

Ultra-High Temperature Ceramic Composites for Leading Edges - 2004

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Ultrahigh temperature ceramics (UHTC) have performed unreliably due to material flaws and attachment design. These deficiencies are brought to the fore by the low fracture toughness and thermal shock resistance of UHTC. If these deficiencies are overcome, we are still faced with poor oxidation resistance as a limitation on UHTC applicability to reusable launch vehicles. We have been addressing the deficiencies of UHTC for the past two years via a small task at GRC that is in the Airframe part of the Next Generation Launch Technology Program. Our focus is on composite constructions and functional grading to address the mechanical issues and on composition modification to address the oxidation issue. The progress on approaches to improving oxidation resistance by alloying and functional grading will be reported.

Keywords: ceramics, composites, carbon fibers, borides, oxidation

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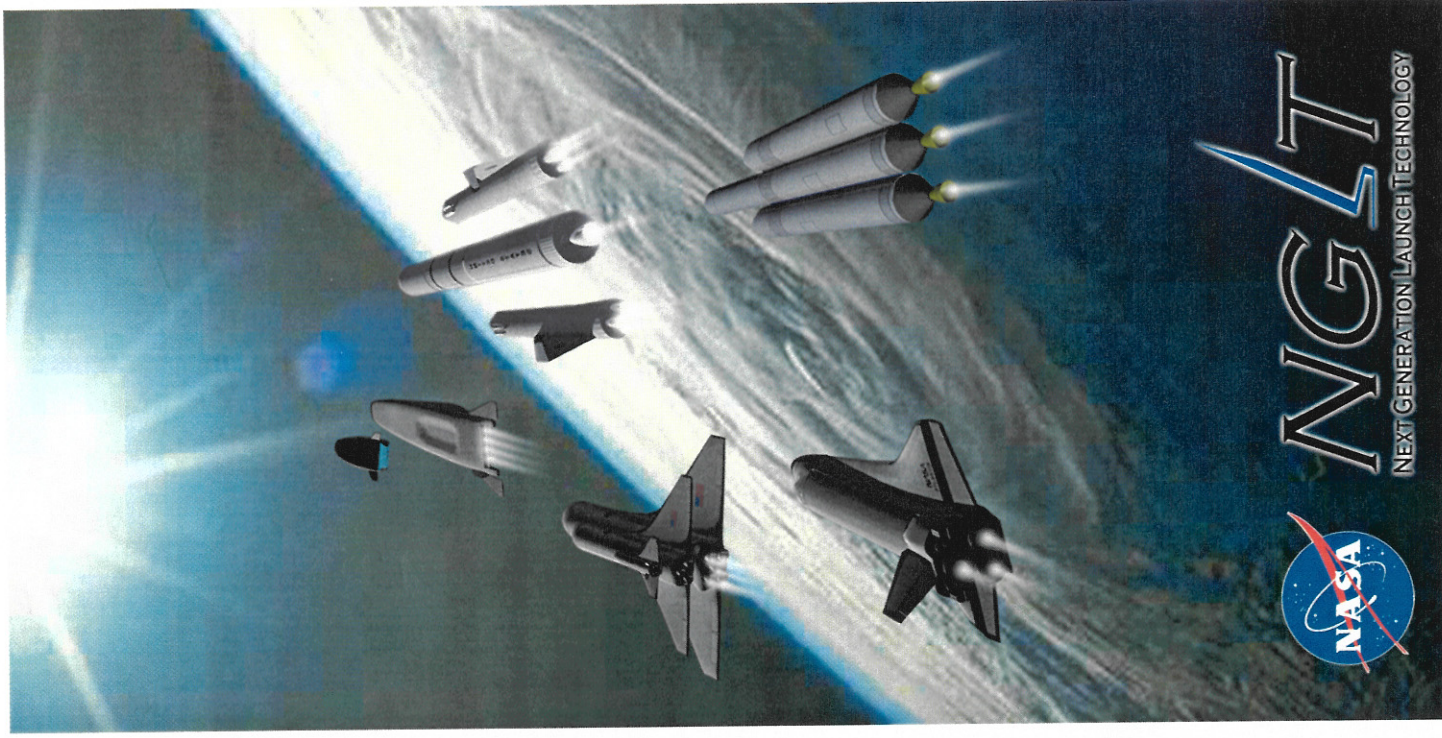
by the

Ceramic, Metal and Carbon Composites Committee (CMC³)
of the

Advanced Composites Working Group (ACWG)

Cape Canaveral, FL

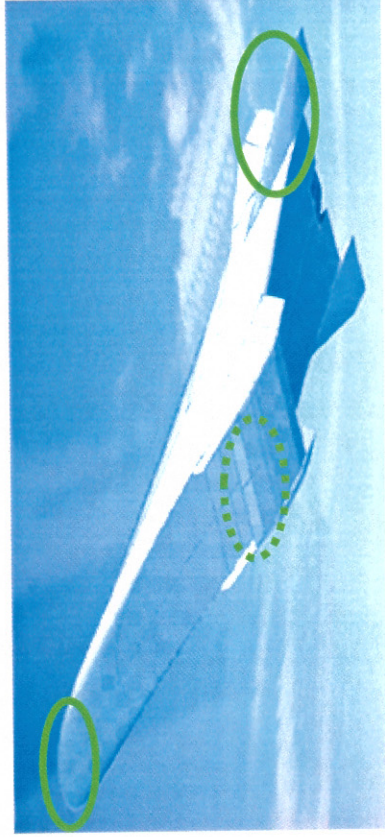
January 25-30, 2004.



OUTLINE

- ◆ Background
- ◆ Objective
- ◆ Ta Modification of ZrB_2 - SiC
 - Furnace oxidation
 - Arc jet test
- ◆ UHTCC
 - Processing
 - Characterization of Starfire UHTCC
- ◆ Concluding Remarks

Ultra High Temperature Ceramic Composites (UHTCC) for Leading Edges



Key Issues

- ◆ Thermal stress resistance
- ◆ Oxidation resistance
- ◆ Temperature capability
- ◆ Architecture optimization

Objective

- ◆ Develop UHTCC for $\geq 3600^{\circ}\text{F}$, reusable, hypersonic vehicle leading edges



Mechanisms for ZrO₂ Protective Scale Enhancement via Ta₂O₅ Additions

- ◆ **Ta₂O₅ as a glass modifier**
 - Talmy et al
- ◆ **Ta⁺⁵ as a dopant in ZrO₂ lattice**
 - Fill O⁻² vacancies
 - Decrease O⁻² transport
- ◆ **Ta₂O₅ as a major oxide scale constituent**
 - Phase V
 - Low melting point

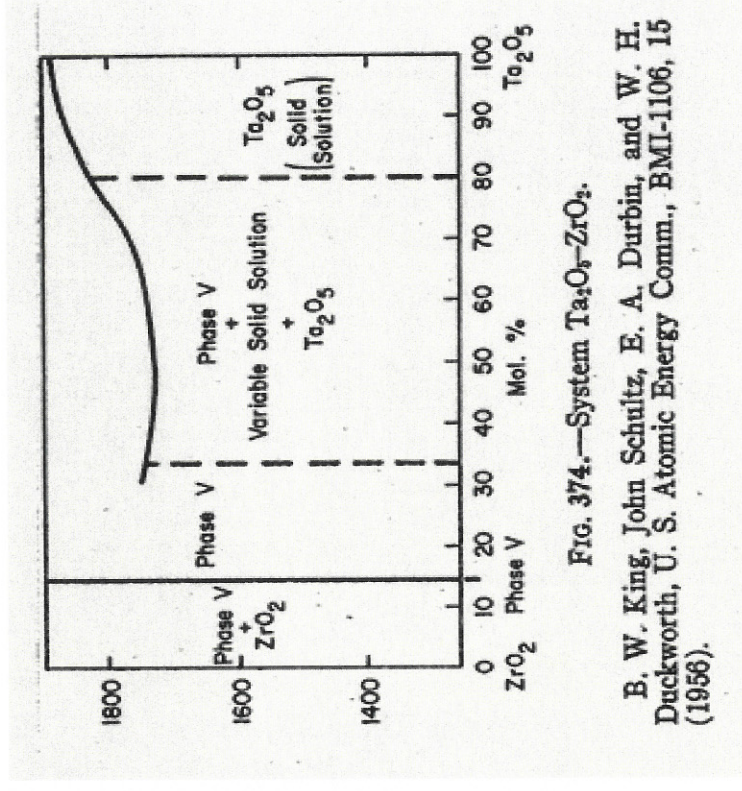


FIG. 374.—System Ta₂O₅-ZrO₂.

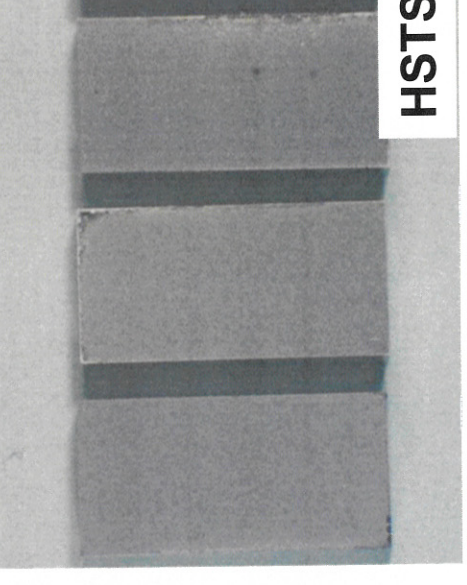
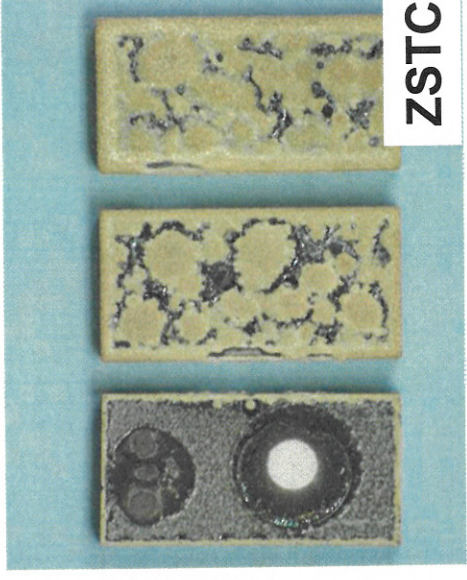
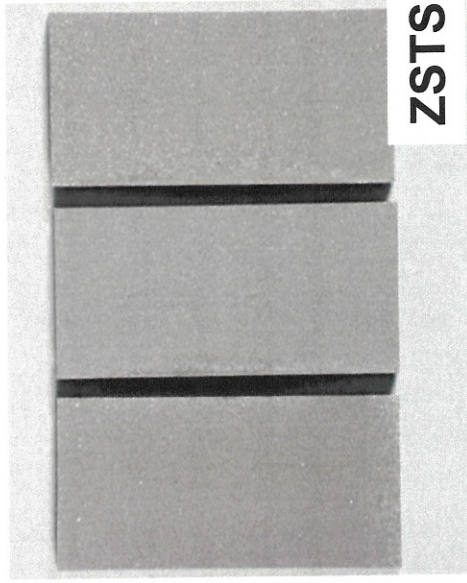
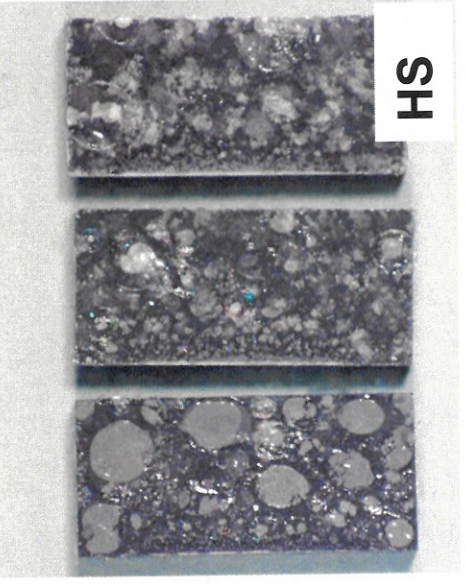
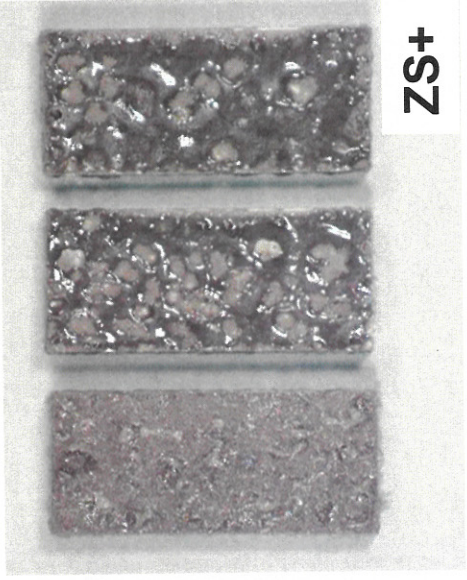
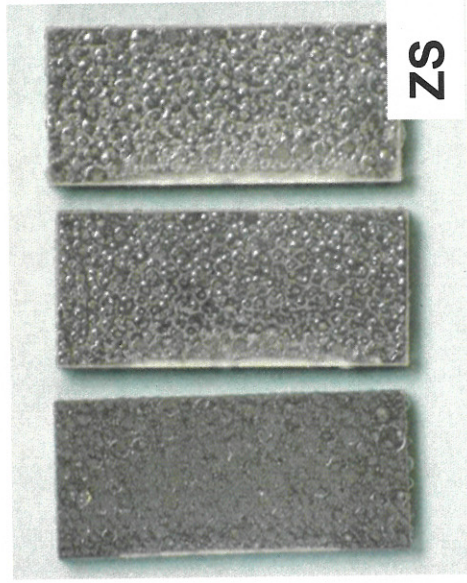
B. W. King, John Schultz, E. A. Durbin, and W. H. Duckworth, U. S. Atomic Energy Comm., BMI-1106, 15 (1956).

Materials Studied

COMPOSITION	DESIGNATION
ZrB ₂ + 20v/o SiC	ZS
HfB ₂ + 20v/o SiC	HS
ZrB ₂ + 20v/o SiC + 20v/o TaSi ₂	ZSTS
ZrB ₂ + 33v/o SiC	ZS+
ZrB ₂ + 20v/o SiC + 20v/o TaC	ZSTC
HfB ₂ + 20v/o SiC + 20v/o TaSi ₂	HSTS

- ◆ powders ball milled, hot pressed ~ 2000°C, 10 ksi, 2h, vacuum
- ◆ 2.54 x 1.2 x 0.3 cm coupons machined from hot pressed plates
- ◆ coupons cleaned, weighed, surface area determined

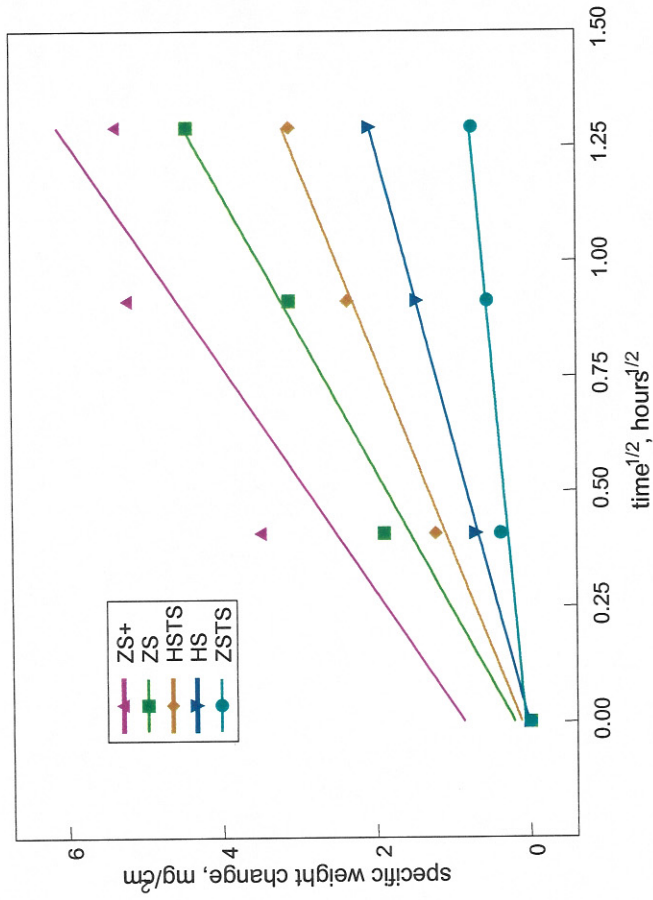
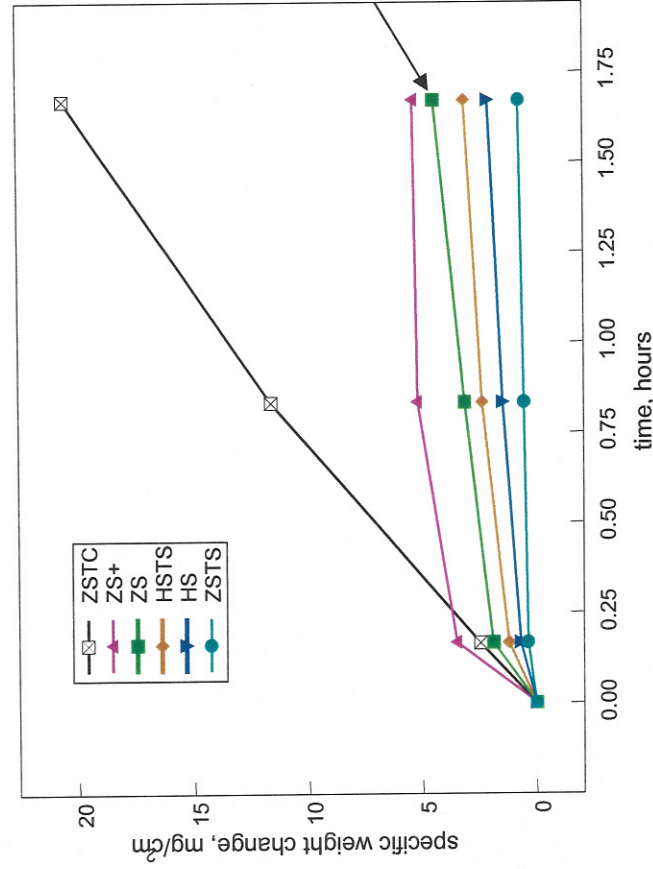
**UHTC Coupon Appearance After Oxidation
1627°C, Stagnant Air**



Left to right: 1, 5, and 10 ten-minute cycles

Ta-containing compositions show less glass formation

Weight Change of UHTC After Oxidation 1627°C, Stagnant Air



- ◆ Poor results for ZS+ relative to ZSTS show that Ta-addition, not additional Si, is responsible for improved oxidation resistance of ZSTS.
- ◆ TaC additions do not improve oxidation resistance at 1627°C.
- ◆ TaSi₂ additions do not improve HS.

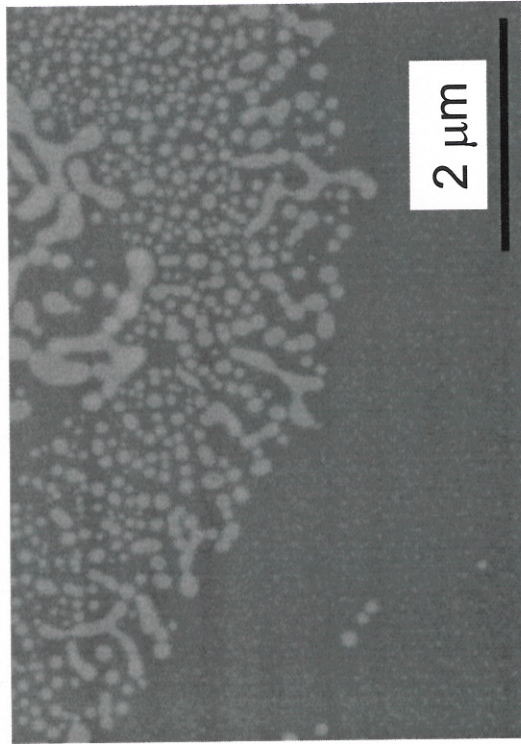
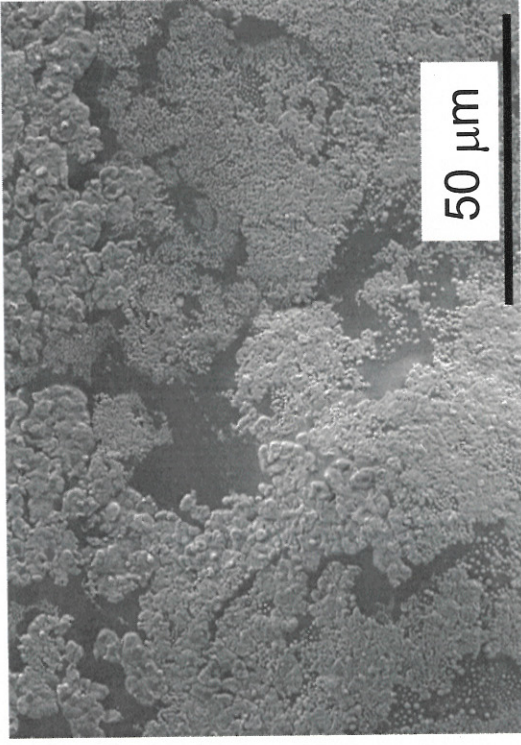
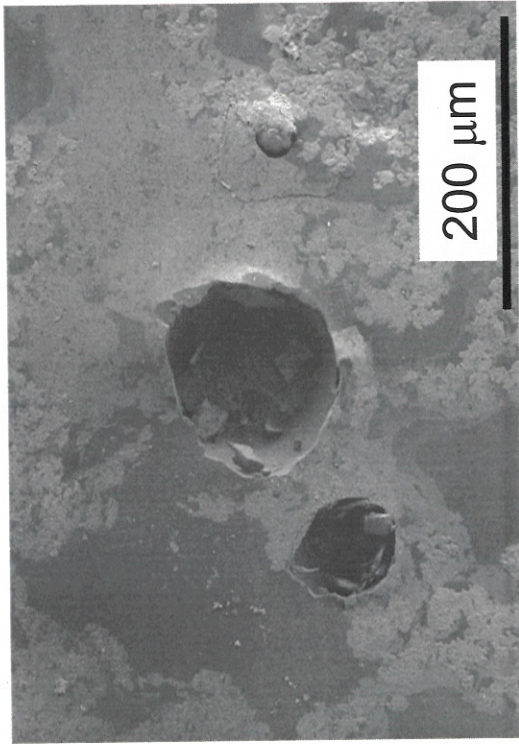
XRD Results for UHTC After Oxidation at 1627°C in Stagnant Air for 100 Min.

composition	phases present
ZS	ZrO ₂ (m), ZrO ₂ (c)
HS	HfO ₂ (m), HfO ₂ (c), HfSiO ₄
ZSTS	ZrO ₂ (m), ZrO ₂ (c)
ZS+	ZrO ₂ (m), ZrO ₂ (c)
ZSTC*	ZrO ₂ (t), ZrO ₂ (m)
HSTS	HfO ₂ (m), HfO ₂ (c), HfSiO ₄

bold = major phase

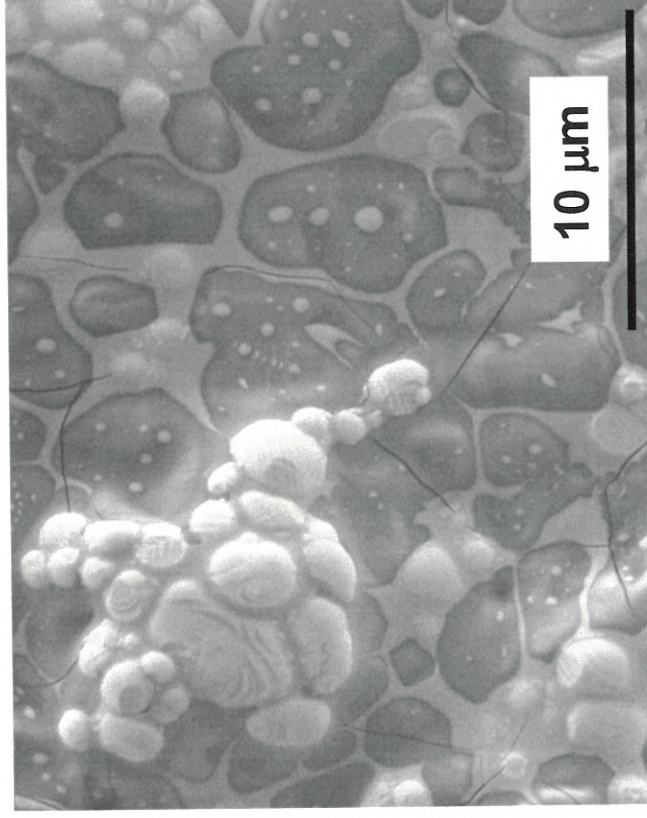
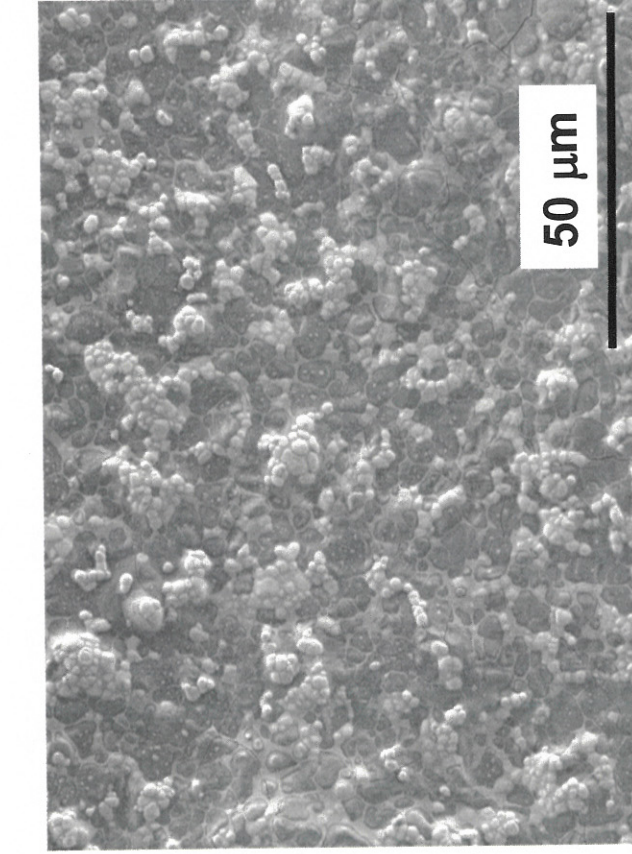
Ta₂O₅·6ZrO₂ (orthorhombic) difficult to distinguish from ZrO₂(c)

Surface Microstructure of ZS After Oxidation at 1627°C in Stagnant Air



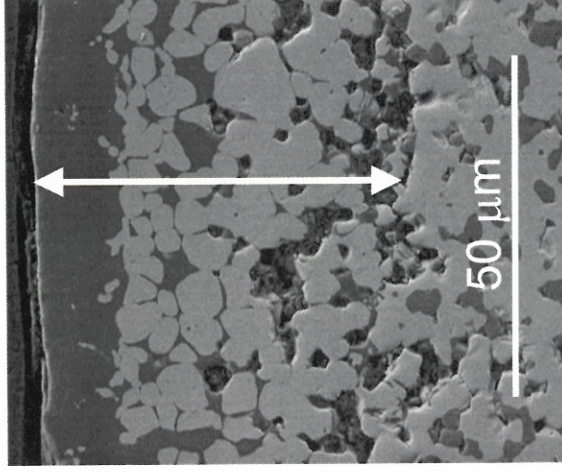
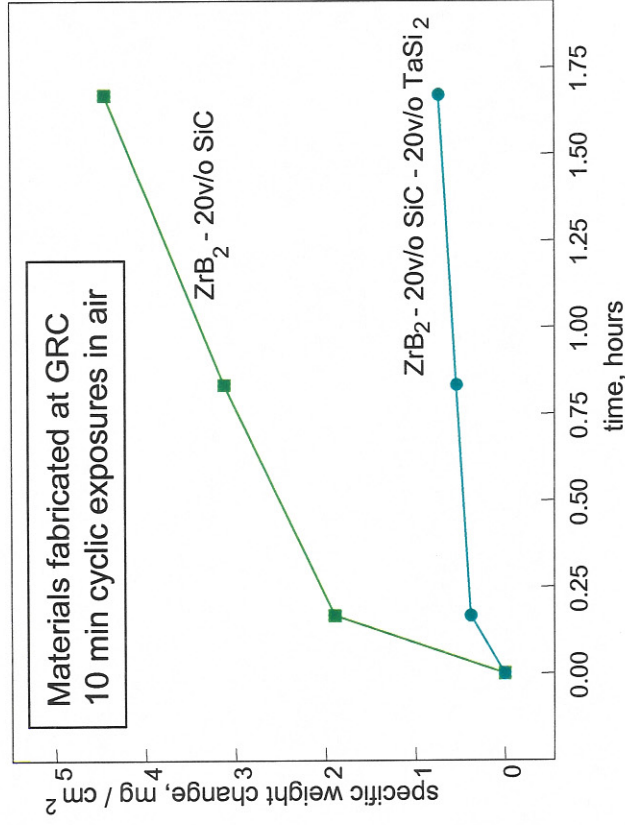
- ◆ Non-uniform dispersion of surface oxide phases.
- ◆ Fine dispersion of second phase in glassy areas.

Surface Microstructure of ZSTS After Oxidation at 1627°C in Stagnant Air

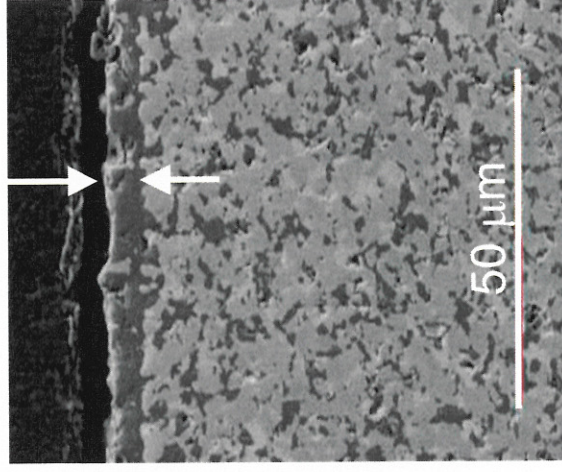


- ◆ Uniform dispersion of surface oxides
- ◆ Evidence of glass immiscibility

Tantalum Additions Improve Oxidation Resistance of ZrB₂-20v/o SiC at 1627°C



ZrB₂ - 20v/o SiC

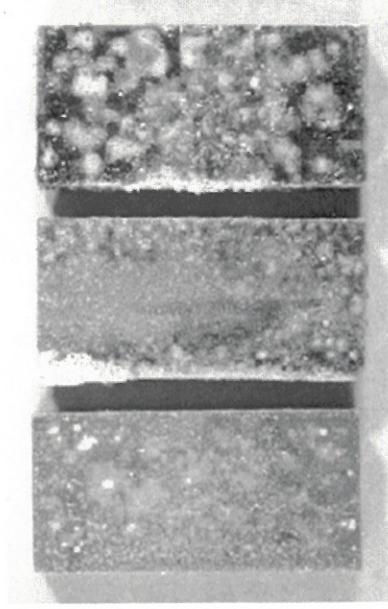


ZrB₂ - 20v/o SiC - 20v/o TaSi₂

UHTC Furnace Oxidized in Air

ZrB₂ + 20 v/o SiC

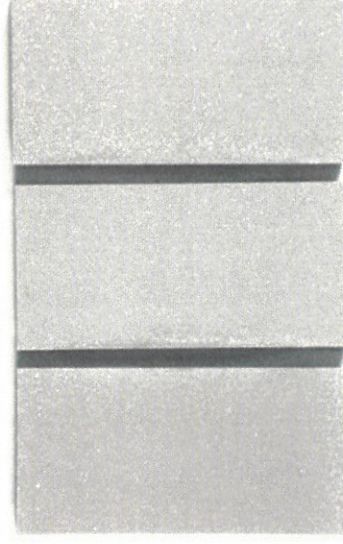
1* 5 10



1627°C

ZrB₂ + 20 v/o SiC + 20 v/o TaSi₂

1 5 10



5



1



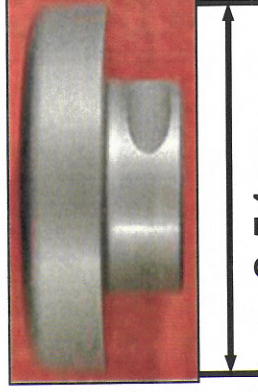
1927°C



5 cycle specimen
after attempted
removal from setter

* # of cycles (1 cycle = 10 minutes hot & 10 minutes cool)

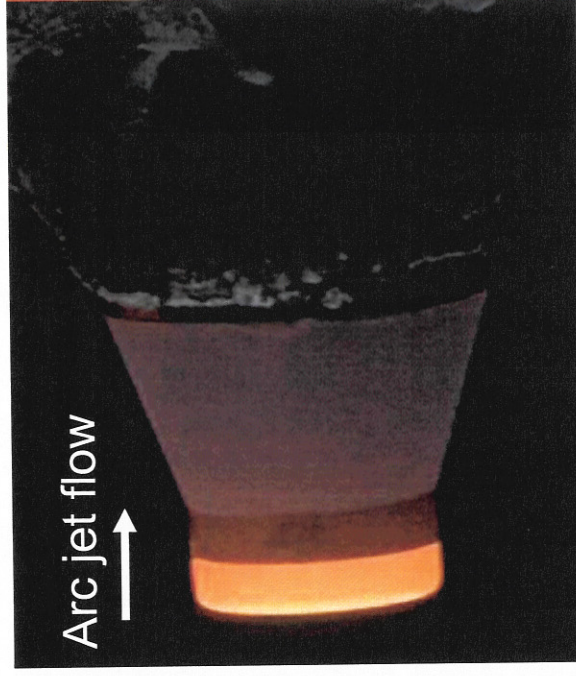
Arc Jet Test of ZrB_2 - 20 v/o SiC - 20 v/o $TaSi_2$



Specimen



Specimen mounted in
graphite holder



Specimen and graphite holder
mounted in arc jet sting

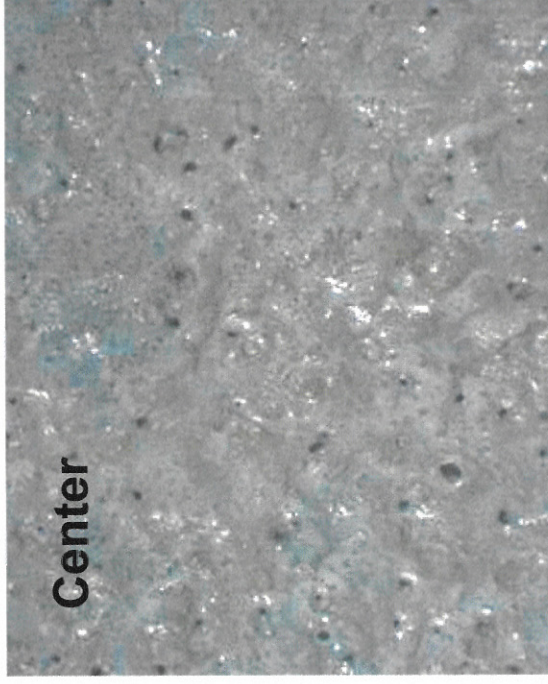
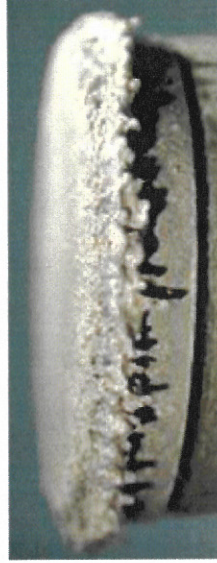
Test Conditions

350 W/cm²
0.07 atm.
600 seconds
% Δ wt = -1.4

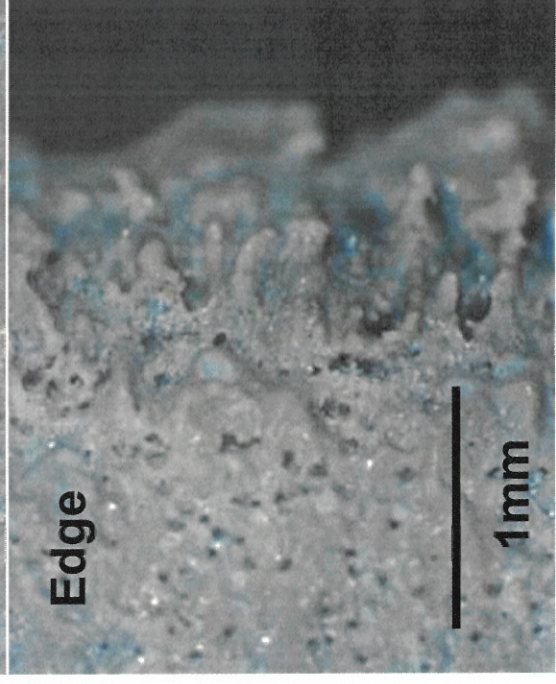
Temperatures and Heat Flux

Measured Temperature ~1800 °C
Edge Heat Flux Estimate ~ 600 W/cm²
Edge Temp Estimate ~1950 to 2000°C

Images of GRC Model After Arc Jet Test



Center



Edge

1mm

XRD Results

- ZrO₂ (m)
- ZrO₂ (c)
- Ta₂O₅ ↑

Some Answers

- ◆ Is Ta or Si in TaSi₂ responsible for the improved oxidation resistance of ZrB₂ – 20v/o SiC – 20v/o TaSi₂? **Tantalum.**
- ◆ Does the benefit of TaSi₂ additions observed at 1627°C extend to higher temperatures? **No, not at 20v/o addition levels.**
- ◆ Are TaSi₂ additions the best way to add Ta to ZrB₂-based UHTC? **TaC additions are not effective at 1627°C.**
- ◆ Can TaSi₂ additions improve the oxidation resistance of HfB₂-based UHTC which are already superior to ZrB₂-based materials? **No, not at 20v/o addition levels.**
- ◆ Can anything be learned about the mechanism by which Ta-additions improve the oxidation resistance of ZrB₂-SiC materials at 1627°C? **Tantalum effects both glass phase and ZrO₂.**

OBJECTIVES

- ◆ Characterize a UHTC composite plate fabricated by Starfire Systems, Inc.
 - CAVEAT: Recognize that little or no development effort went into fabrication of this material. It was a best effort fabrication for NASA LaRC
- ◆ Reveal some of the issues associated with the UHTCC concept

Starfire UHTCC Plate

◆ Constituents

- ◆ Zoltek Panex® 30 Carbon Fabric PW06
- ◆ Starfire Systems' SP-Matrix Polymer (Allylhydridopolycarbosilane (AHPCS))
- ◆ HfB₂ Powder
- ◆ SiC Powder

Processing of Part Number 000928-6-64

◆ Initial Cycle:

- For the initial lay up the **bottom 6 layers of cloth are coated with a SiC/AHPCS slurry** and the **top 5 layers are coated with a HfB₂ /AHPCS slurry** and assembled in a mold.
- Cured to 400°C and fired to 850°C under inert gas to pyrolyze.

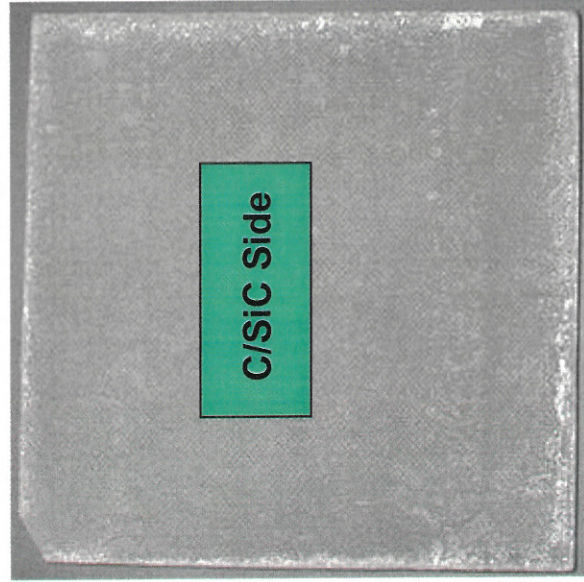
◆ Cycle 2:

- **Coat the HfB₂ side of the plate with more HfB₂ /AHPCS slurry.**
- Fire directly to 850°C under inert gas.

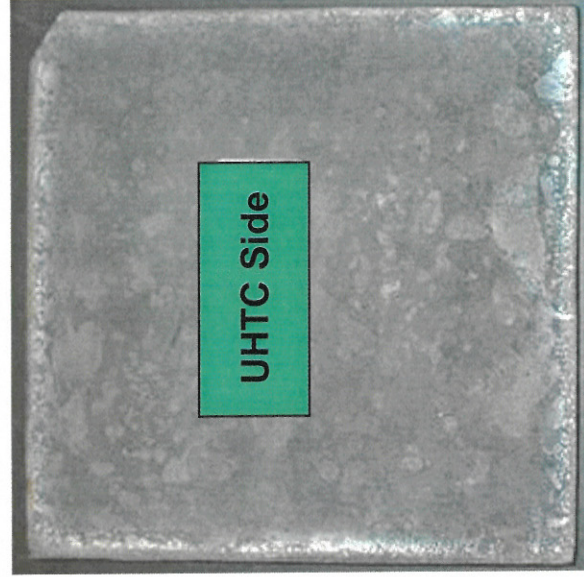
◆ Cycle 3: Repeat cycle 2

◆ Cycle 4 - 10:

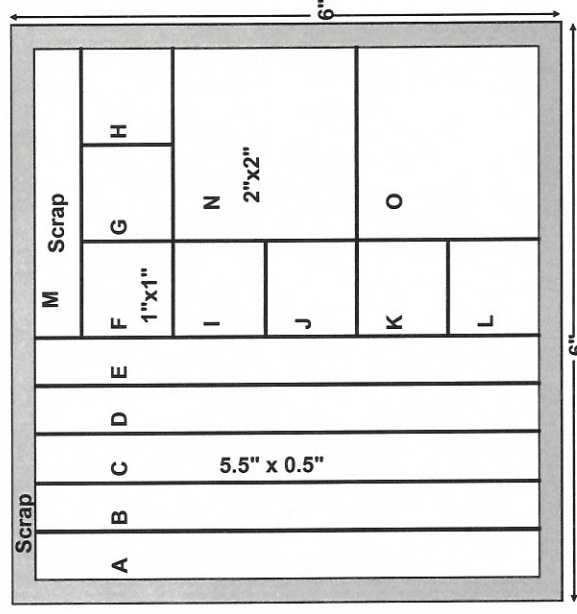
- **Vacuum infiltrate with AHPCS only.**
- Pyrolyze directly to 850°C under inert gas, no clamping necessary.



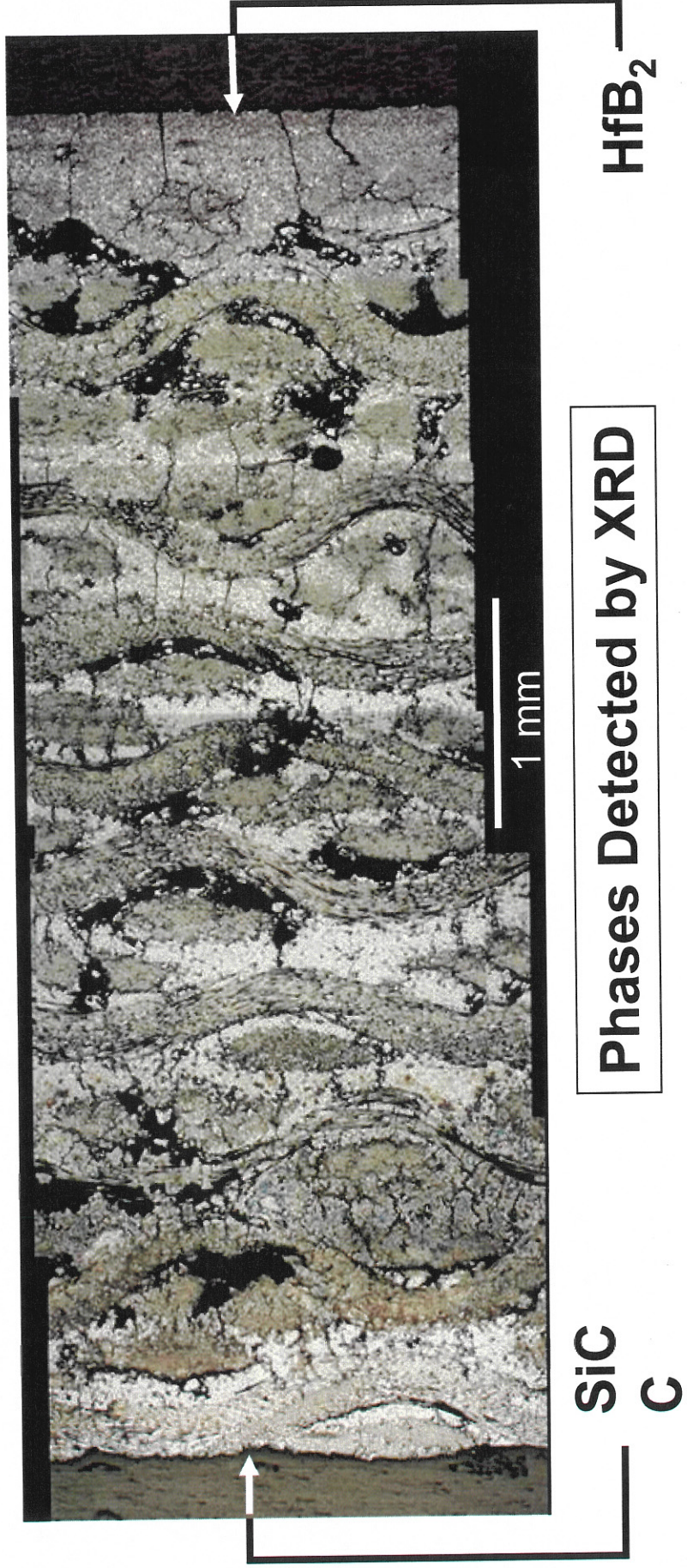
C/SiC Side



UHTC Side

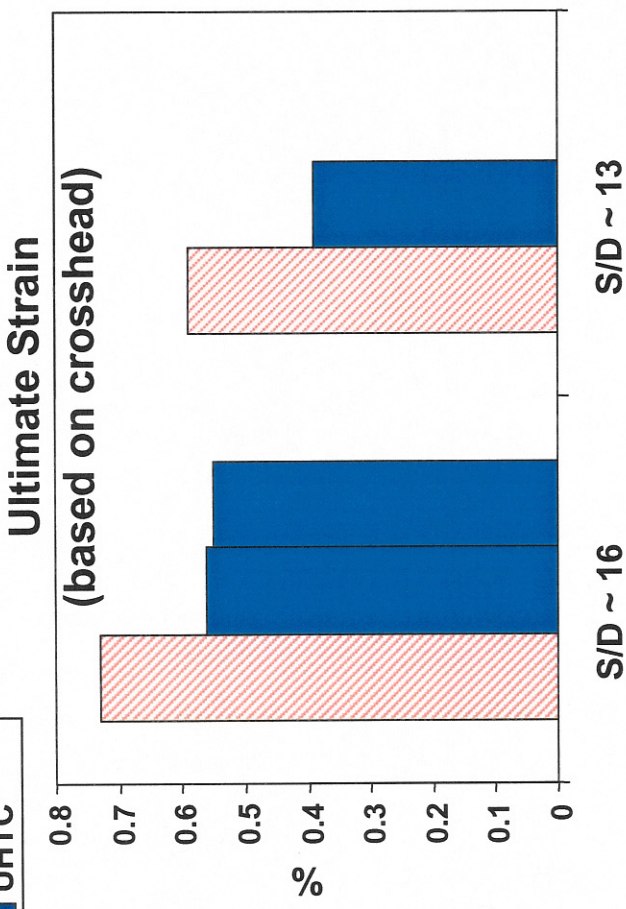
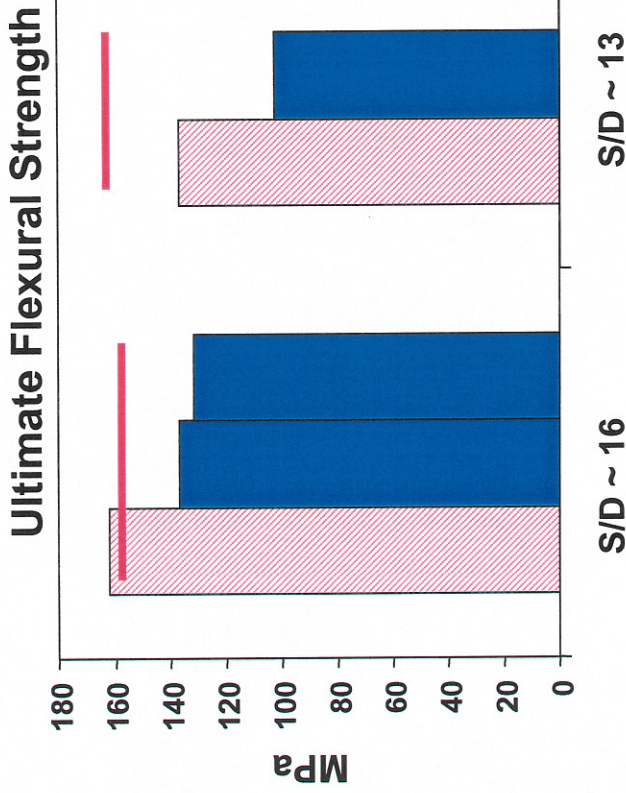


UHTCC Cross-section



UHTCC Flexural Strength Results

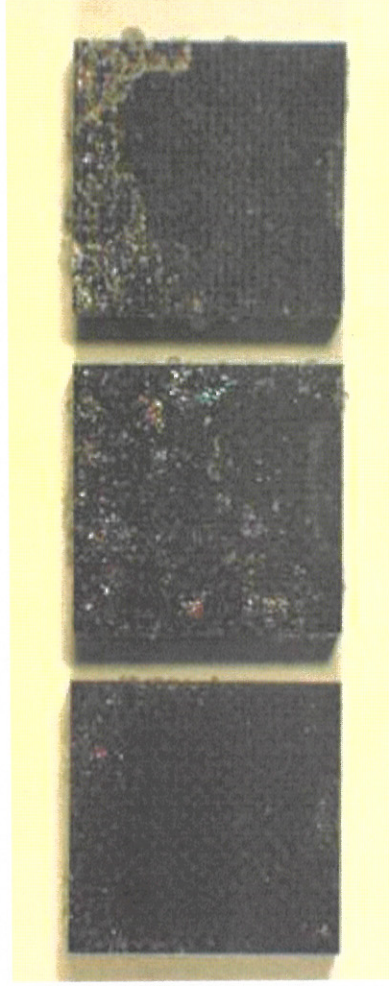
Tension Side
 — Prediction
 ▨ C/SiC
 ■ UHTC



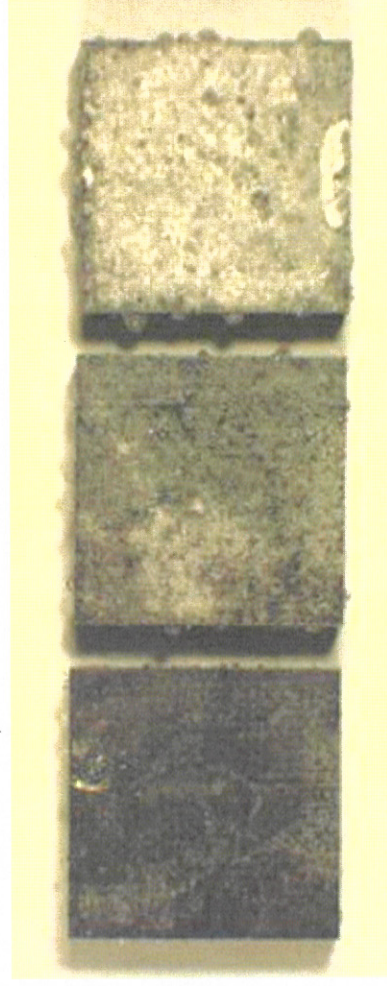
Note: S/D ≥ 16 necessary for valid 4 point flexural test

- ◆ Predictions Based on Beam Theory
- ◆ Calculated load at 0.7% strain
- ◆ Panex 30 minimum property: E = 193 GPa
- ◆ Rule of mixtures with no matrix contribution

UHTCC After 1627°C Furnace Oxidation



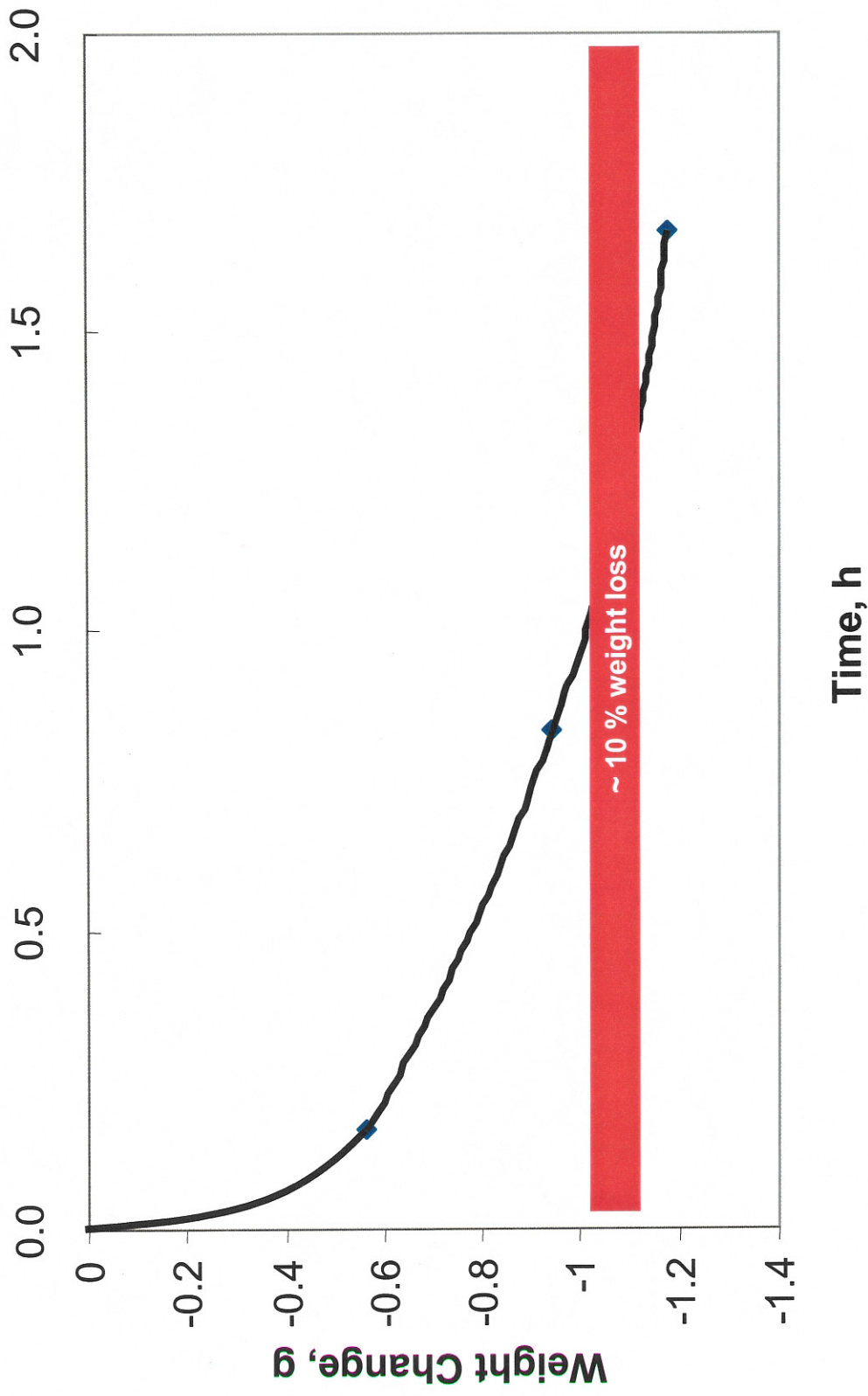
**C/SiC
Side**



**HfB₂
Side**

Cycles	1	5	10
Hours	0.167	0.833	1.667

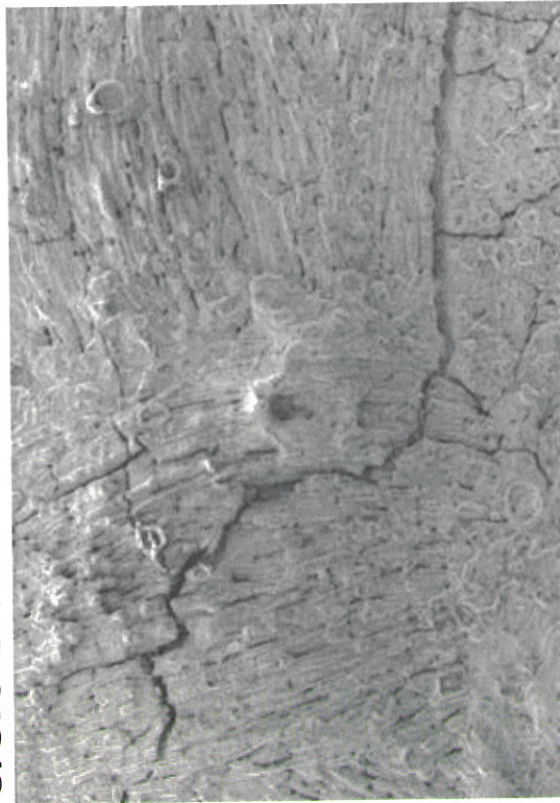
Furnace Oxidation of UHTCC at 1627°C



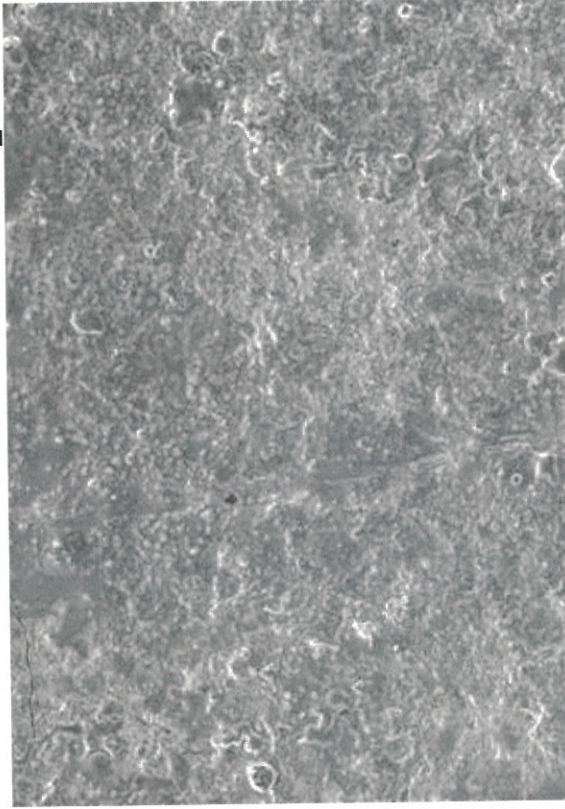
UHTCC After 10 Ten-minute Cycles in Air at 1627°C

C/SiC Side

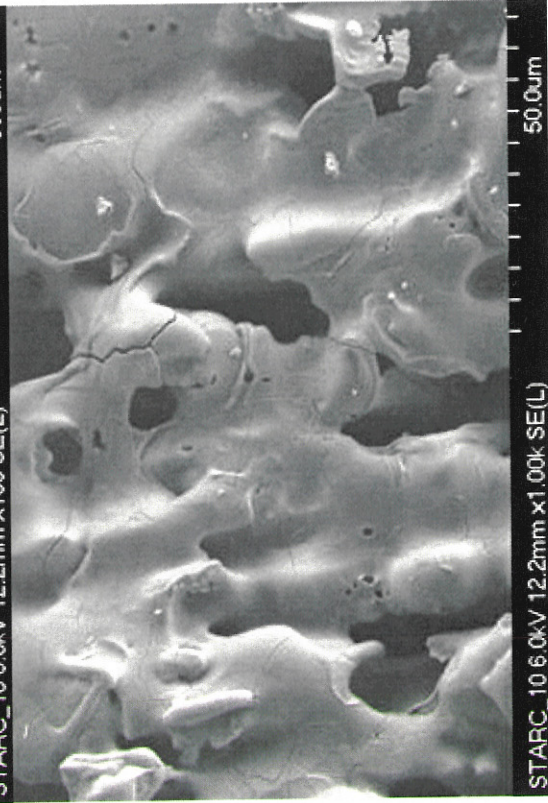
HfB₂ Side



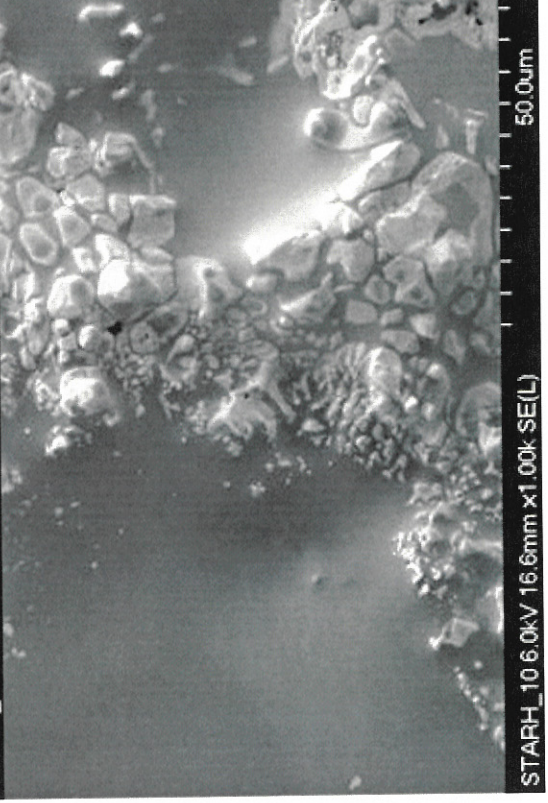
STARC_10 6.0kV 12.2mm x100 SE(L)



STARH_10 6.0kV 12.1mm x100 SE(L)



STARC_10 6.0kV 12.2mm x1.00k SE(L)



STARH_10 6.0kV 16.6mm x1.00k SE(L)

UHTCC Oxy-Acetylene Torch Test

- ◆ **Sample O: One 4 min. cycle to 1805°C**
 - Temps with Ircon 2 color pyrometer, 980-1760°C range
 - Weight loss = 0.79 g, or 1.9%
- ◆ **Sample N: Three ~4 min. cycles**
 - Cycle 1 max temp 1815°C
 - Cycle 2 max temp 1915°C
 - Cycle 3 max temp 2015°C
 - Weight loss = 1.95 g, or 4.6%

Sample O	
Time, min.	Temp, °C
0.5	1720
1.0	1750
1.5	1750
2.0	1755
2.5	1765
3.0	1775
3.5	1790
4.0	1805



0 sec

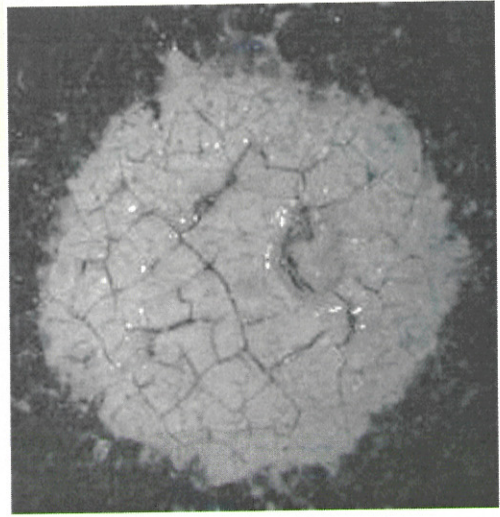
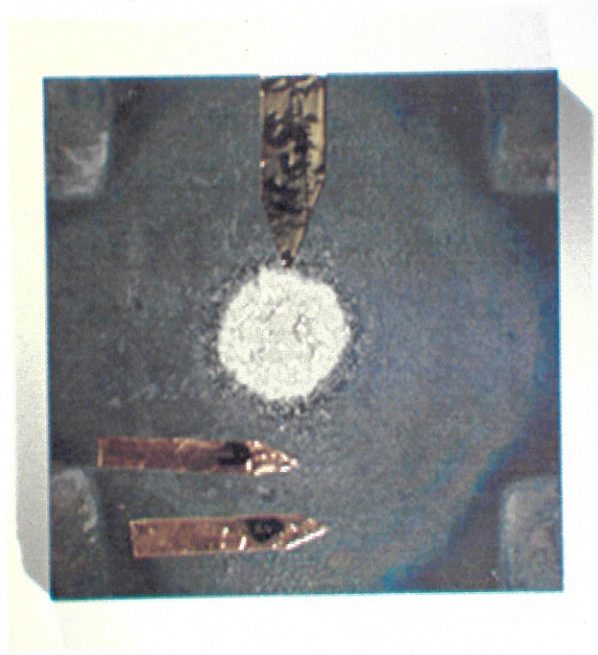
10 sec

20 sec

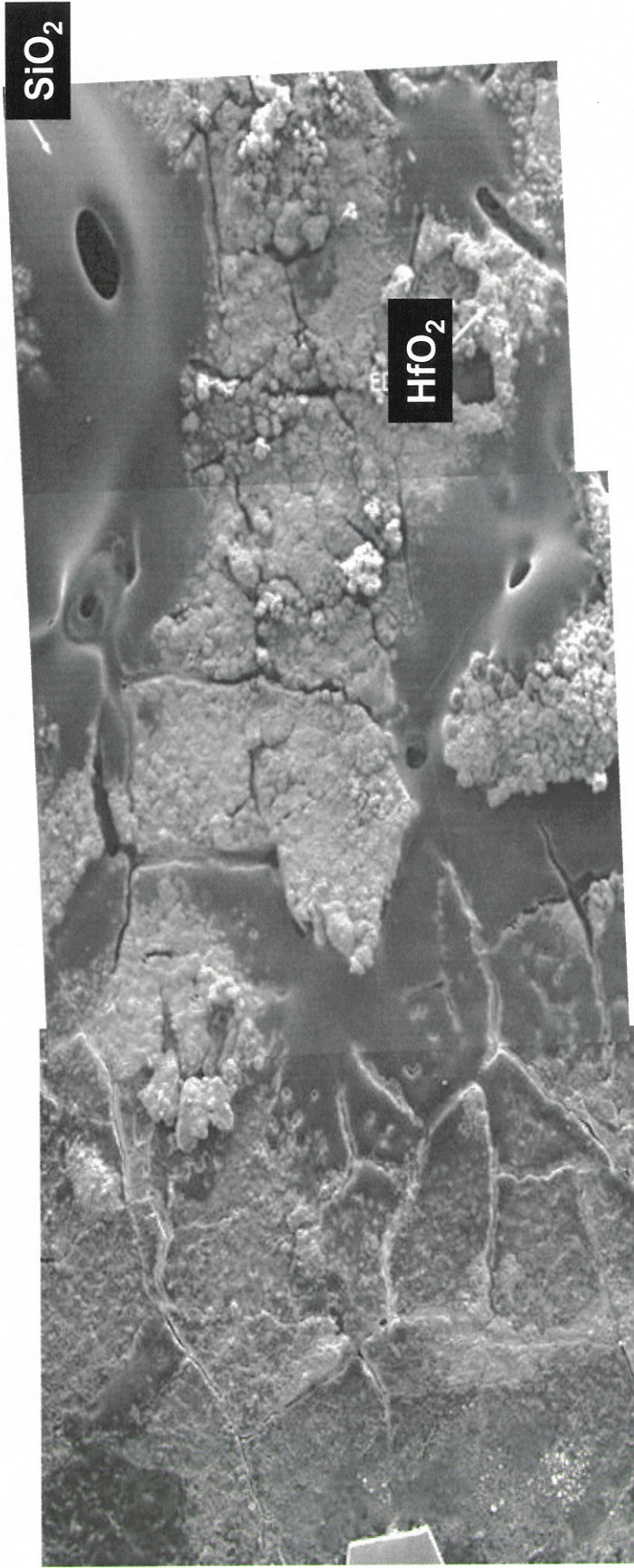
30 sec

Specimen "O" during cool-down

UHTC Surface After Three 4-Minute Torch Cycles to 1815 to 2015°C



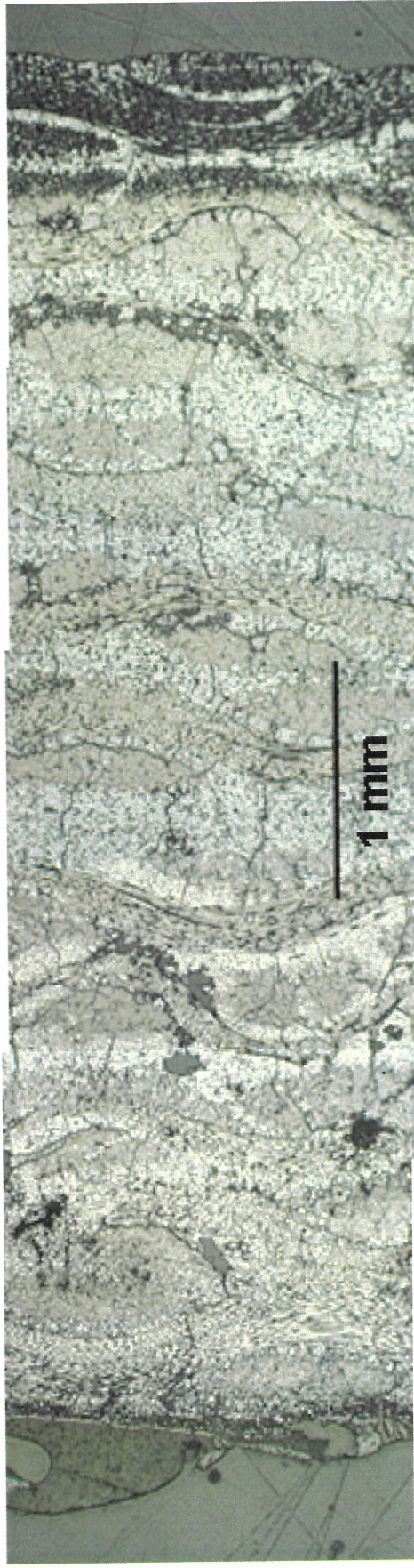
SEM of Center of UHTC Surface After Three Torch Cycles



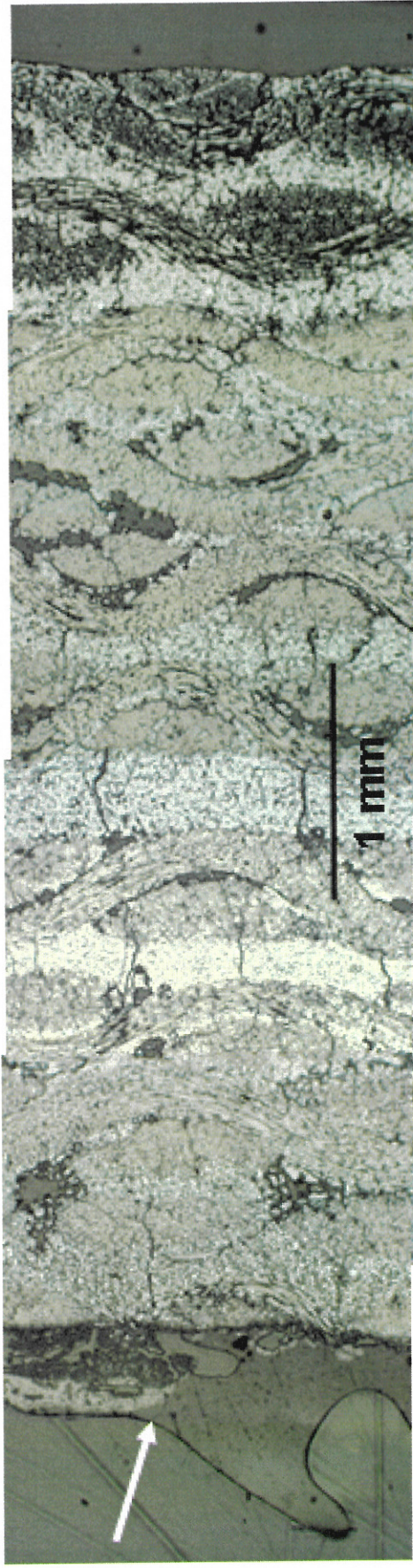
UHTCC Specimen Center Cross Sections After Torch Test

HfB₂

C/SiC

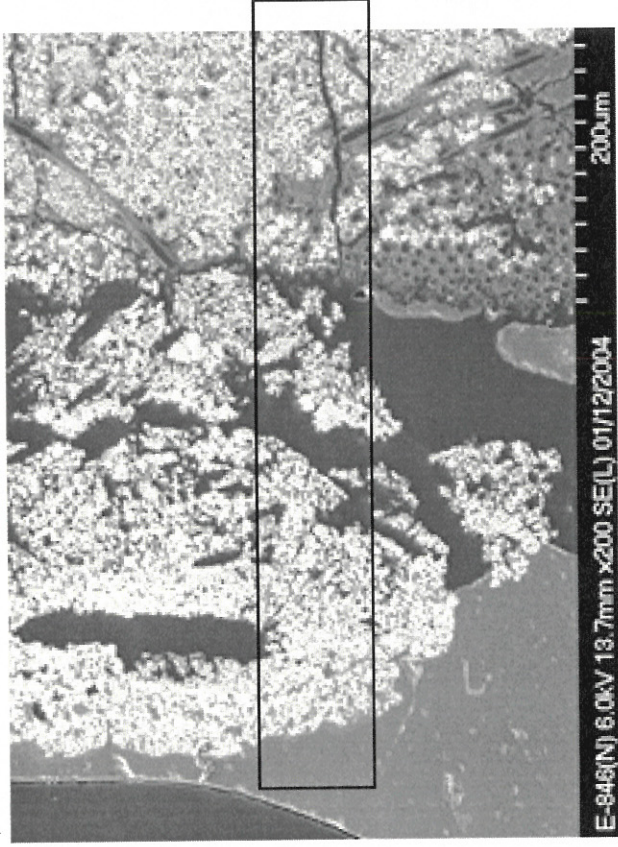
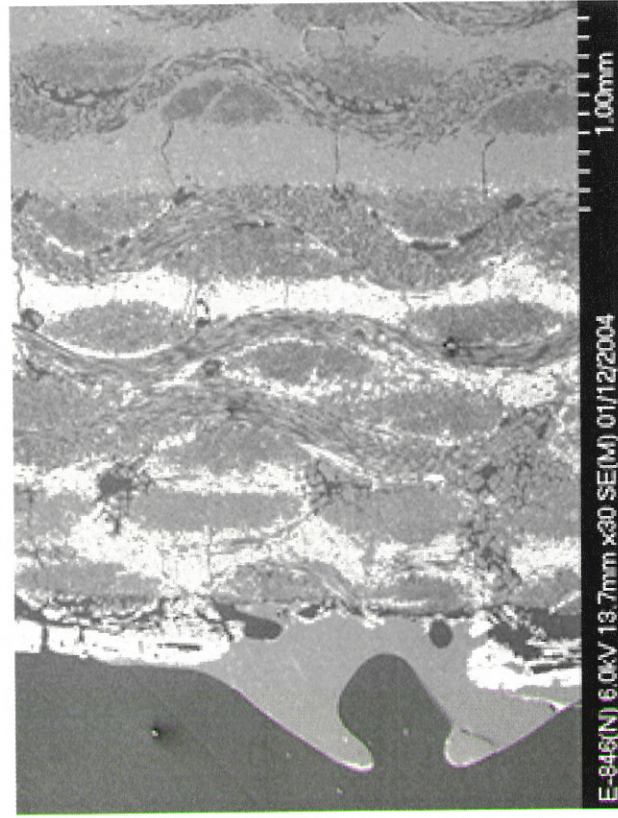


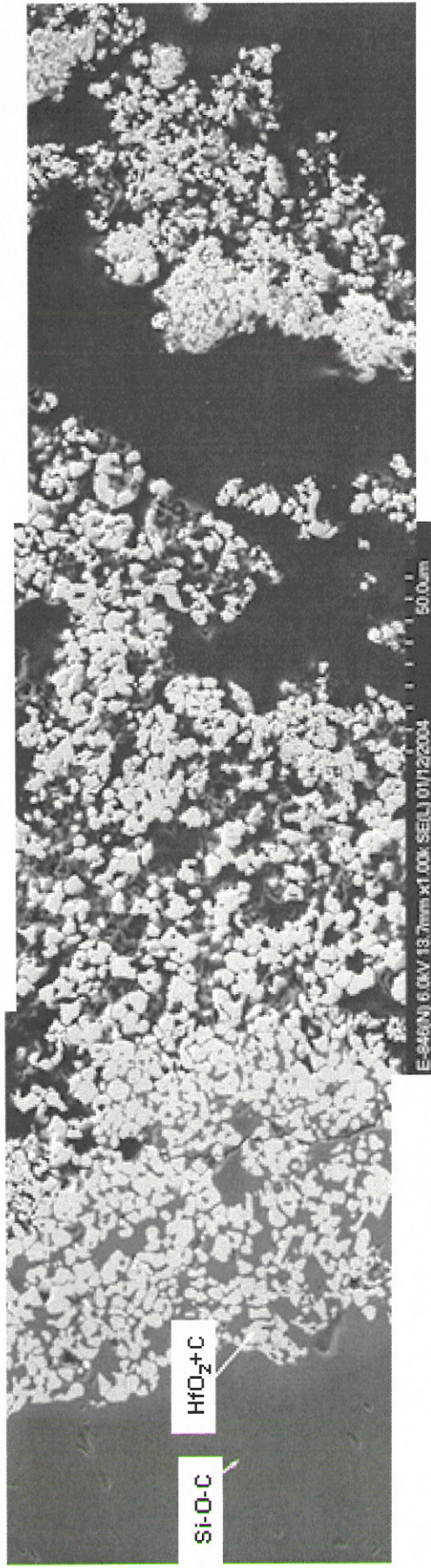
One 4-Minute Cycle to 1805°C



Three 4-Minute Torch Cycles to 1815 to 2015°C

UHTC Side, Center Hot Zone





Conclusions

- ◆ **TaSi₂ Additions**
 - Good results at 1627°C, but oxide scale too fluid at > ~ 1800°C
 - Look at lower levels of additive
- ◆ **UHTCC**
 - **Processing**
 - Uniform and through thickness graded microstructure achieved
 - Matrix cracking due to thermal expansion mismatch between C fibers and matrix constituents is a concern
 - **Mechanical Properties**
 - Flexural strength was close to expected values based on rule of mixtures with no matrix contribution
 - Some evidence of composite behavior
 - **Furnace Oxidation**
 - Weight loss and metallography indicated that carbon fiber oxidation occurred rapidly
 - **Torch Test**
 - Based on observed temperature spikes during test, adherence of the HfO₂-rich scale is an area of concern
 - Material withstood ~2000°C (~3600°F), severe heat-up and thermal gradients with no major visible distress, but with significant HfB₂ coating and carbon fiber oxidation revealed by metallography

Future Work

- ◆ **Complete oxidation studies focused on lower levels of Ta addition to achieve doping without low melting phase formation**
- ◆ **Continue UHTCC evaluation**
 - Complete metallography on Starfire specimens
 - Evaluate other NASA and industry developed materials
- ◆ **Continue UHTCC development**
 - Fiber coatings need to be incorporated to address fiber oxidation issues
 - Advanced SiC fibers need to be evaluated to address oxidation and thermal expansion mismatch issues

Acknowledgements

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- ◆ Thanks to QSS employees Terry R. McCue for scanning electron microscopy support and Ronald E. Phillips for assistance with testing at GRC.
- ◆ Thanks to David Glass of NASA Langley for providing the Starfire UHTCC plate.
- ◆ Thanks to Walt Sherwood of Starfire Systems Inc. for providing processing details and for permission to present this study.
- ◆ Thanks to Sarah E. Beckman and Jerome W. Ridge (Eloret Inc.) of NASA Ames Research Center for assistance with arc jet testing.