Atomistically Informed Materials Design of Ultrahigh Temperature Ceramics for Improved Mechanical Behavior in Oxidizing Environments

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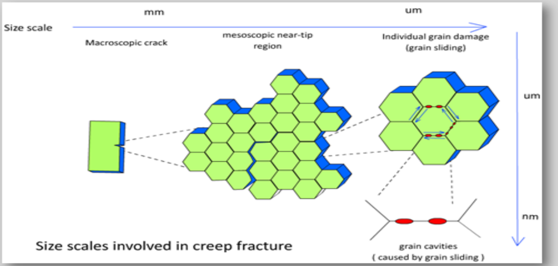
Overview

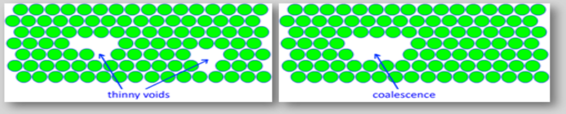


Size scales involved in creep fracture

A multi scale creep study : creep deformation of interconnected hard particles in a flowing matrix may require voids or cracks to accommodate the large deformations. This requires consideration of atomic scale mechanisms (interfaces, diffusion, and vacancies), microstructures (grains, boundaries, additional phases), as well as the continuum damage development at the macroscale.

✓Void nucleation Growth & coalescence

occur due to large grain rotations resulting from grain boundary sliding. Void growth and coalescence are known precursors to fracture in ductile metals and glasses.



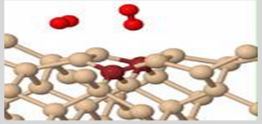
- Grain boundary cavities
  - Nucleation (on the order of ~2 nm) associated with stress concentrations in the form of ledges, dislocation pile-ups, reinforcement phase due to grain boundary sliding or vacancy diffusion along grain boundaries[1,7].
  - Growth is a result of classical creep mechanisms such as diffusion, dislocation motion, grain boundary sliding [7].
- Pocket cavities
  - Formed at pockets of the amorphous secondary phase between multi-grain junctions of primary phase. [5]
  - Growth is limited by viscous motion of the secondary phase.
  - Size is limited by pocket size.

✓Stress redistribution

Grain boundary sliding or diffusion leads to a redistribution of local vacancy concentration, and therefore stress . Because of this process , overall steady state creep rates may occur in a larger stress range

✓Oxidation

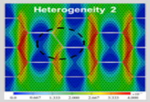
the effect of oxygen transport phenomenon, controlling the oxidation rates and the sensitivity of the oxygen diffusivity to the oxide grain size and composition is studied

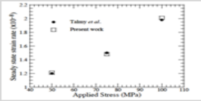


Main Achievements

✓ Atomistic & Micromechanics

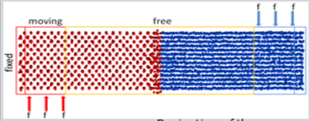
- Micromechanics framework to model creep damage is ready



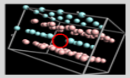


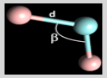
Predicting fracture (left) and creep (right) behavior of monolithic ZrB_2

- ZrB_2, HfB_2 interatomic ReaxFF potential is also ready. Can now atomistically investigate (in future) oxidation, thermo-mechanical properties, grain boundary behavior, diffusion constants.
- An algorithm that can handle slow-strain rate creep atomistic calculations is ready---Grain boundary sliding successfully modeled at realistic strain rates. A dramatic contrast is found when compared with conventional approaches
- Use the developed potential to gain insights into ZrB_2 and HfB_2 creep deformation and damage behavior---computation of deformation mechanisms map in progress
- Study of void nucleation studies in ZrB2 is in progress
- Make connections with experiments:
  - Comparison with bi-crystal experiments
  - Atomistically informed micromechanical model validated against polycrystal creep rupture experiments



Projection of the model on y-z plane

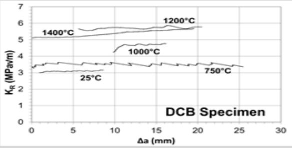




ZrB_2 heat of formation energy		
	QM	ReaxFF
β[degree]	113.23	113.12
d [A°]	2.58	2.61

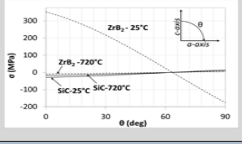
✓Fracture Behavior

- Double Cantilever Beam (DCB) R-Curve experiments conducted through 1600°C

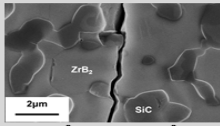


- Intergranular fracture path increases with temperature
- ZrB_2 TEA becomes isotropic while remaining non-cubic.
- High temperature fracture behavior
  - T < 700° C TEA is offset by lack of ZrB_2 Intergranular fracture
  - 700° C < T < 1200° C Bridging is geometric dominant up to creeping temperature
  - T > 1200° C creep zone development contributes most to toughening

Average TEA Residual stress[2,3,4]



SiC particle bridging example



700° C < T < 1200° C
SiC-ZrB_2 thermal expansion mismatch contributes to crack bridging

Main Achievements/Current Impact

✓Creep Characterization

- 4-pt flexure creep experiments conducted at 16, 20, 30, 54, 72, 97 MPa from 1400°C to 1800°C.

T ≤ 1500°C:

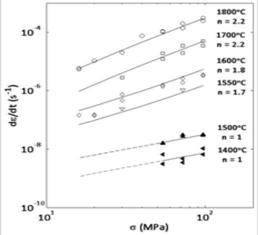
$$\dot{\varepsilon} = \frac{AbG^nD}{KT}\left(\frac{b}{d}\right)^p\left(\frac{\sigma}{G}\right)^n$$

T > 1500°C:

$$\dot{\varepsilon}_{gbs} = \frac{\beta G b^2 D_l}{dKT}\left(\frac{\sigma}{G}\right)^2$$

$$\dot{\varepsilon}_c = \left[{}^{3\beta\sigma^{(n+1)}}/_{4G}\right]\exp\left(-\frac{Q}{RT}\right)$$

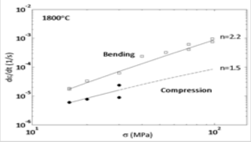
Temperature	Slope #	Stress Range	Activation Energy (KJ/mol)
1600 - 1820°C	1	54-97 MPa	639 ± 1
	2	16-30 MPa	568 ± 10
1400 - 1500°C	5	54-97 MPa	364 ± 93

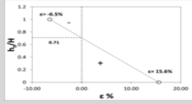


- Cavitation observed in all creep specimens T>1500°C.
  - Cavitation contributes 5-10% of overall creep strain
  - ZrB_2-SiC interphase boundaries accounted for > 75% cavitation observed.
  - Stress dependent cavity nucleation and growth kinetics observed. σ ≤ 30MPa –Growth and σ > 30MPa – Nucleation controlled
- Steady State Creep Mechanisms [4][5]
  - Low Temperature: Diffusion (n=1) accommodated ZrB_2 and ZrB_2-SiC g.b. sliding mechanism.
  - High Temperature: Rate controlled ZrB_2 and ZrB_2-SiC g.b. sliding accommodated by dislocations and partially by cavitation (1.5<n<2/3).

✓Creep Behavior

- Outer-fiber strains indicate creep behavior differences in compression and tension.





Large Strain Bending Creep

1800C_16MPa – 7.75 hrs

✓Future Goals

- Creep model development: OIM grain statistics and texture development analysis.
- Micromechanical modeling of ZrB_2-SiC composites
- Complete high temperature tensile creep experiments

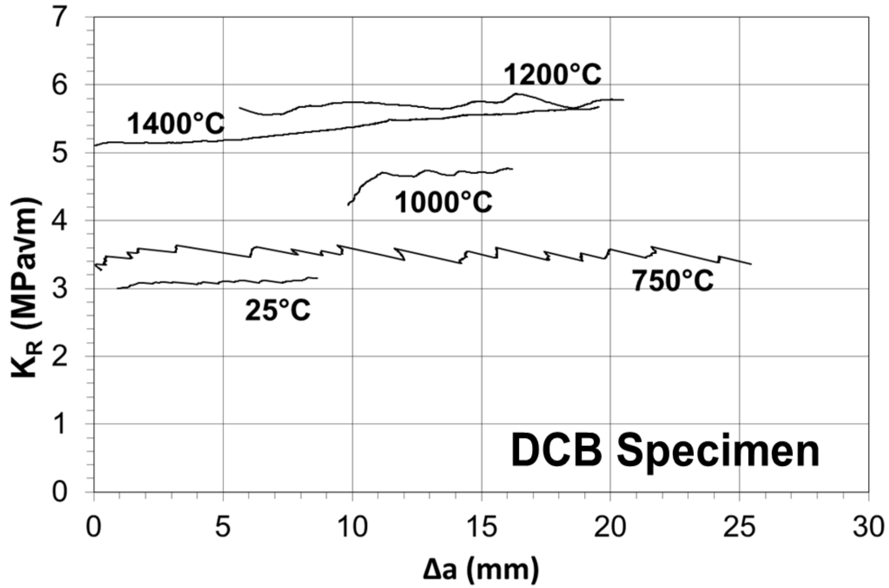
✓Publications

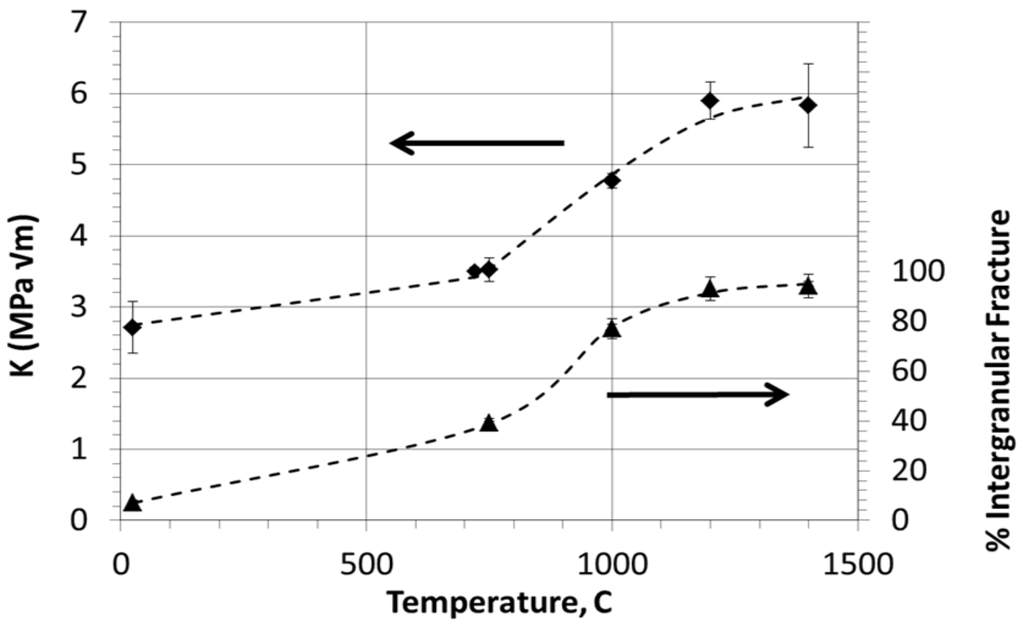
- M.W. Bird, R.P. Aune, A.F. Thomas, P.F. Becher, K.W. White, "Temperature-Dependent Mechanical and Long Crack Behavior of Zirconium Diboride-Silicon Carbide Composite," J. Eur. Ceram Soc, 32 (2012) 3453-62
- C-H. Yu, C-W. H, C-S. Chen, Y. Gao, C-H Hsueh, *Effects of grain boundary heterogeneities on creep fracture studied by rate-dependent cohesive model*, Eng. Frac. Mech., 93, 48-64 (2012)
- C. Mi, D.A. Buttry, P. Sharma, D.A. Kouris, "Atomistic insights into dislocation-based mechanisms of void growth and coalescence, "Journal of Mechanics and Physics of Solids, 59 (2011) 1858-1871
- A. Goussien, W. Fan, A. Van Duin, P. Sharma, *A Reactive Force-Field for Zirconium and Hafnium Di-Boride*, accepted for publication in Computational Materials Science, 2013
- . M.W. Bird, R.P Aune, F. Yu, P.F. Becher, K.W. White, *Creep Behavior of a Zirconium Diboride-Silicon Carbide Composite*, J. Eur. Ceram Soc., Submitted
- R. Sarangi, A. Goussiem, R. Sarangi, Grain boundary Sliding Constitutive Law from Atomistics, *Physical Review Letters*, submitted
- C. H. Yu, C. W. Huang, C. S. Chen, Y. Gao, and C. H. Hsueh, "A Micromechanics Study of Creep Fracture of Zirconium Diboride," *J. Euro. Ceram. Soc.*, Submitted

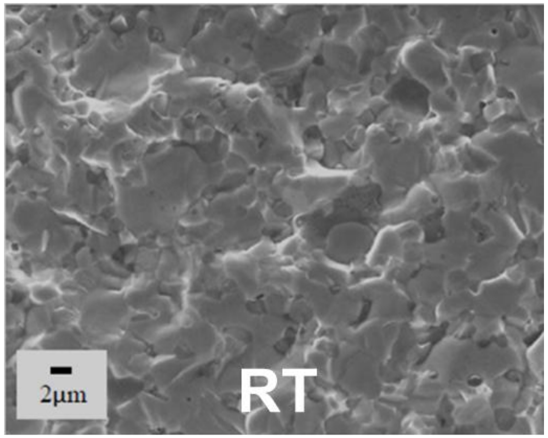
References

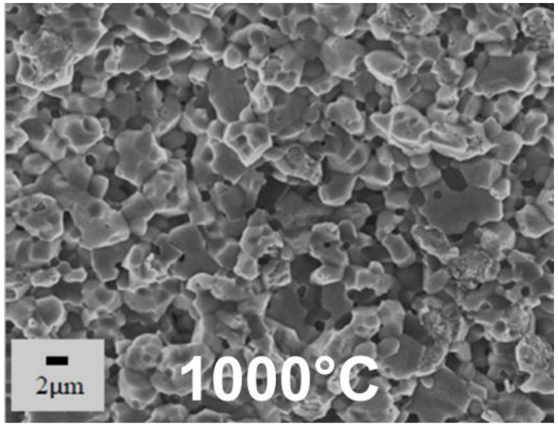
[1]. Onck, van der Geissen. "Growth of an initially sharp crack by grain boundary cavitation"
[2] White KW, Hay JC., J Am. Ceram. Soc., 77 (9), (1994) 2283-8
[3] Kusakari M, Tanaka K, Inui H,Otani S., Okamoto NL., Acta Mater, 58, (2010) 76-84
[4] Bradt RC, Li Z, J. Am. Ceram. Soc., 69 (12), (1986) 863-6
[5] Cannon, W.R. Langdon, T. G., J. of Mat. Sci., 1988, 23, 1-20
[6] Langdon, T. G., Philosophical Magazine 1970, 22, 689-700
[7] Evans, A. G., Rana, A., Acta Metal., 1979, 28, 129-141

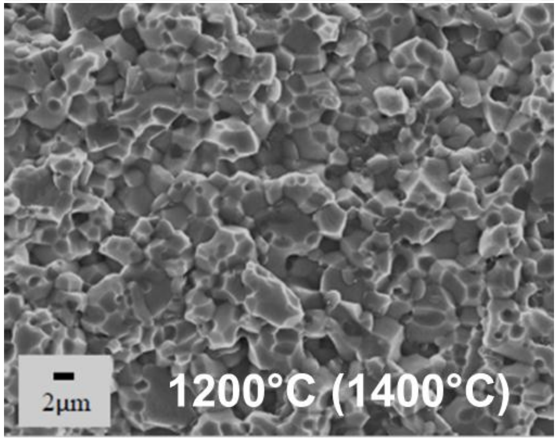
LONG CRACK (R-CURVE) ASSESSMENT





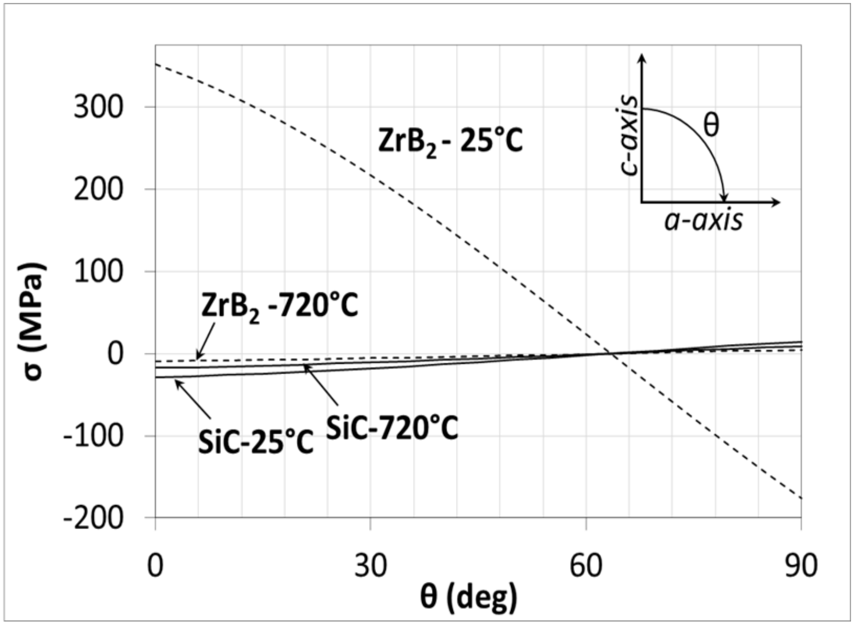


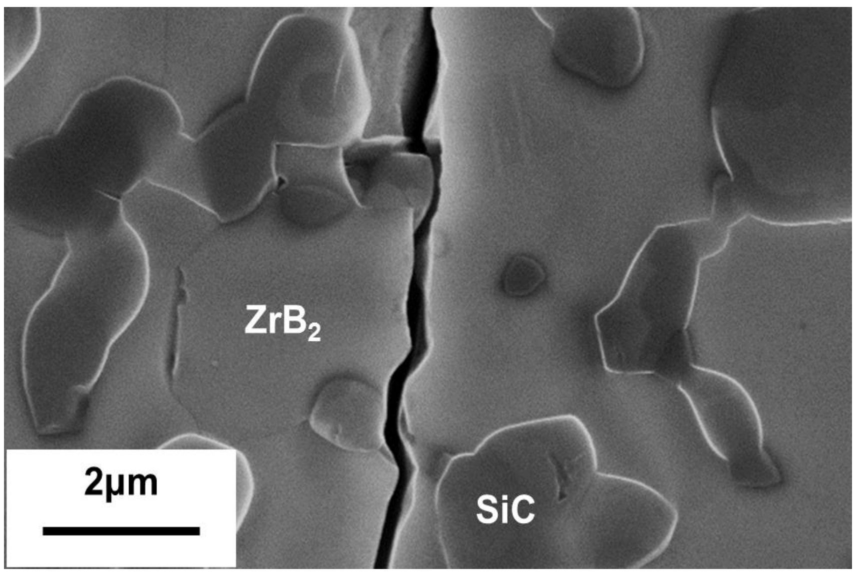




LONG CRACK (R-CURVE) ASSESSMENT

Average Residual stress





- ZrB_2 TEA becomes isotropic while remaining non-cubic.
  - < 700C TEA residual stress are superimposed upon thermal expansion mismatch stresses.
  - > 700C Bridging is geometric dominant up to creeping temperatures
- Low temperature bridging
  - TEA is offset by lack of ZrB_2 Intergranular fracture
  - Thermal expansion mismatch between ZrB_2-SiC contributes most to toughening

Example of SiC frictional pullout

Thermal Expansion Mismatch

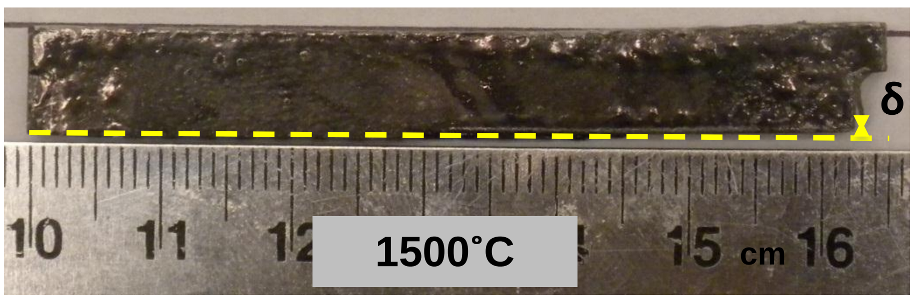
[1]White KW, Hay JC., *J Am Ceram Soc* 1994;**77**(9):2283–8.
[2]Kusakari M, Tanaka K, Inui H, Otani S, Okamoto NL.,*Acta Mater* 2010;**58**:76–84.
[3]Bradt RC, Li Z., *J Am Ceram Soc* 1986;**69**(12):863–6

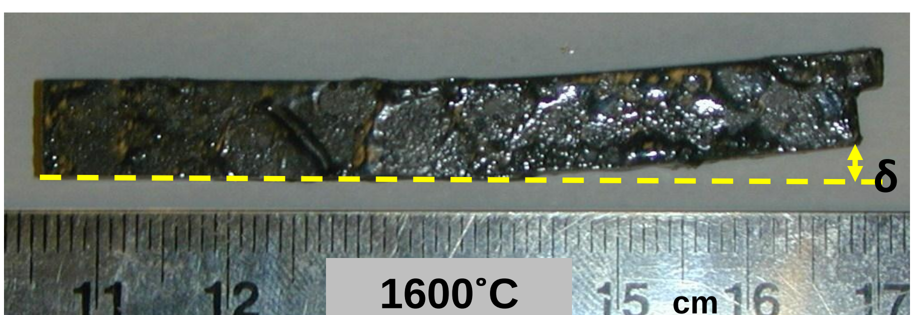
LONG CRACK (R-CURVE) ASSESSMENT

- At 1200˚C, LEFM compliance model begins to break down.

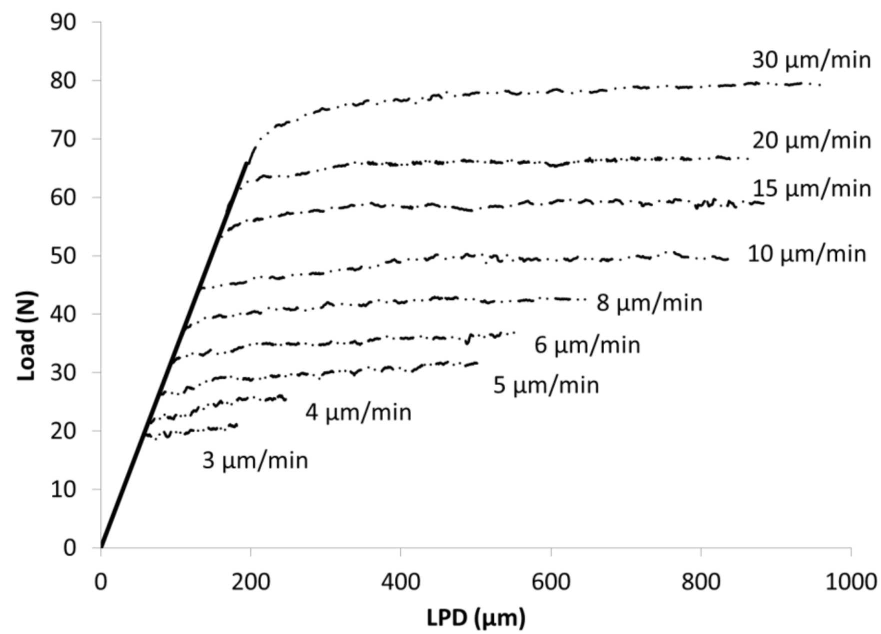
$$\delta_{tot} = \delta_{crack} + \delta_{creep}$$

- Large component of toughness attributed to creep
- Compliance crack 5% (1200˚C) and 14% (1400˚C) greater than measured crack



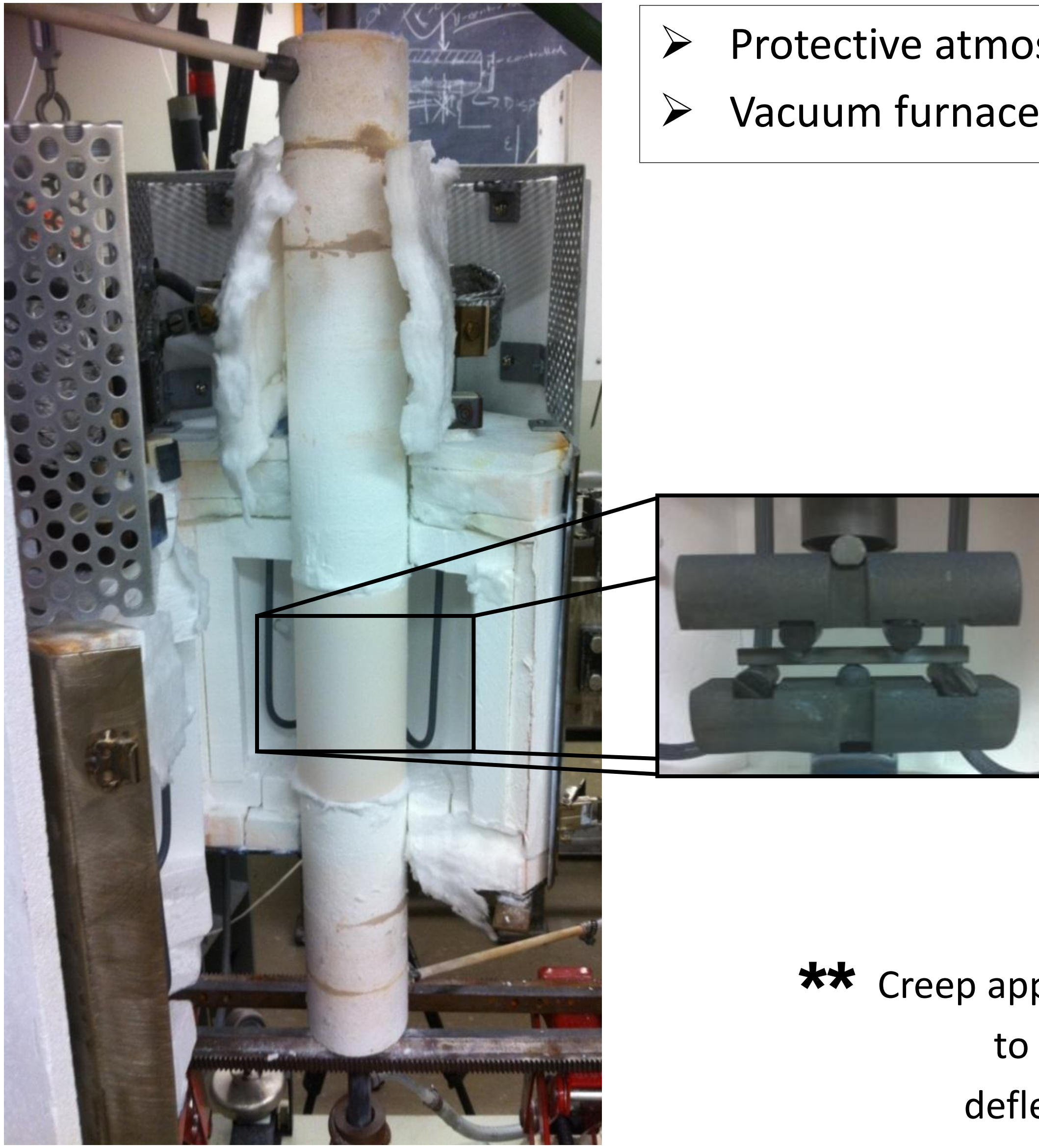


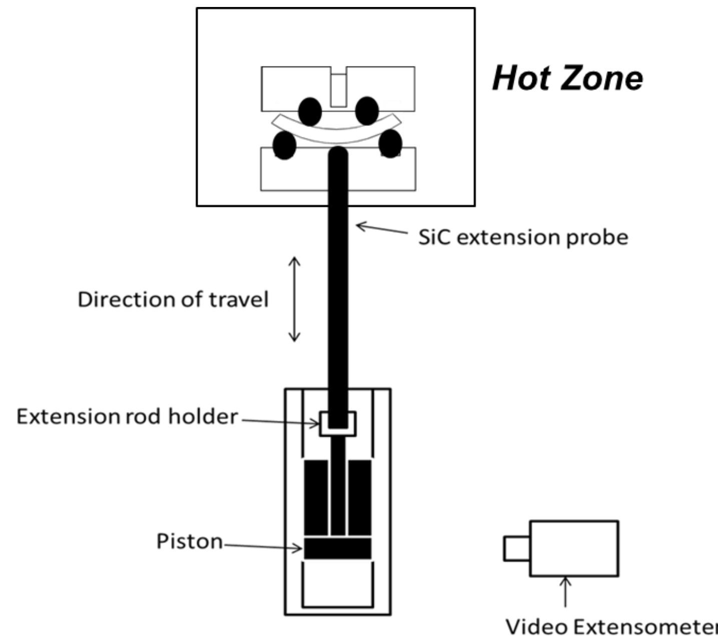
1600˚C DCB



Current Work

- Protective atmosphere (flowing argon) conditions.
- Vacuum furnace-Inert conditions





** Creep apparatus reduces oxidation scales **
to < 50 μm with continuous
deflection/strain measurement

UHTC ZrB_2-20SiC CREEP

Talmy *et al.* work*

- ❖ Creep rate increases with:
  - ➢ SiC content, temperature (1200 -1500˚C), and stress (30 -180 MPa) increases
  - ➢ decreasing SiC particle size (2 µm, 10 µm)
- ❖ Proposed steady state creep mechanisms
  - ➢ G.B. Sliding for 50% vol SiC content (n~2)
  - ➢ Diffusional for 0-25% vol SiC content (n~1)

Wei-Ming Guo *et al.* work‡

- ❖ Creep rate increased with temperature 1500- 1600 ˚C; 1 - 7 (x 10^{-9})1/s, 19 MPa, 24 to 100 hrs.
- ❖ Cavity nucleation observed in all specimens.
  - ➢ G.B. triple junctions cavitation (wedge shaped).
  - ➢ Predominate cavitation along SiC-ZrB_2 interphase boundaries.

*Talmy, I.G. *et al*, J. Am. Ceram. Soc., 91, 2008, pp. 1441-1447.

‡ W-M Guo, *et al., High-temperature flexural creep of ZrB_2-SiC ceramics in argon atmosphere, Ceram. Int . (2011) in press*

UHTC ZrB_2-20SiC CREEP

Kats *et. al.* *

- ZrB_2-ZrC (2-4 µm grain sizes) Compressive Creep rate increases with:
  - ZrC content, temperature (1700 -2420˚C), and stress (5 -30 MPa) increases
  - Measured creep rates of $10^{-6} – 10^{-4}$ S^{-1}
- Diffusion accommodated deformation, n=1

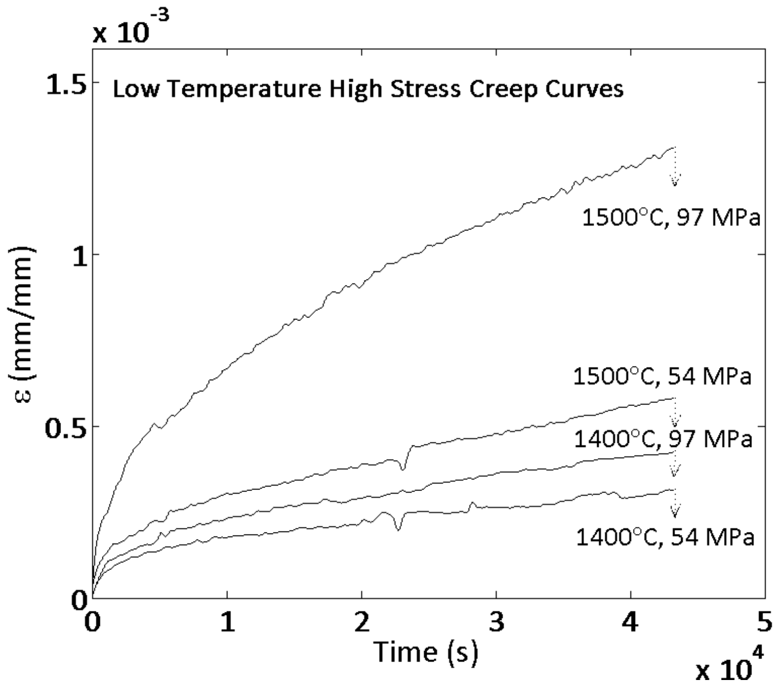
Spivek *et. al.*[ᵻ]

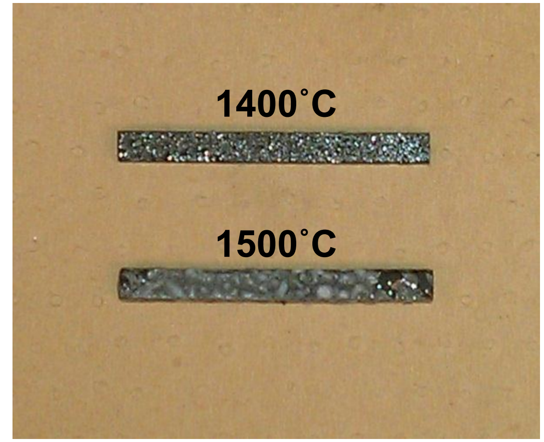
- ZrB_2-ZrN and TiB_2-TiC Bending Creep 2000-2300 ˚C;
  - ZrB_2-20vol%ZrN, grain sizes 24 and 46 µm, respectively
  - TiB_2-20 vol% TiC, grain sizes of 5 and 6 µm, respectively
  - Creep rate ratio, TiB_2TiC/ ZrB_2-ZrN = 15
  - Fine grained TiB_2-TiC: Superplastic creep behavior.

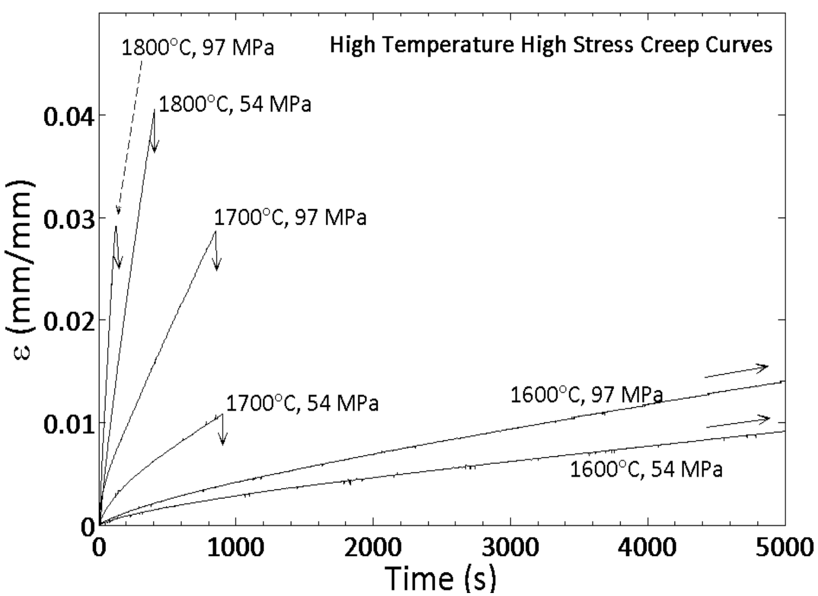
*S.M. Kats *et al,* Compressive Creep of Alloys of the ZrC-ZrB2 and TiC-TiB2 Systems. Soviet Powder Metallurg Metal Ceram. 1981, 20 (12), 886-890

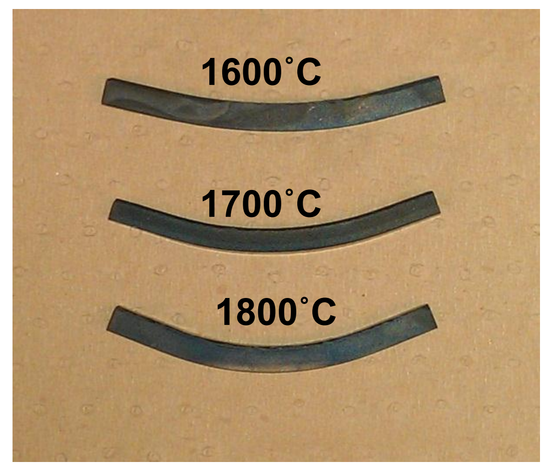
ᵻI.I. Spivak *et al,* Creep in the Binary Systems TiB2-TiC and ZrB2-ZrN. Soviet Powder Metallurg Metal Ceram. 1974, 13 (8), 617-620.

BENDING CREEP









Time = 4 $x10^4$s

Time = 1 $x10^4$s

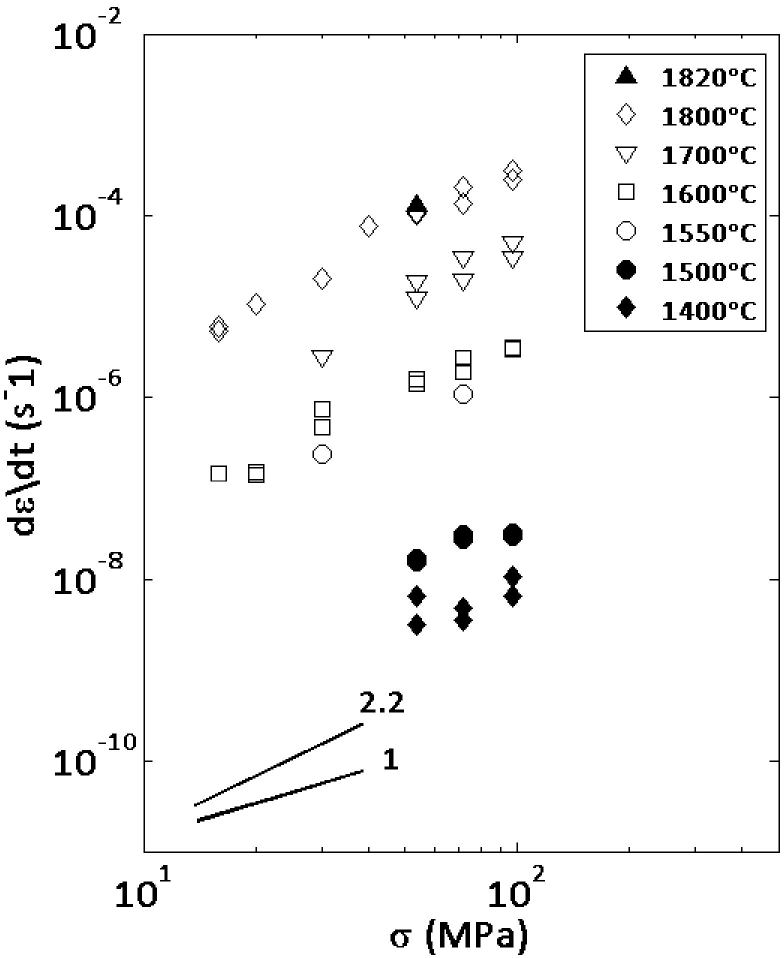
Time = 1 $x10^2$s

Dotted Arrow = time constraints

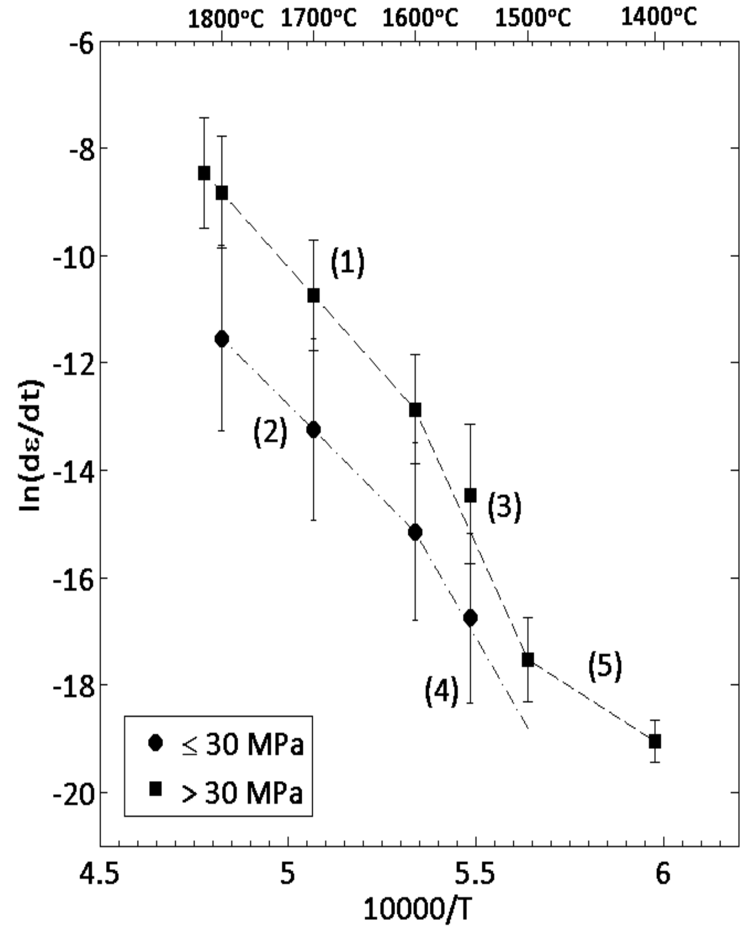
Solid Arrow = deflection constraints

BENDING CREEP

Strain-rate Stress Dependence



Strain-rate Temperature Dependence



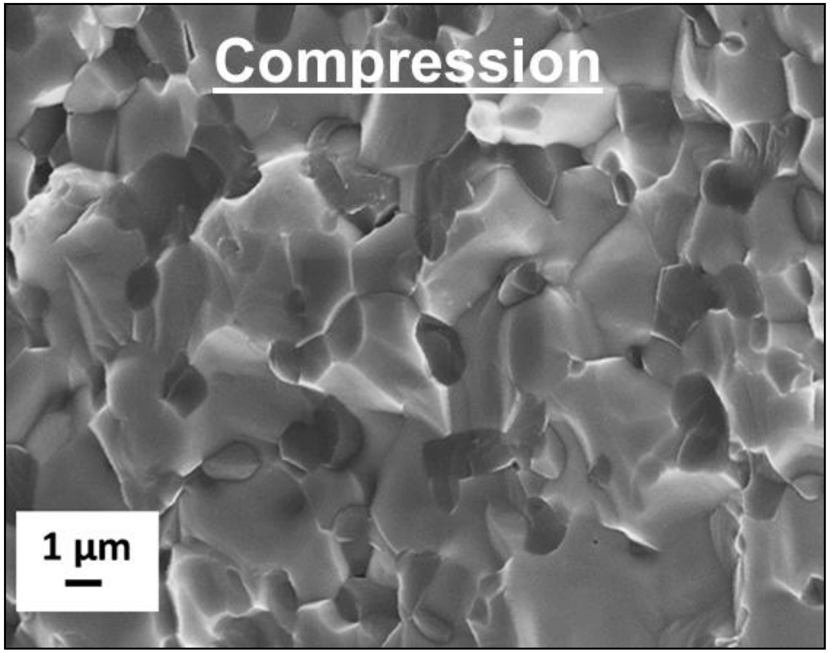
1500° C<T<1600° C

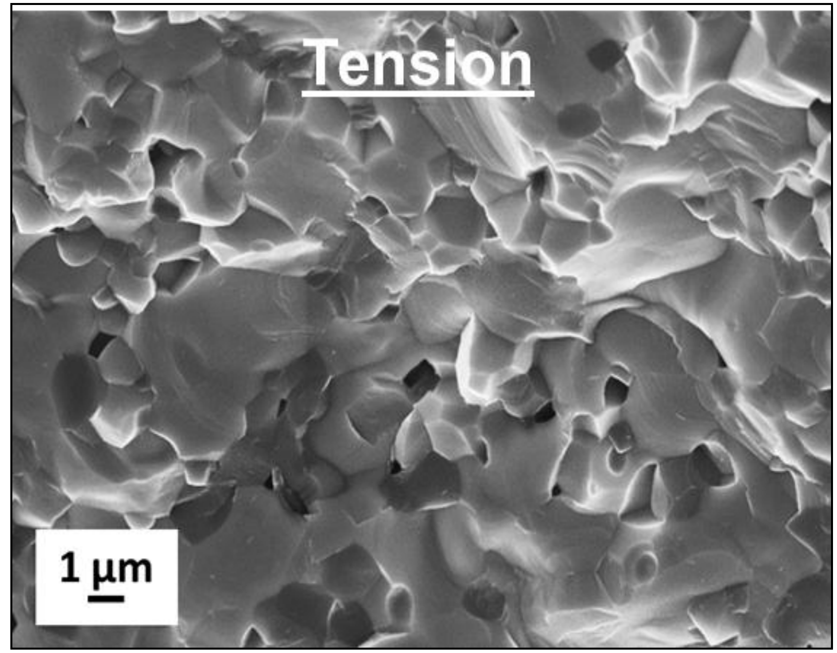
1.5 decade strain-rate increase

Error bars represent 95% CI

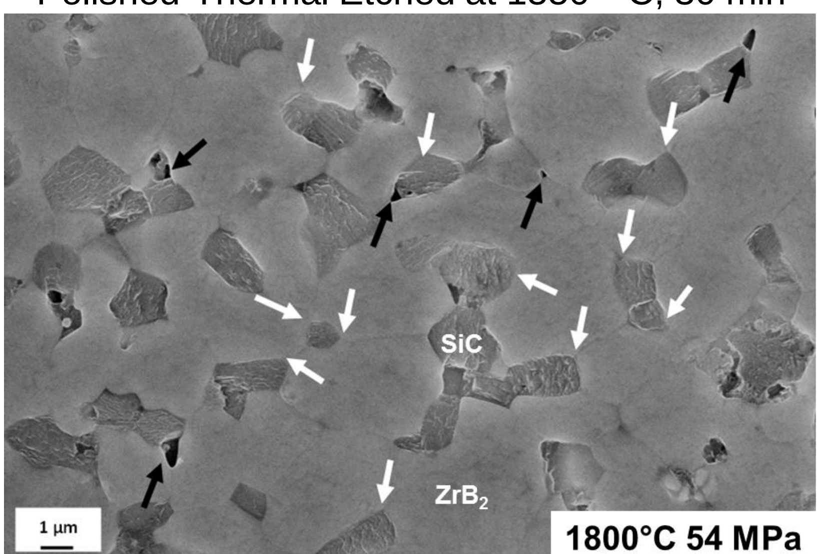
Temperature	Slope #	Stress Range	Activation Energy (KJ/mol)
1600 - 1820°C	1	54-97 MPa	**639 ± 1**
	2	16-30 MPa	**568 ± 10**
1400 - 1500°C	5	54-97 MPa	**364 ± 93**

BENDING CREEP





Polished-Thermal Etched at 1550° C, 30 min



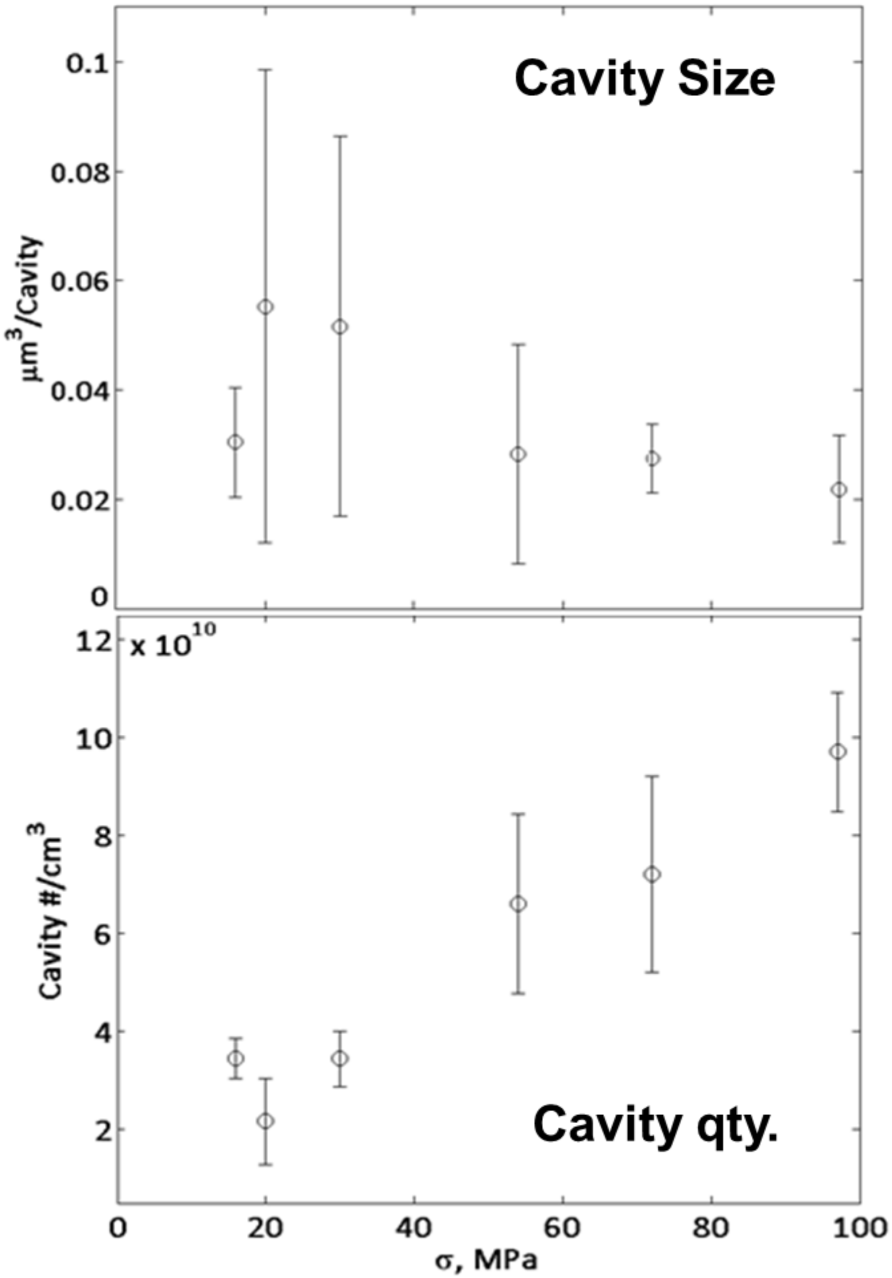
Cavitation Strain Contribution

5-10% of overall creep strain

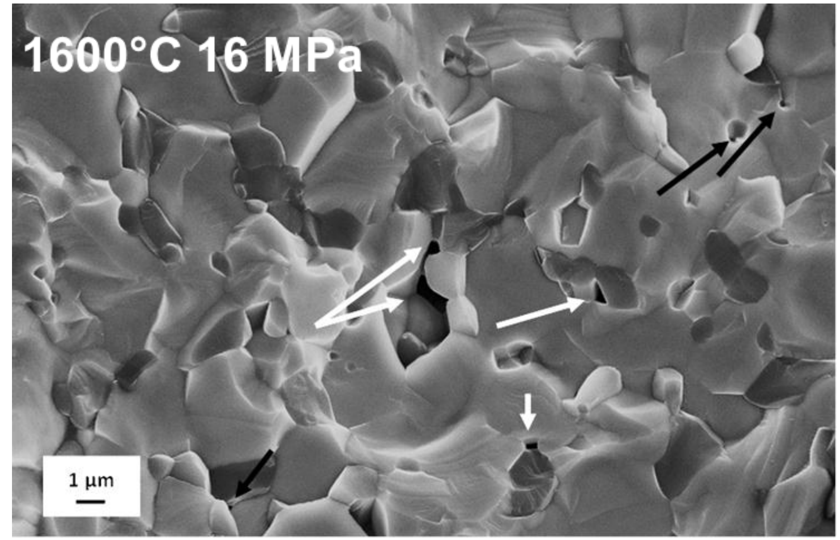
> 75% Z-S triple point cavities

White arrows = Continuous triple point
Black arrows = Cavitated triple point

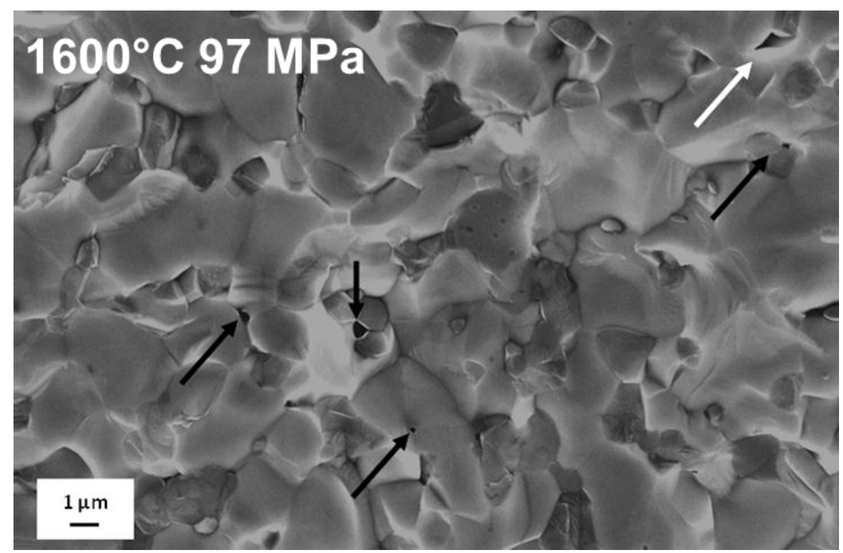
BENDING CREEP



Growth Dominant



Nucleation Dominant



STEADY STATE CREEP MECHANISM(S)

LOW TEMPERATURE

- Diffusion (n=1) accommodated ZrB_2 and ZrB_2-SiC g.b. sliding mechanism:
  - Rule out following:
    - Solution Precipitation via interphase glass film network (n=1).
    - Viscous flow at g.b. (n=1): TEM reports occasional amorphous phase along SiC-ZrB_2 boundaries.
    - Harper-Dorn creep (n=1) require large grain sizes ~400 µm and texture development (Large mobile dislocation density)

HIGH TEMPERATURE

- Rate controlled ZrB_2 and ZrB_2-SiC g.b. sliding accommodated by dislocations and partially by cavitation ($1.5<n<2/3$)
  - Rule out following:
    - Lattice dominated mechanism require $3<n<5$ (i.e. intragranular dislocation glide); Expect ZrB_2 grain texture development and grain shape change.
    - n = 5 refers to fully ductile behavior (i.e. intragranular slip); n = 3 refers to dislocation climb when slip is restricted.

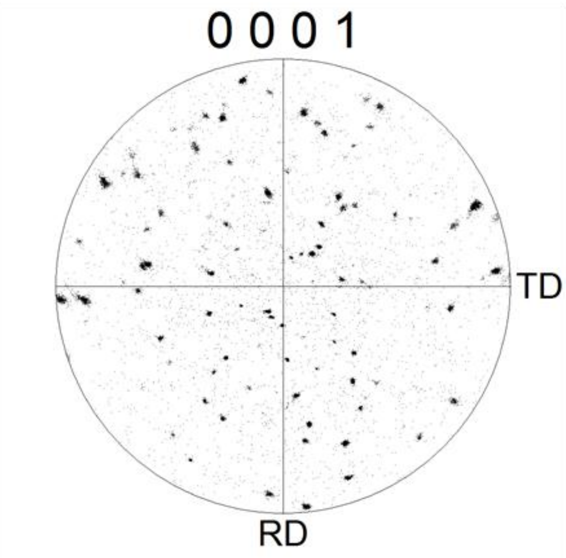
[1]Cannon, W. R.; Langdon, T. G. J. of Mat. Sci 1988, 23, 1-20.

Bending Creep: Texture and Grain Size Analysis

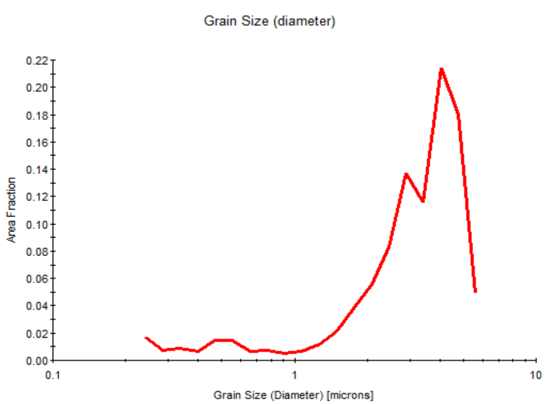
ZrB2

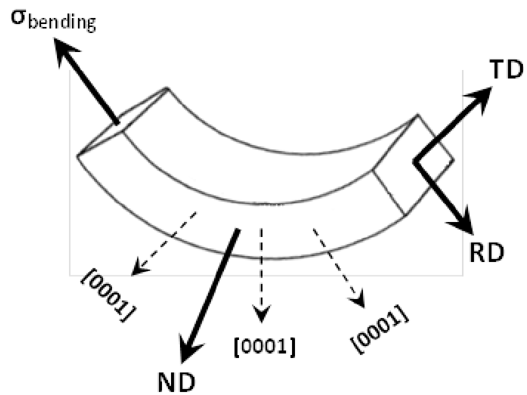
1500°C , Neutral Axis

($\varepsilon_{outer\text{-}fiber}$ = 0.13%)



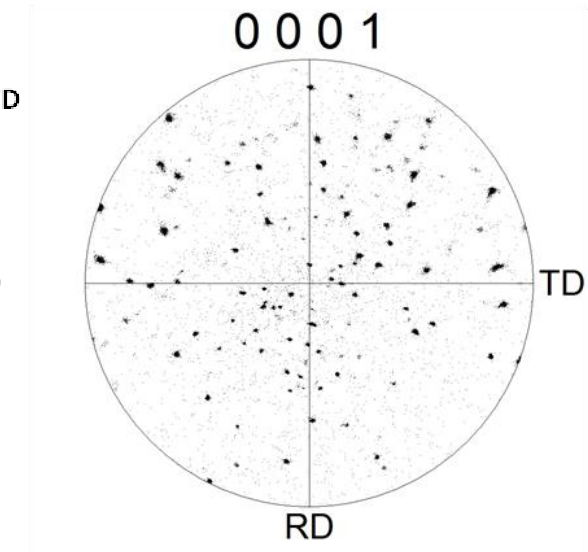
Aspect Ratio = 0.574±0.0044



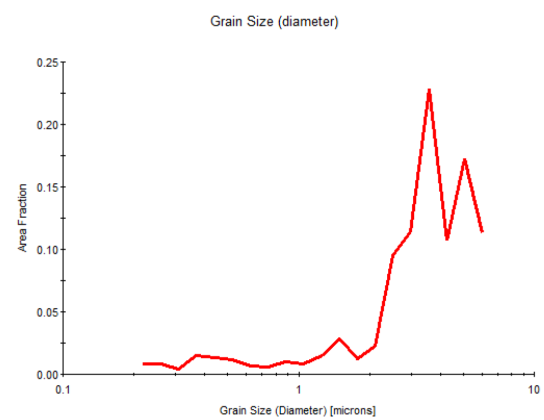


1800°C , Tensile Edge

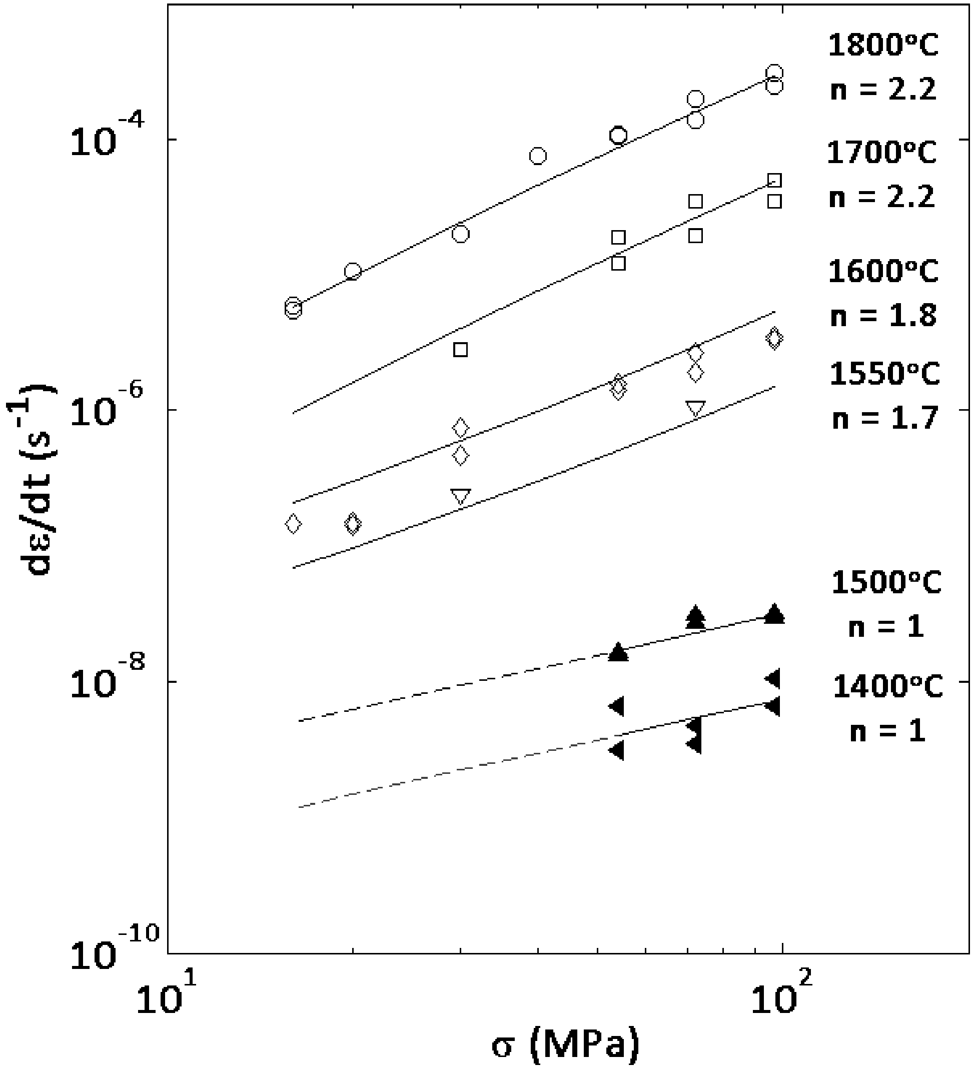
($\varepsilon_{outer\text{-}fiber}$ = 4.47%)



Aspect Ratio = 0.577±0.0044



BENDING CREEP



Solid lines are model fits

Dashed lines are extrapolated values

Grain boundary sliding and cavitation models

2 $$\dot{\varepsilon}_{gbs} = \frac{\beta G b^2 D_l}{dKT}\left(\frac{\sigma}{G}\right)^2$$

3 $$\dot{\varepsilon}_c = \left[{}^{3\beta\sigma^{(n+1)}}/_{4G}\right]\exp\left(-\frac{Q}{RT}\right)$$

Diffusion accommodated by g.b. sliding

1 $$\dot{\varepsilon} = \frac{AbG^n D}{KT}\left(\frac{b}{d}\right)^p\left(\frac{\sigma}{G}\right)^n$$

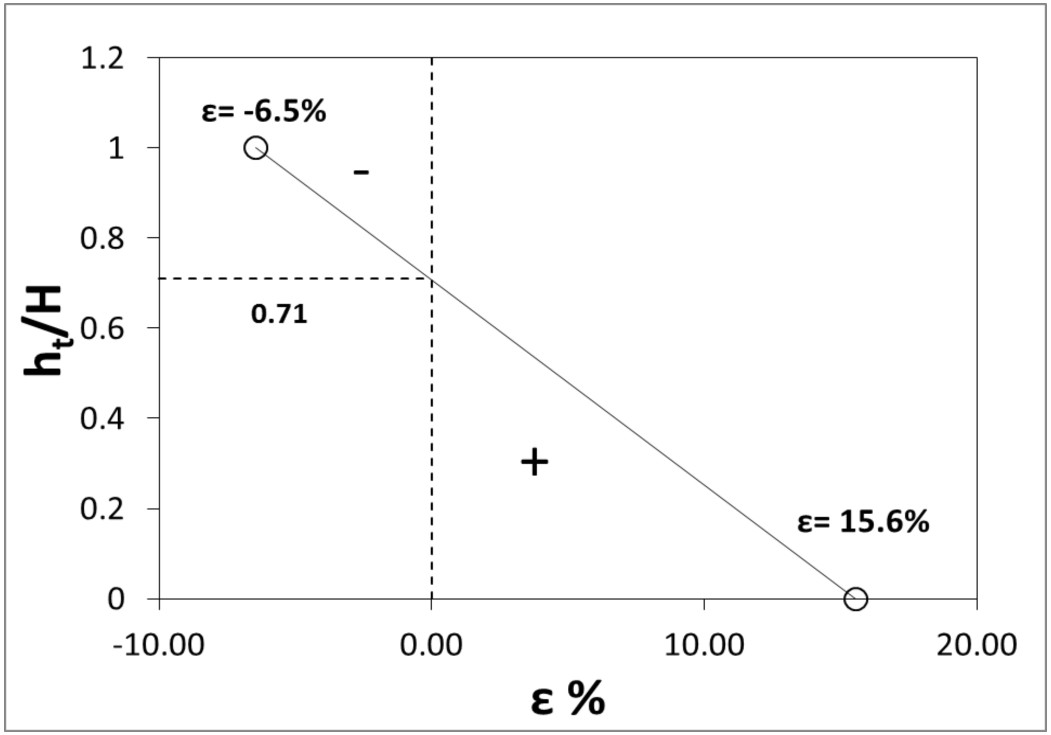
[1]Cannon, W. R.; Langdon, T. G. J. of Mat. Sci 1988, 23, 1-20.
[2]Langdon, T. G. Philosophical Magazine 1970, 22, 689-700.
[3]A.G. Evans, A. Rana, Acta Metal. 1979, 28, 129-141.

CREEP BEHAVIOR

Large Strain Bending Creep

1800C_16MPa – 7.75 hrs

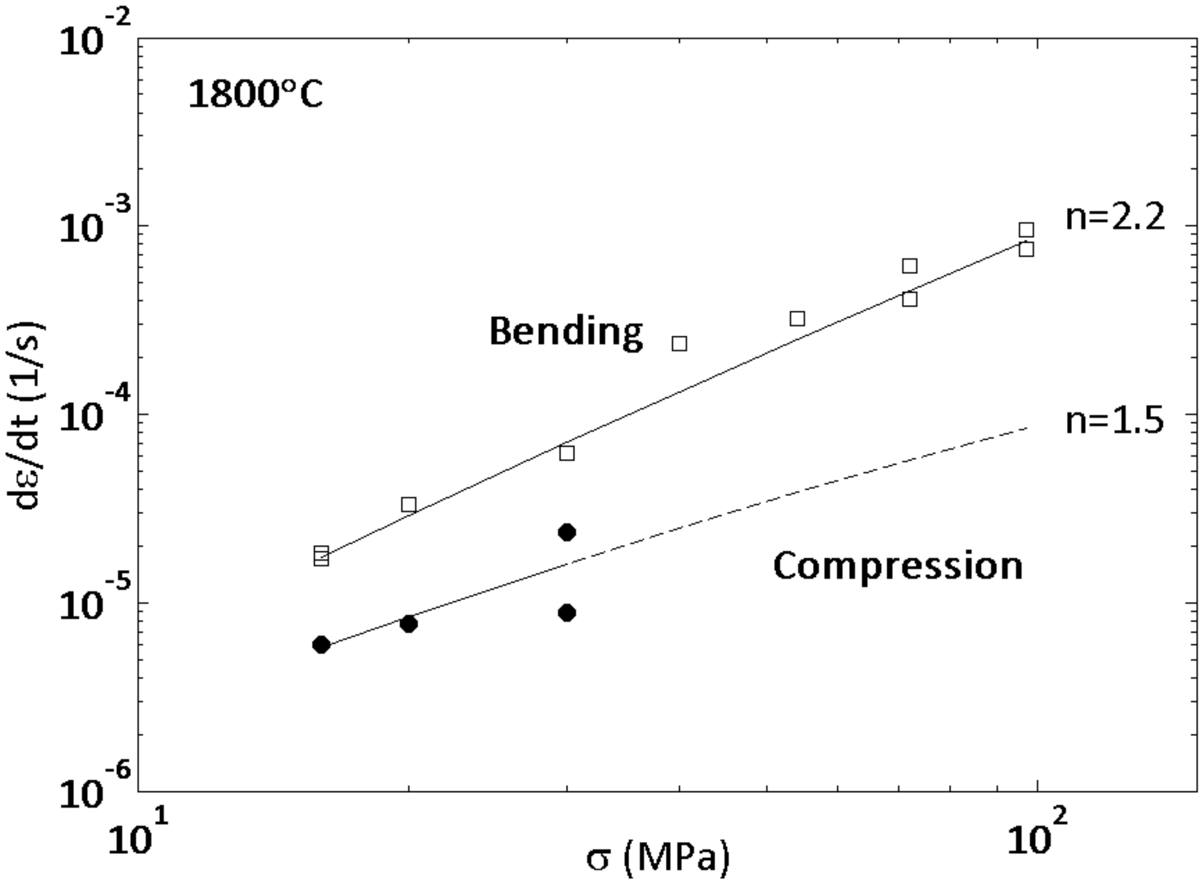
OUTER FIBER STRAIN DISTRI BUTION



Optically measured between inner load span

- Curvature radii measurements show two distinct creep behaviors between compression and tension zones.

CREEP BEHAVIOR



Global Behavior

Bending

$$\frac{1}{\dot{\varepsilon}_{Total}} = \frac{1}{\dot{\varepsilon}_{gbs}} + \frac{1}{\dot{\varepsilon}_{c}}$$

Compression

$$\frac{1}{\dot{\varepsilon}_{Total}} = \frac{1}{\dot{\varepsilon}_{gbs}} + \frac{1}{\dot{\varepsilon}_{Diff}}$$

where

$$\dot{\varepsilon}_{Diff} = \dot{\varepsilon}_{Coble} + \dot{\varepsilon}_{N-H}$$

Local Behavior

Grain Boundaries

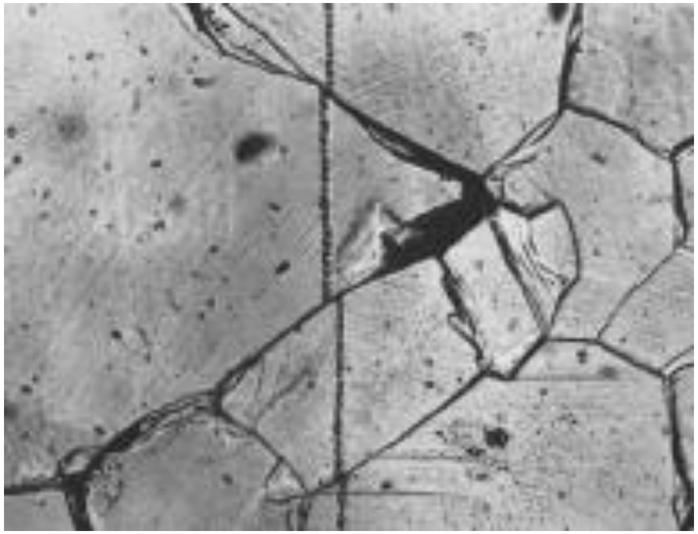
$$\frac{1}{\dot{\varepsilon}_{Mechanism}} = \frac{1}{\dot{\varepsilon}_{Z}} + \frac{1}{\dot{\varepsilon}_{S}} + \frac{1}{\dot{\varepsilon}_{ZS}}$$

Lattice

$$\frac{1}{\dot{\varepsilon}_{Mechanism}} = \frac{1}{\dot{\varepsilon}_{Z}} + \frac{1}{\dot{\varepsilon}_{S}}$$

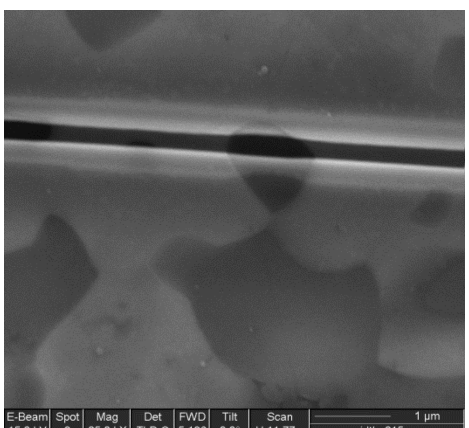
GRAIN BOUNDARY SLIDING CREEP BEHAVIOR

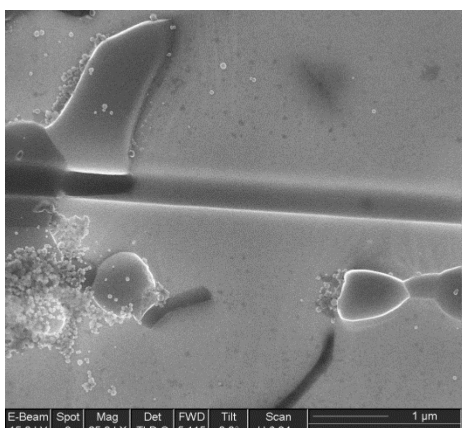
MOTIVATION



R.L. Bell, T.G. Langdon, J. Mat. Sci., 2 (1967) 313-23

CURRENT FIB SCRIBE





- ❖ Our grain sizes 10 x smaller
  - ➢ Scribe width dimensions must be 10 x smaller.
  - ➢ Machining scribe requires advanced equipment
- ❖ Focused Ion Beam (FIB) technology can machine 200-300 nm wide scribes.
- ❖ Machine scribe on flat polished surface parallel to the bending stress.
- ❖ Creep test under vacuum – inert back filled enviornment.

DIMENSIONS AND PARAMETERS

- **300 nm x ~500 nm x 1 mm**
- **500 pA, 30 kV**
- **1μs dwell**
- **Milling time 1 hr/scribe**

EXPERIMENTAL FUTURE GOALS

Creep model development:

- Complete OIM creep strain analysis on large strain (>10%) creep specimens.
- Complete high temperature tensile creep experiments and compare with predicted tensile creep from bending experiments.
- Complete grain boundary sliding experiment
- Complete Microstructure Characterization

Creep Fracture Study:

- Creep Fracture Mechanisms unclear. Literature assumes cavitation nucleated cracks.
- Experiments: WLDCB, Crack Length via resistance methods .
- Link to fracture and creep regime data using C*