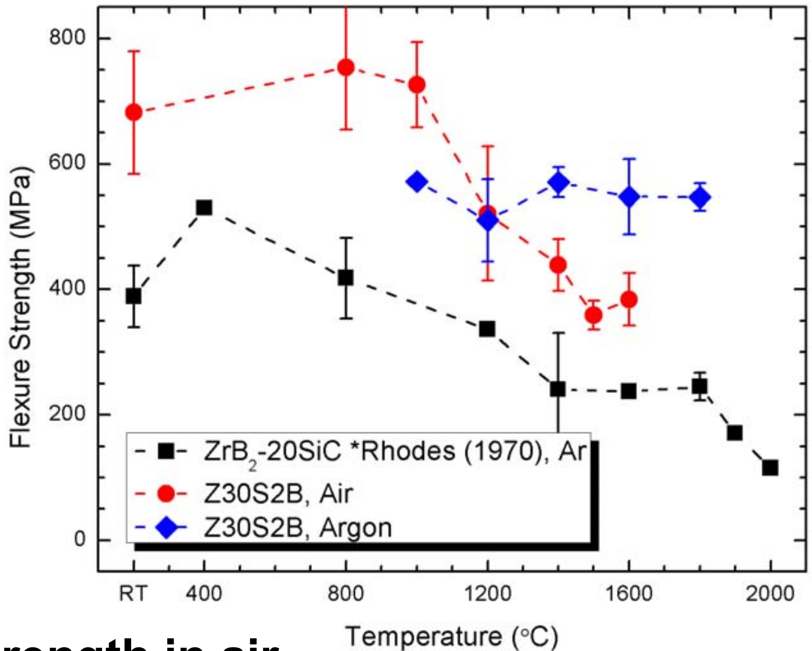


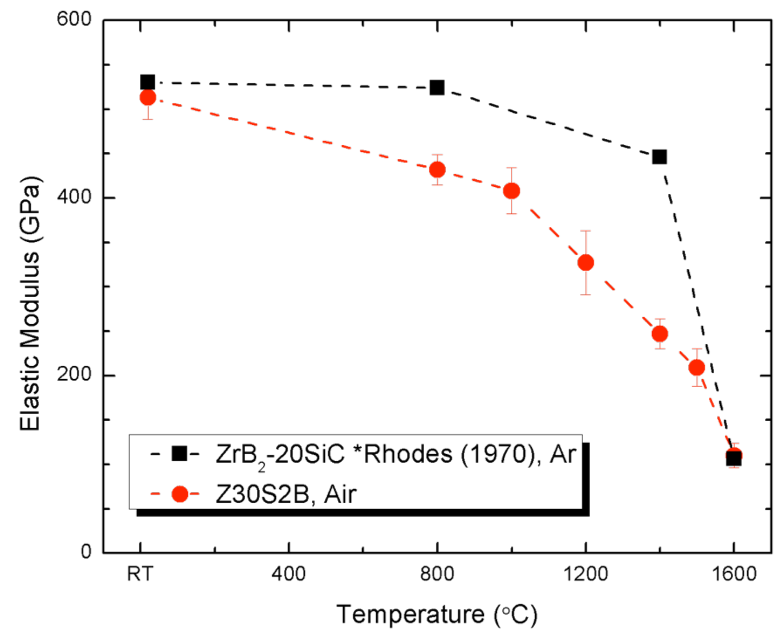
- **Nominal composition**
  - **ZrB_2 + 30 vol% SiC**
  - **About 2 vol% B_4C sintering aid**

Microstructure	
Density	>99.9%
ZrB_2 Grain Size	1.9 ± 0.9 µm
SiC Grain Size	1.2 ± 0.5 µm
SiC Cluster Size	6.1 ± 4.4 µm
B_4C Cluster Size	1.2 ± 1.0 µm
Max SiC Cluster Size	59.1 µm
Max B_4C Cluster Size	14.4 µm

- **Microcracking observed in matrix**
  - **CTE mismatch**

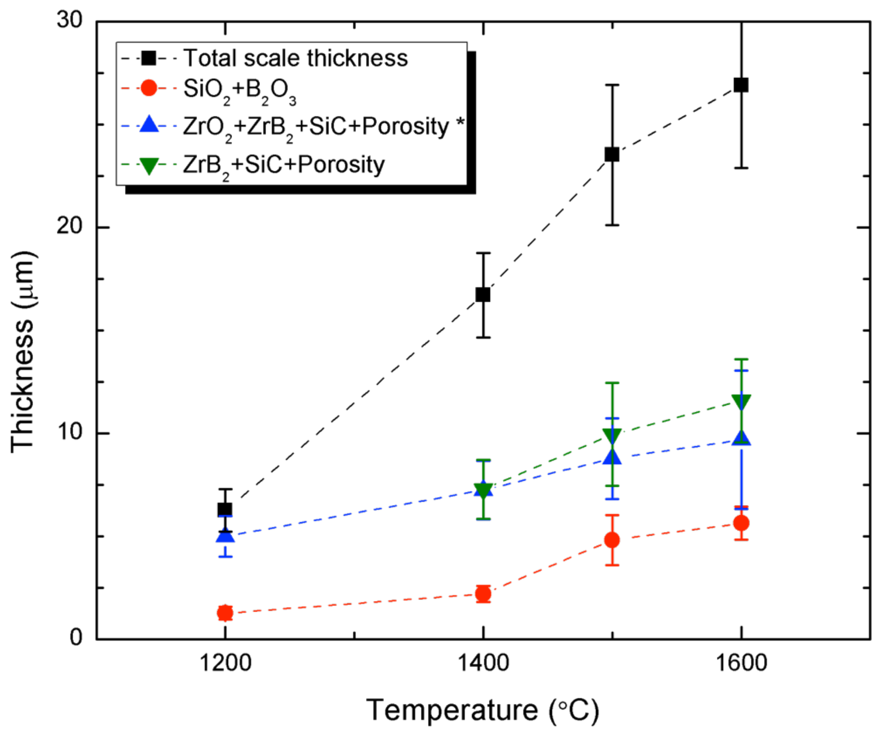
ZrB_2-SiC Strength and Modulus

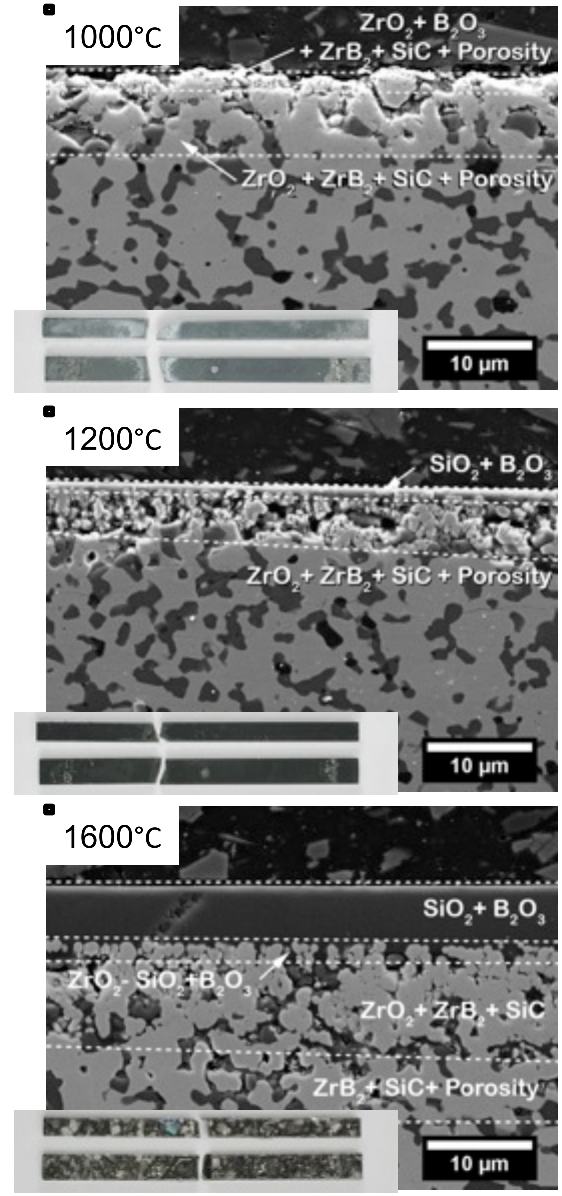




- **Strength in air**
  - **Increases up to ~1200°C (flaw healing) decreases above (oxidation)**
- **Strength in argon**
  - **Stable up to at least 1800°C**
- **Higher modulus from Rhodes study may be due to larger grain size**
  - **More resistant to creep and grain boundary sliding**

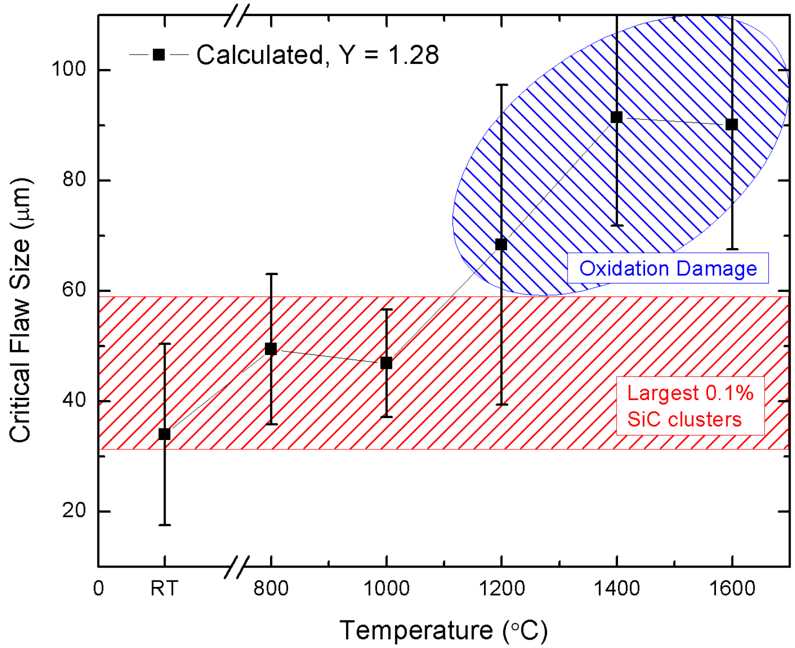
Effect of Oxidation

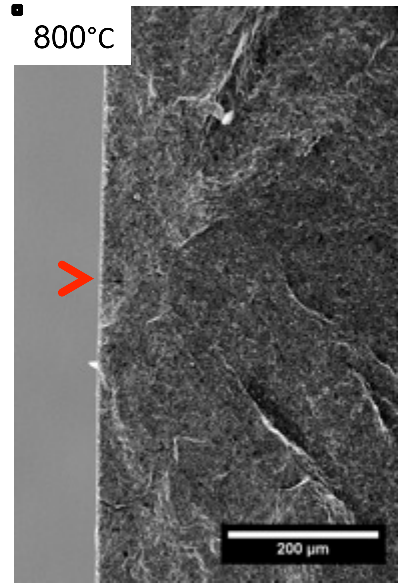


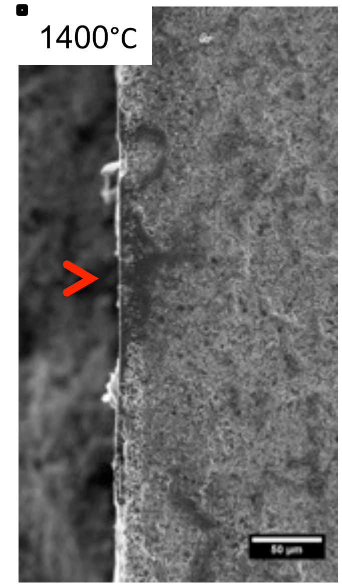


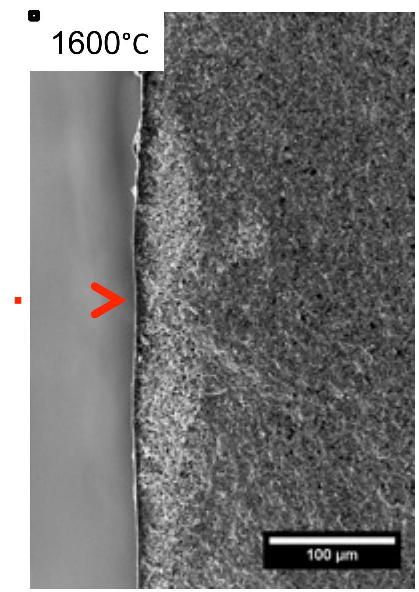
- **Oxide scale structure evolves with temperature**
  - **Flaw healing below ~1200°C**
  - **Increasing depth of damage at higher temperatures**
  - **Scale thickness is not uniform**

ZrB_2-SiC Failure Analysis



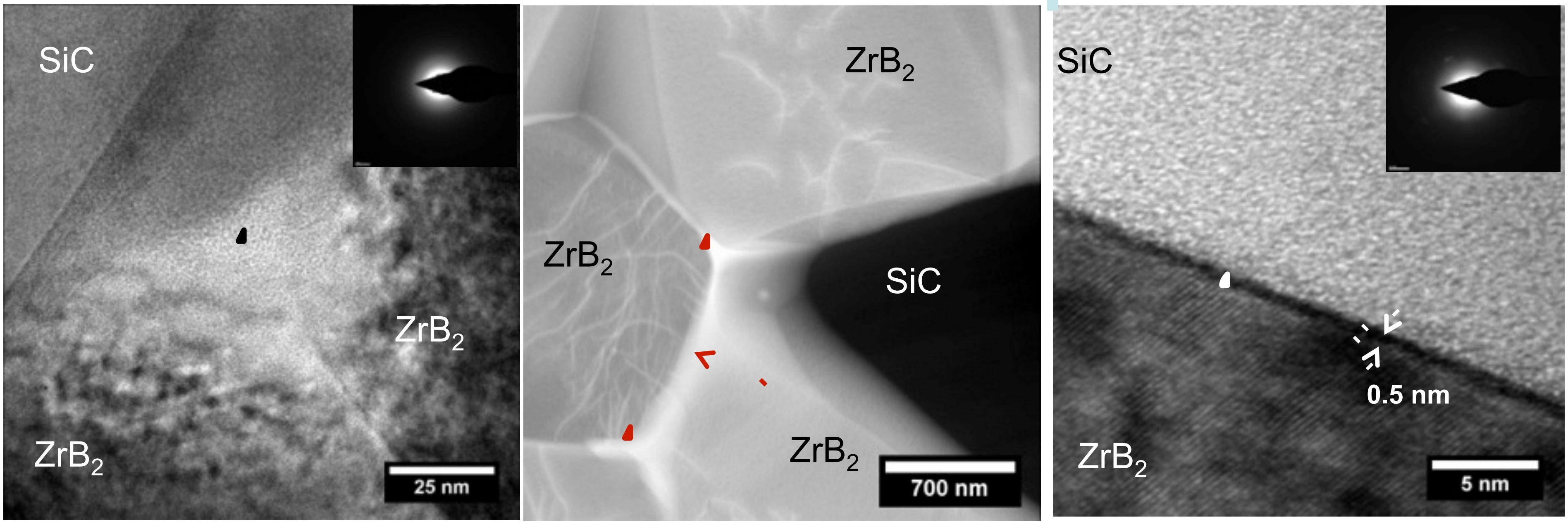






- **Below 1000°C, SiC clusters are the critical flaw**
- **Oxidation damage controls strength at 1200°C and above**
- **Observed fracture origins are consistent with size of calculated critical flaws**
- **Strength could be improved by reducing SiC cluster size or reducing oxidation damage**

TEM Analysis of ZrB_2-SiC



- Performed at Imperial College, London (thanks to Prof. W.E. Lee)
- Amorphous C-rich phase observed at some ZZS and ZSS triple junctions
- Fe and Co-rich phase observed at grain boundaries and triple junctions
  - Impurities from starting powders (Fe) and milling (Co) with WC media
- Amorphous film containing Zr, C, O, and Si at ZS grain boundaries
- Would reducing impurity content improve resistance to creep?

Continuing Research

- Test pure ZrB_2 at higher temperatures
  - Need a different test fixture material
  - ZrB_2-ZrC fixture being fabricated
- Complete analysis of ZrB_2-SiC in argon
  - Does minimization of oxidation change strength or modulus?
  - What is the strength-limiting flaw when oxidation is suppressed?
- Produce ZrB_2 and ZrB_2-SiC with improved purity
  - Can grain boundary phases be eliminated?
  - Will controlling grain boundary chemistry improve elevated temperature strength and resistance to creep?

2012 Accomplishments

- Thermal property testing
  - Produced matrix of compositions for additive study
  - Completed thermal property testing on ZrB_2 with Ti, Hf, Nb, and W
- Mechanical property testing
  - Completed ultra-high temperature mechanical test system
  - Analyzed nominally pure ZrB_2
    - First property measurements above 1800°C since 1970s
  - Characterized mechanical behavior of ZrB_2-SiC in air
    - Strength below 1200°C controlled by SiC cluster size
    - Strength above 1200°C controlled by oxidation damage
- 3 papers published, 2 accepted and published on-line
- 7 presentations