ULTA-HIGH TEMPERATURE CERAMIC COMPOSITES FOR LEADING EDGES

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ABSTRACT

Ultra-high 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. In particular, initial tests of tantalum additions have shown potential for major improvement. Results for additional tests at higher temperatures will be presented. These oxidation improvements are being incorporated in the composites approaches. Two fabrication approaches are being pursued to produce carbon fiber reinforced UHTC composites: prepregging and rigid perform infiltration. Fabrication procedures, microstructures, and initial mechanical property and oxidation results for composites will be reported

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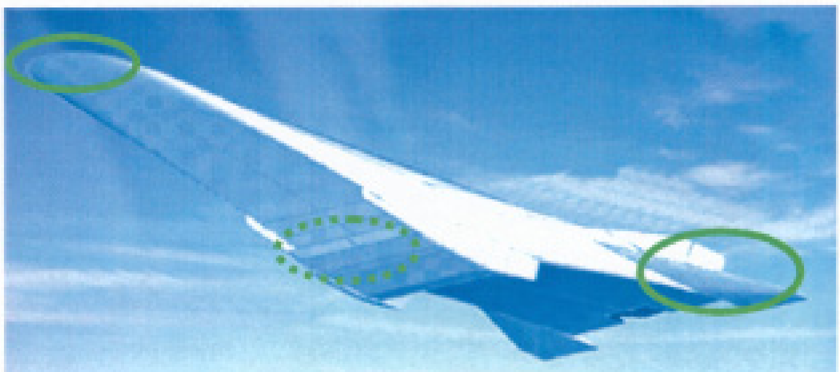
Outline

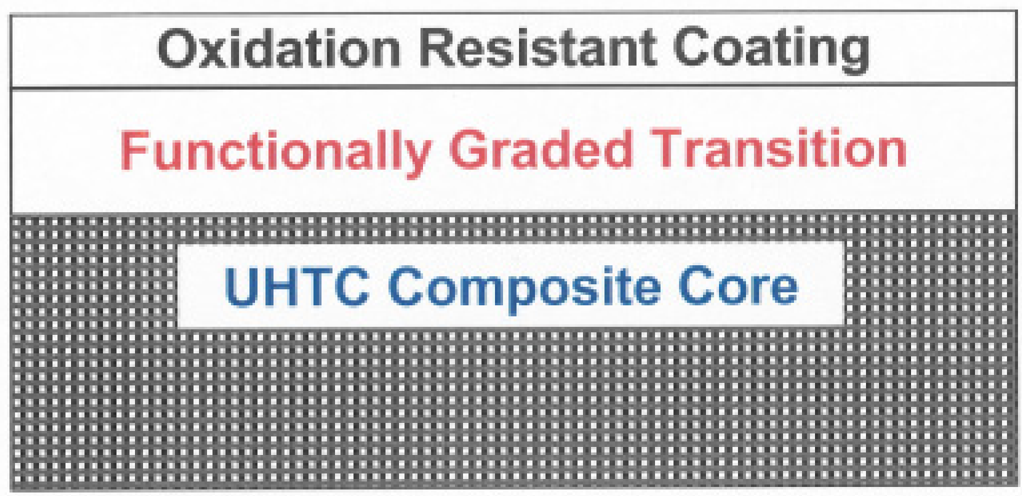
- Background
- Objectives
- Ta Modification of ZrB_2 - SiC
  - Furnace oxidation
  - Arc jet test
- UHTCC
  - Processing
  - Characterization of Starfire UHTCC
- Concluding Remarks

Ultra High Temperature Ceramic Composite (UHTCC) Leading Edge



Key Issues

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



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Mechanisms for ZrO_2 Protective Scale Enhancement via Ta_2O_5 Additions

- Ta_2O_5 as a glass modifier
  - Talmy et al
- Ta^{+5} as a dopant in ZrO_2 lattice
  - Fill O^{-2} vacancies
  - Decrease O^{-2} transport
- Ta_2O_5 as a major oxide scale constituent
  - Phase V
  - Low melting point

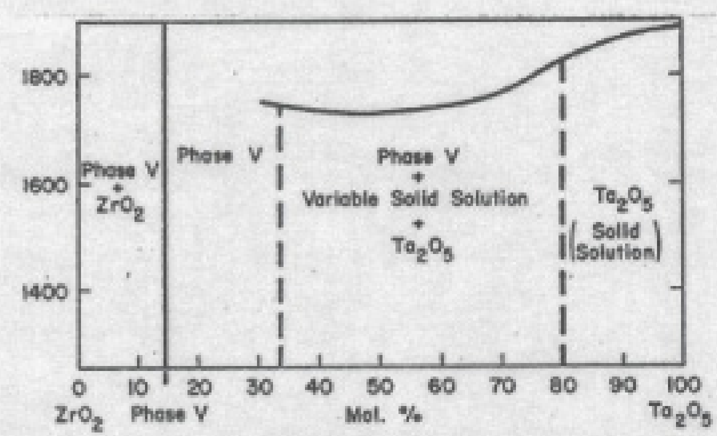


FIG. 374.—System Ta_2O_5–ZrO_2.

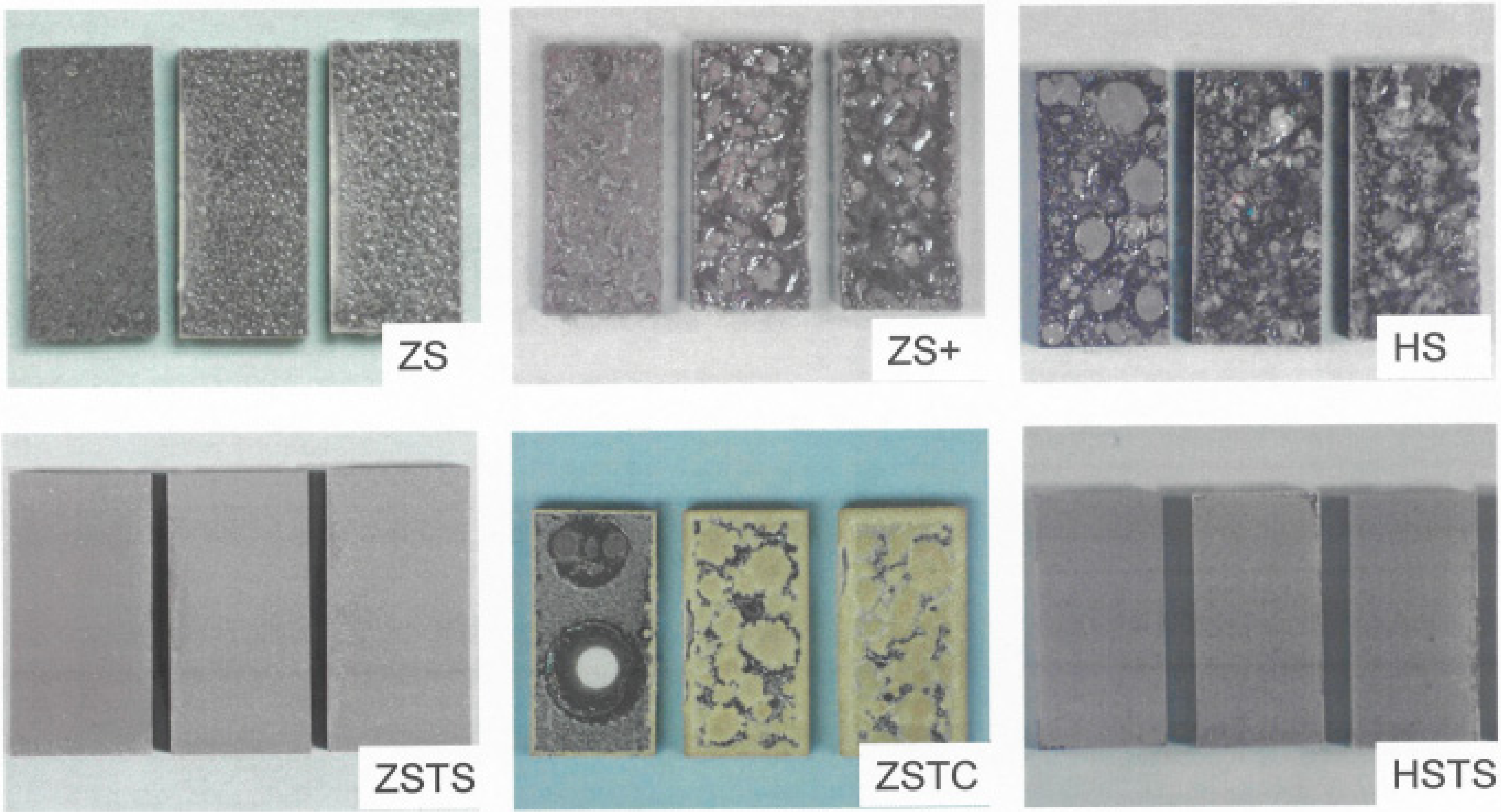
B. W. King, John Schultz, E. A. Durbin, and W. H. Duckworth, U. S. Atomic Energy Comm., BMI-1106, 15 (1956).

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

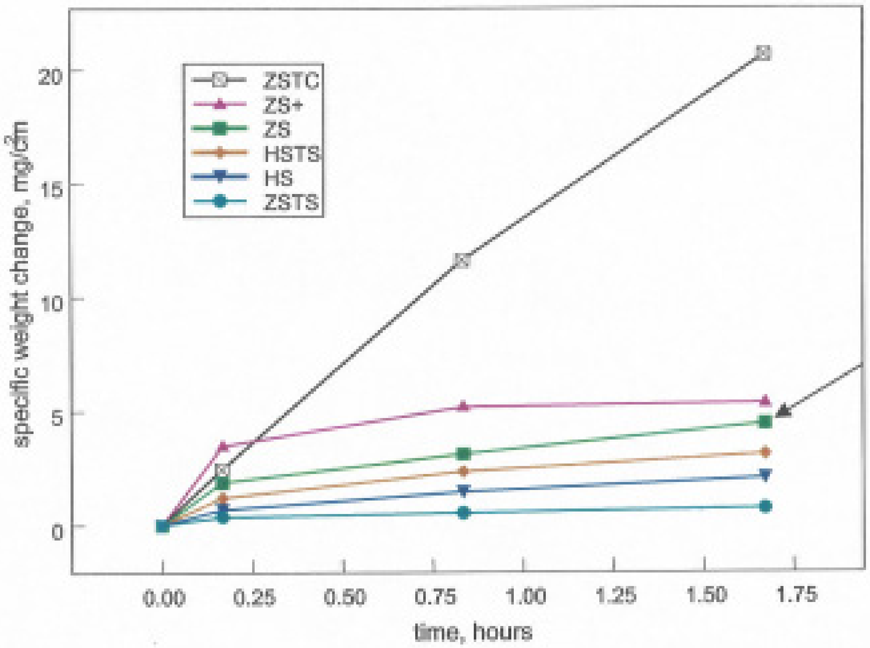
UHTC Coupon Appearance After Oxidation 1627°C, Stagnant Air

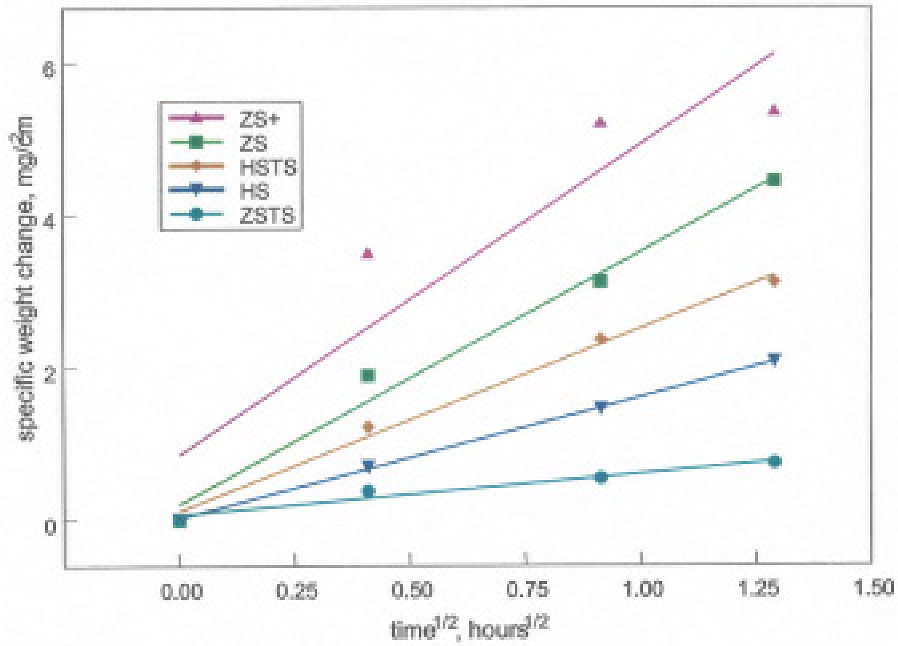


Left to right: 1, 5, and 10 ten-minute cycles

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.
- $TaSi_2$ additions do not improve HS.

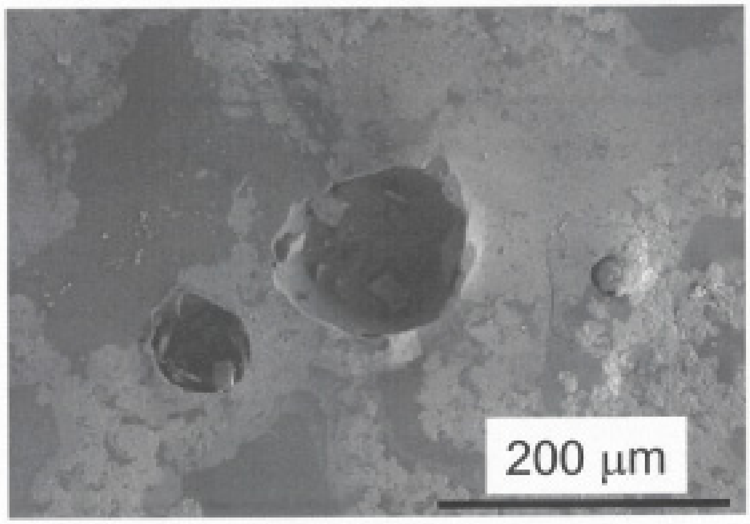
XRD Results for UHTC After Oxidation at 1627°C in Stagnant Air for 100 Min.

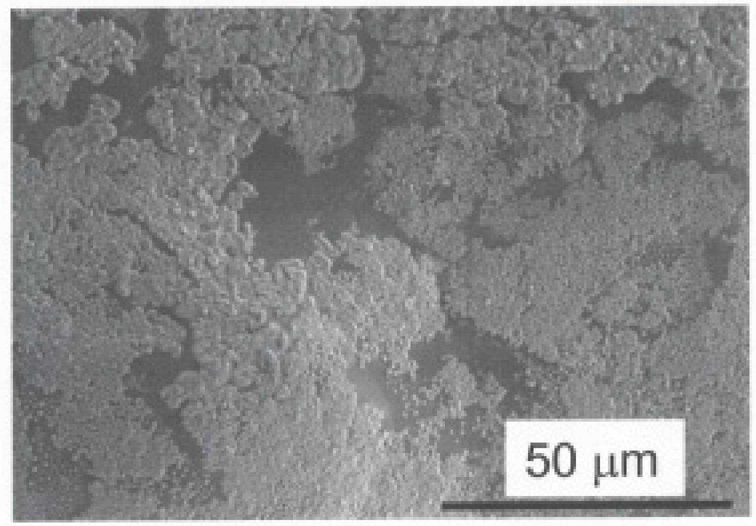
composition	phases present
ZS	**ZrO_2(m)**, ZrO_2(c)
HS	**HfO_2(m)**, HfO_2(c), $HfSiO_4$
ZSTS	**ZrO_2(m)**, ZrO_2(c)
ZS+	**ZrO_2(m)**, ZrO_2(c)
ZSTC*	**ZrO_2(t)**, ZrO_2(m)
HSTS	**HfO_2(m)**, **HfO_2(c)**, **$HfSiO_4$**

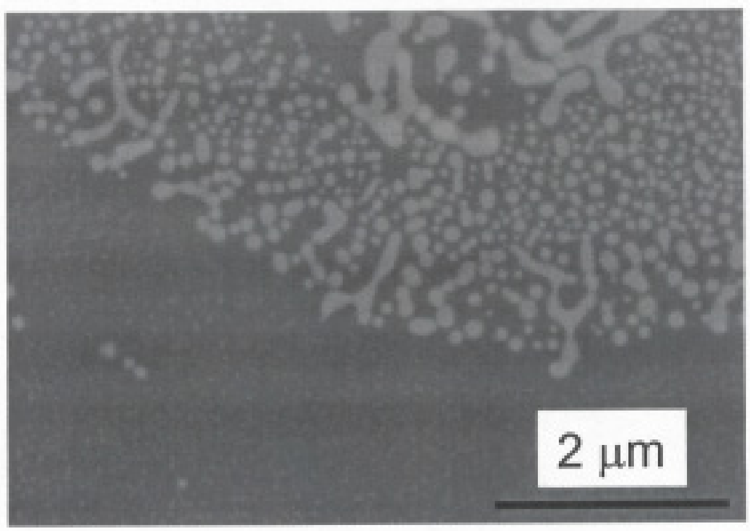
bold = major phase

$Ta_2O_5 \cdot 6ZrO_2$ (orthorhombic) difficult to distinguish from ZrO_2(c)

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

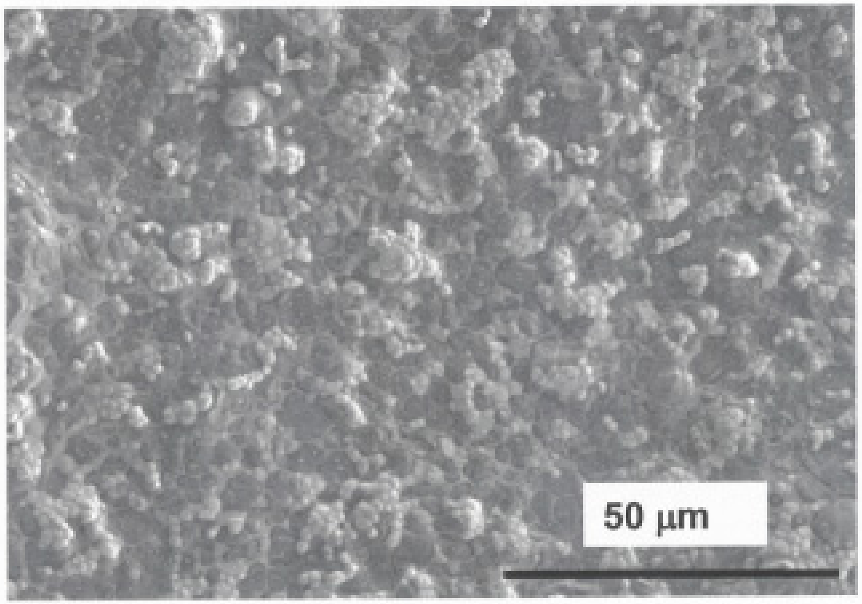


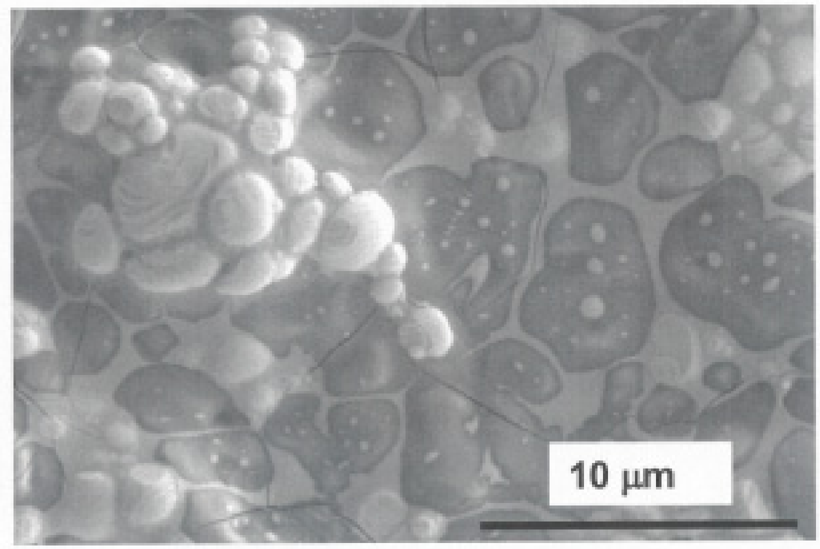




- Non-uniform dispersion of surface oxide phases.
- Fine dispersion of second phase in glassy areas.

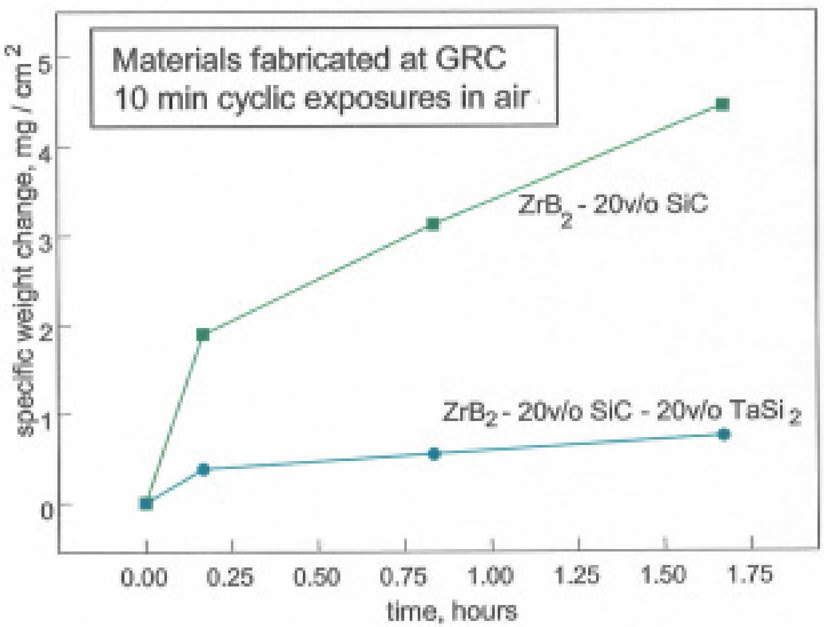
Surface Microstructure of ZSTS After Oxidation at 1627°C in Stagnant Air

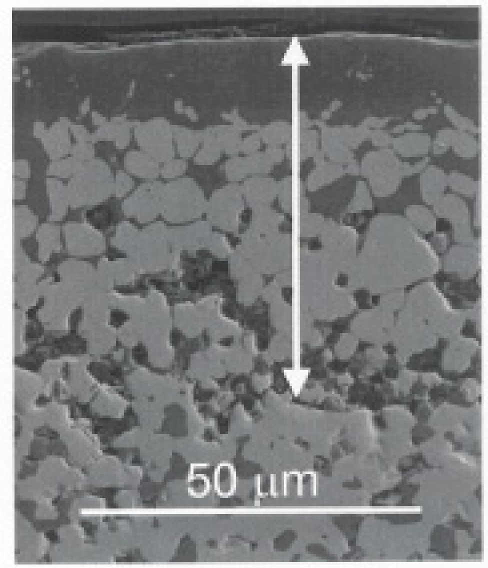




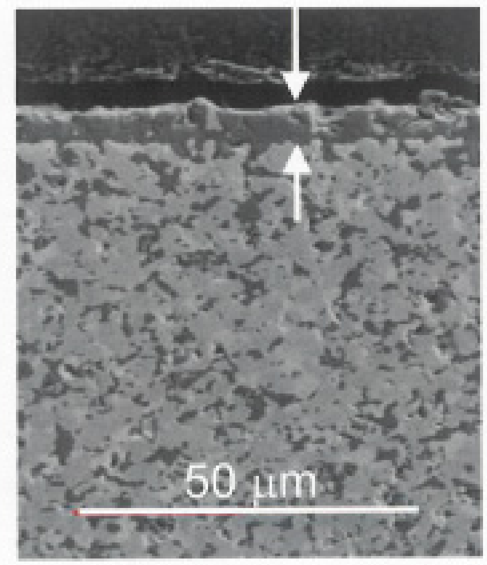
- Uniform dispersion of surface oxides
- Evidence of glass immiscibility

Tantalum Additions Improve Oxidation Resistance of ZrB_2-20v/o SiC at 1627°C





ZrB_2 – 20v/o SiC

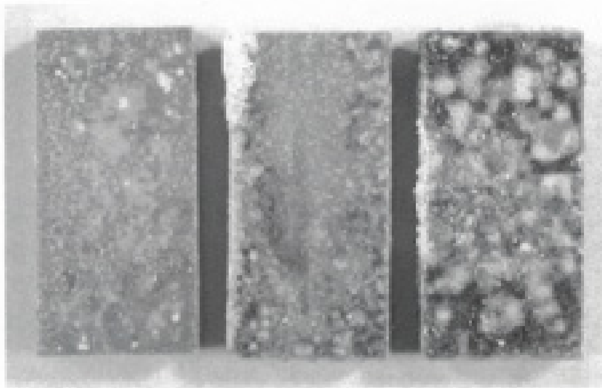


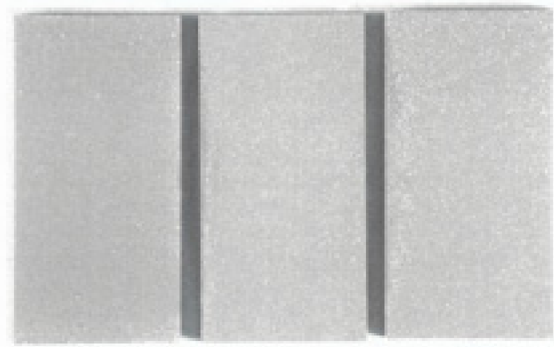
ZrB_2 – 20v/o SiC – 20v/o $TaSi_2$

UHTC Furnace Oxidized in Air

	ZrB_2 + 20 v/o SiC	ZrB_2 + 20 v/o SiC + 20 v/o $TaSi_2$
	1* 5 10	1 5 10

1627°C

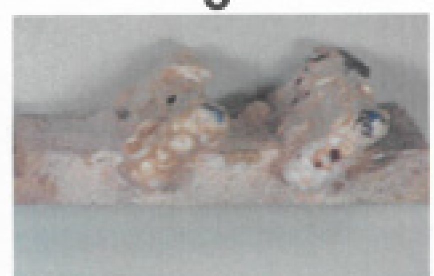




1927°C

1

5



5 cycle specimen after attempted removal from setter

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

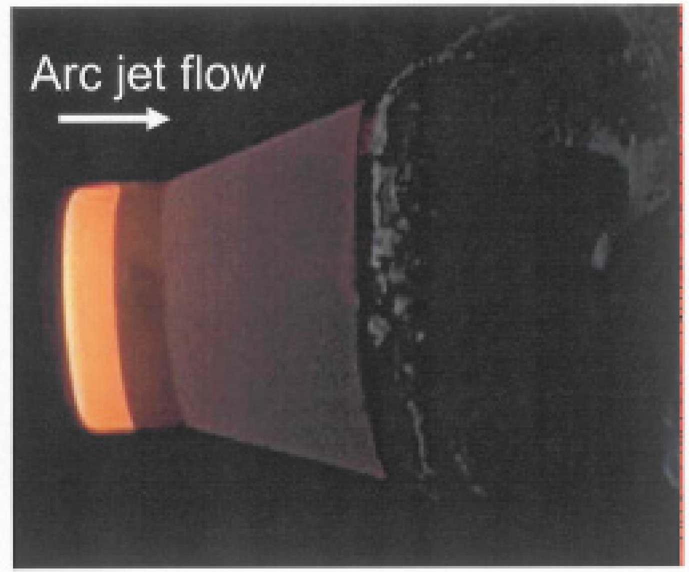
Arc Jet Test of ZrB_2 - 20 v/o SiC - 20 v/o $TaSi_2$


2.54 cm

Specimen

2.54 cm

Specimen mounted in graphite holder



Specimen and graphite holder mounted in arc jet sting

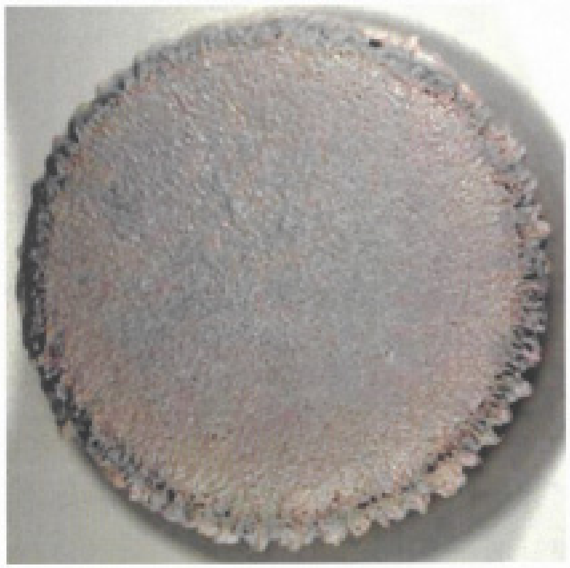
Test Conditions

350 W/cm^2
0.07 atm.
600 seconds
% Δwt = -1.4

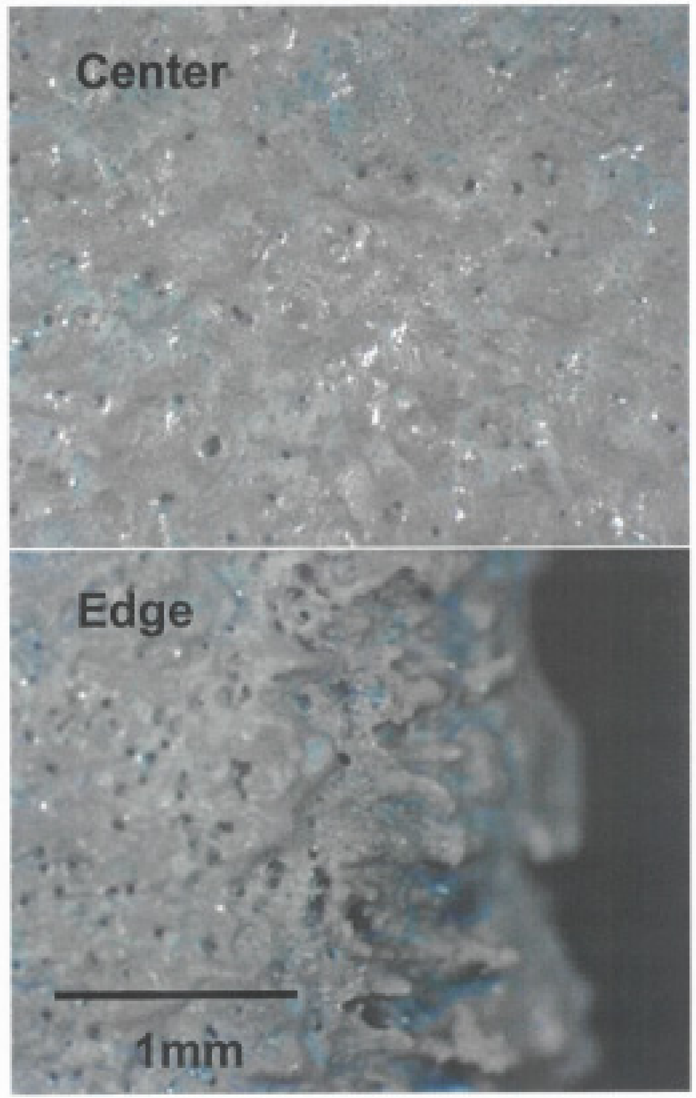
Temperatures and Heat Flux

Measured Temperature ~1800 °C
Edge Heat Flux Estimate ~ 600 W/cm^2
Edge Temp Estimate ~1950 to 2000°C

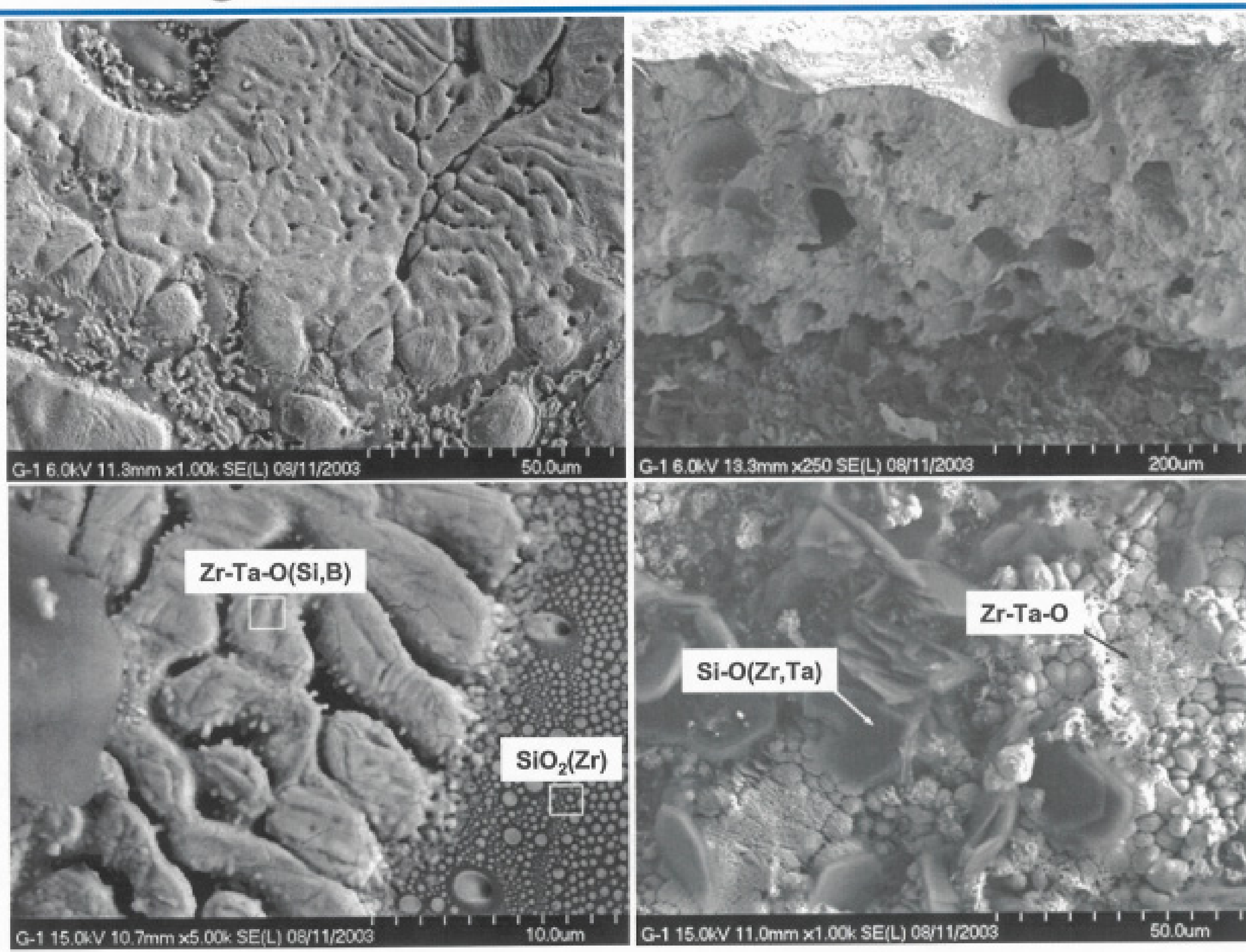
Images of GRC Model After Arc Jet Test



XRD Results
- ZrO_2 (m)
- ZrO_2 (c)
- Ta_2O_5 ↑



SEM Images of Arc Tunnel Tested ZrB_2-SiC-$TaSi_2$



Some Answers

- Is Ta or Si in $TaSi_2$ responsible for the improved oxidation resistance of ZrB_2 – 20v/o SiC – 20v/o $TaSi_2$? Tantalum.
- Does the benefit of $TaSi_2$ additions observed at 1627°C extend to higher temperatures? No, not at 20v/o addition levels.
- Are $TaSi_2$ additions the best way to add Ta to ZrB_2-based UHTC? TaC additions are not effective at 1627°C.
- Can $TaSi_2$ additions improve the oxidation resistance of HfB_2-based UHTC which are already superior to ZrB_2-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 ZrB_2-SiC materials at 1627°C? Tantalum effects both glass phase and ZrO_2.

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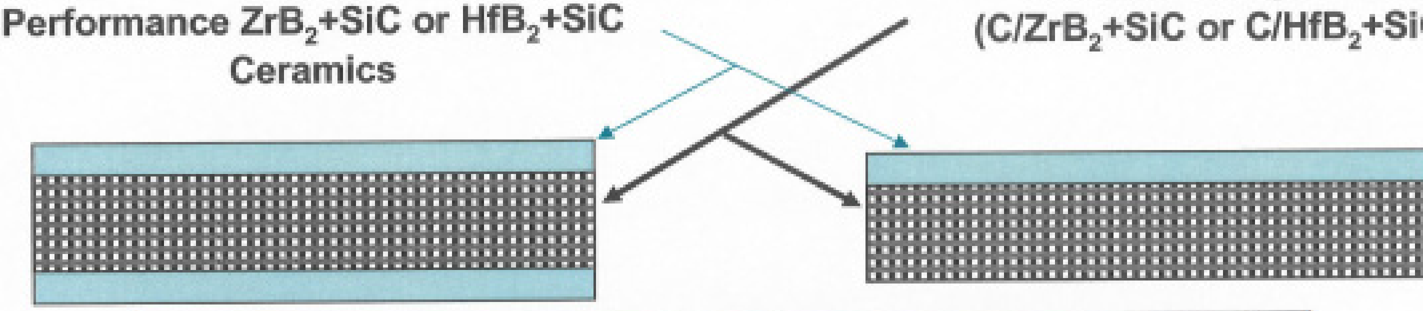
UHTCMC Hybrid System

Coated or Improved Oxidation Performance ZrB_2+SiC or HfB_2+SiC Ceramics

Ceramic Composites (C/ZrB_2+SiC or C/HfB_2+SiC)



Advantages of UHTCMC hybrids

- Thickness and composition of UHTC layers can be changed to suit the application requirements
- Improved toughness
- Improved environmental durability
  - Tailored surface coatings
  - Crack healing matrices
  - Control of residual stresses
- Smooth composite surfaces
  - Low drag
  - Machinable without fiber damage
  - Easier to bond and attach sensors and other devices
  - Critical to good attachments/seals

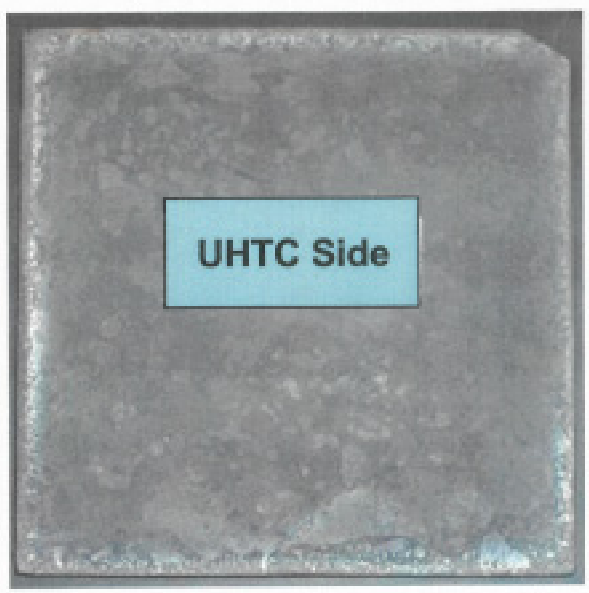
Characterization of an Ultra-High Temperature Ceramic Composite

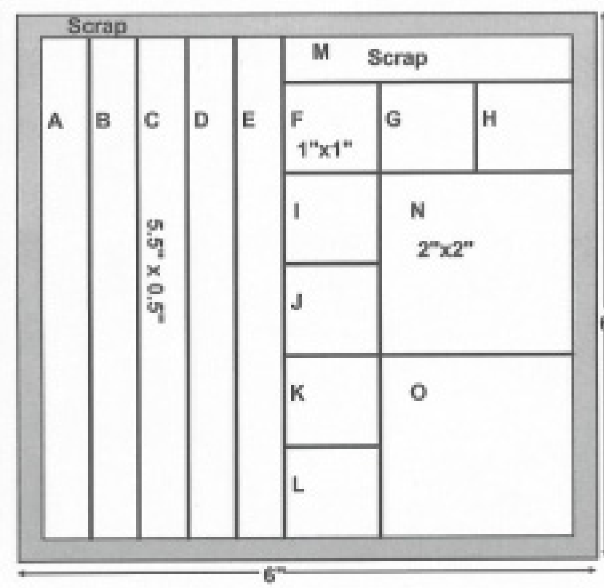
- Objectives
  - Characterize a UHTC composite plate fabricated by Starfire Systems, Inc.
    - CAVEAT: Recognize that little or no development effort went into fabrication of this material. It was a best effort fabrication for NASA LaRC
  - Reveal some of the issues associated with the UHTCC concept

Starfire UHTCC Plate

Constituents
- **Zoltek Panex® 30 Carbon Fabric PW06**
- **Starfire Systems' SP-Matrix Polymer (Allylhydridopolycarbosilane (AHPCS))**
- **HfB_2 Powder**
- **SiC Powder**

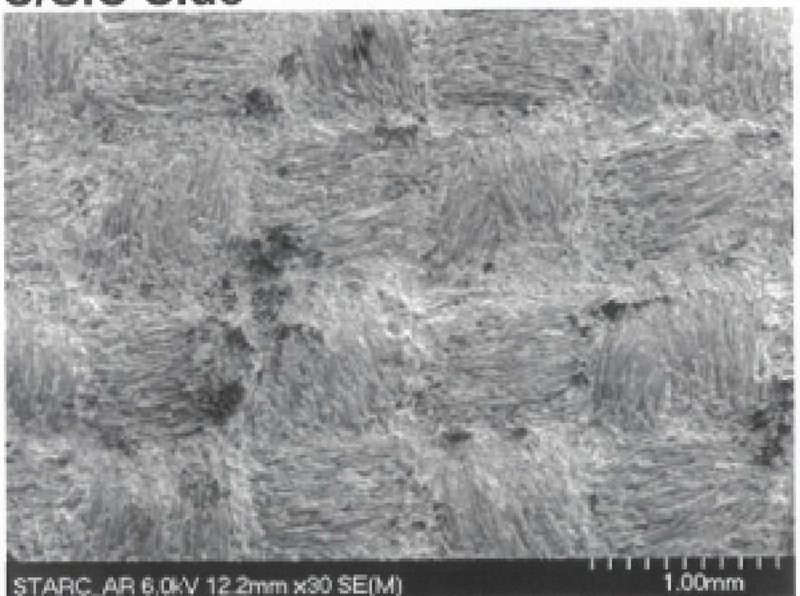
Processing of Part Number 000928-6-64
- **Initial Cycle:**
  - For the initial lay up the **bottom 6 layers of cloth are coated with a SiC/AHPCS** slurry and the **top 5 layers are coated with a HfB_2 /AHPCS slurry** and assembled in a mold.
  - Cured to 400°C and fired to 850°C under inert gas to pyrolyze.
- **Cycle 2:**
  - **Coat the HfB_2 side of the plate with more HfB_2 /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.

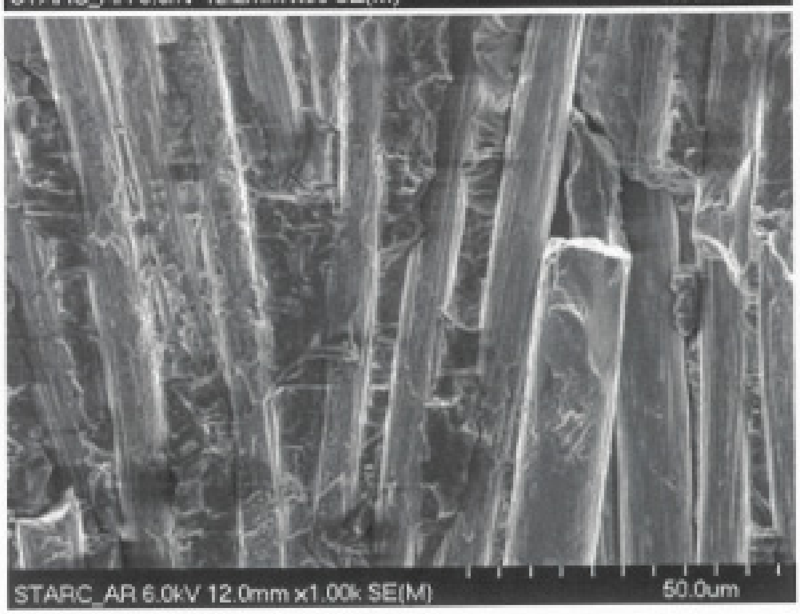




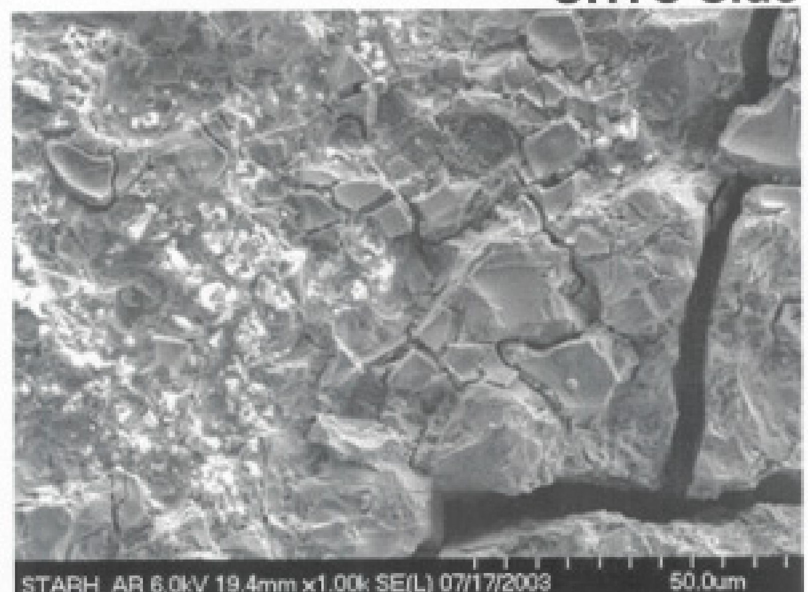
As -Received UHTCC

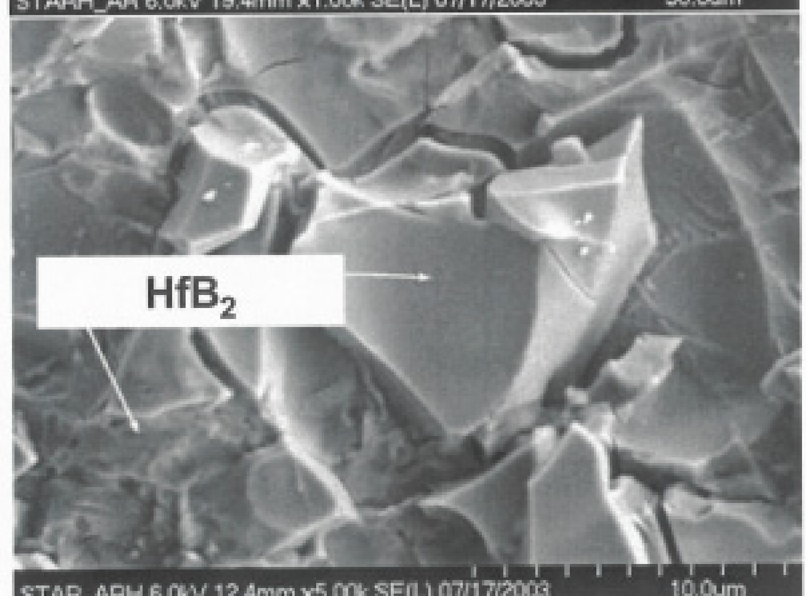
C/SiC Side



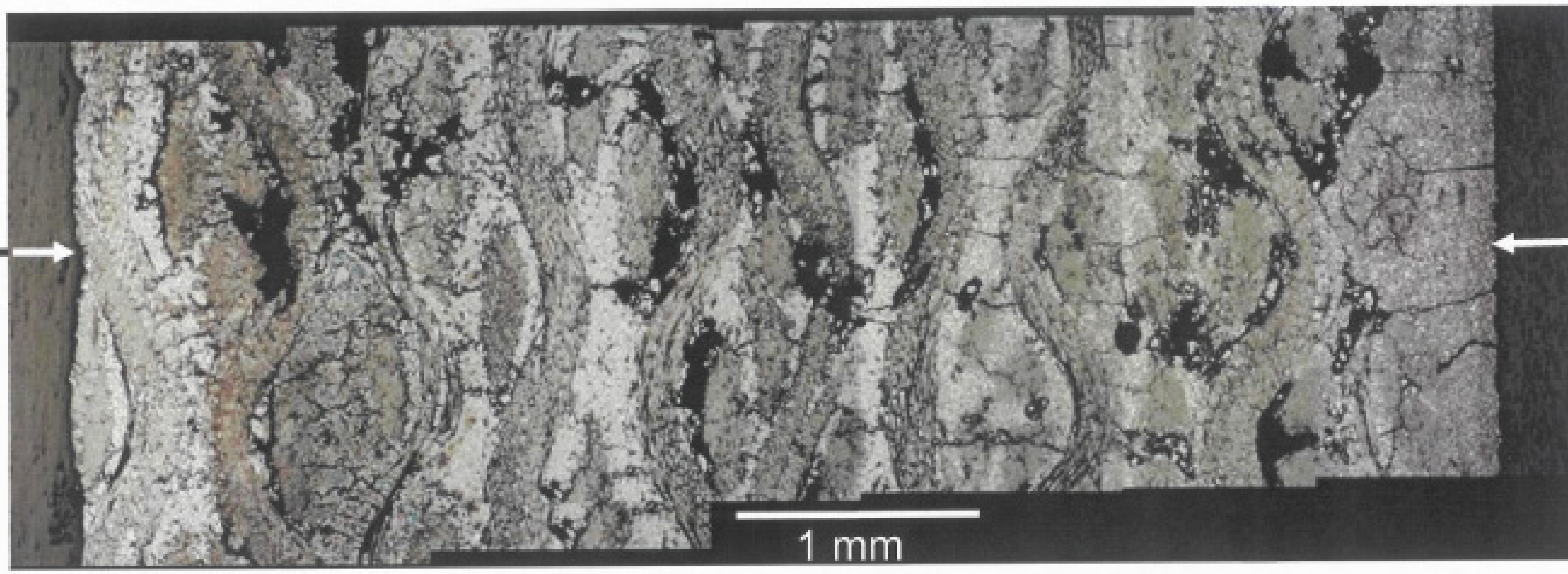


UHTC Side





UHTCC Cross-section



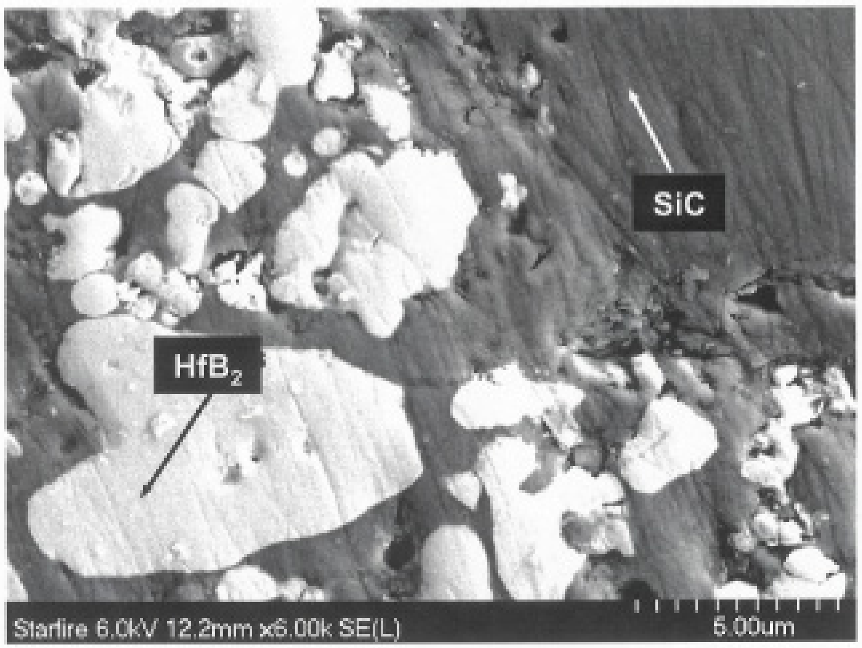
SiC
C

Phases Detected by XRD

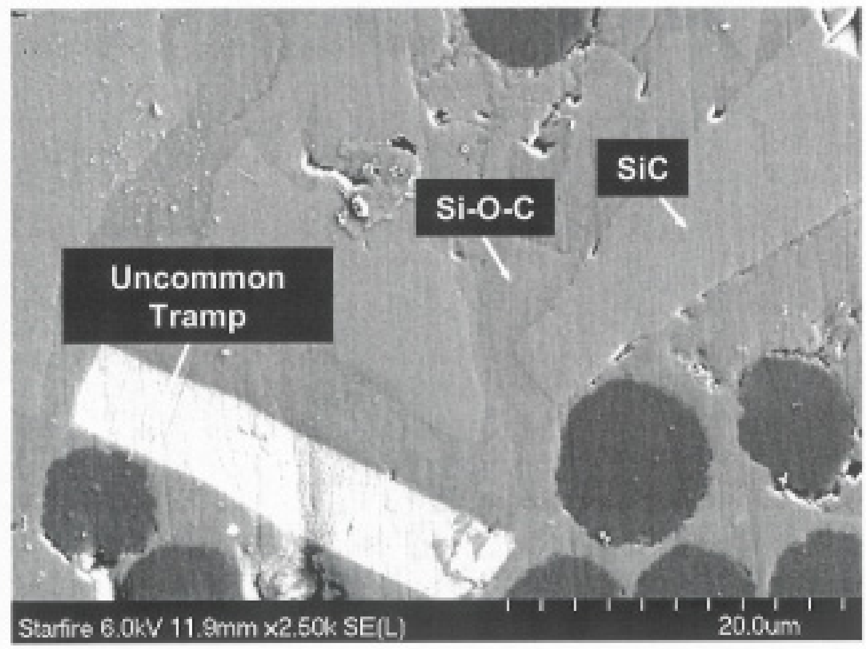
HfB_2

Constituents in As-Received UHTCC

HfB_2 Coating Layer



Matrix on C/SiC Side



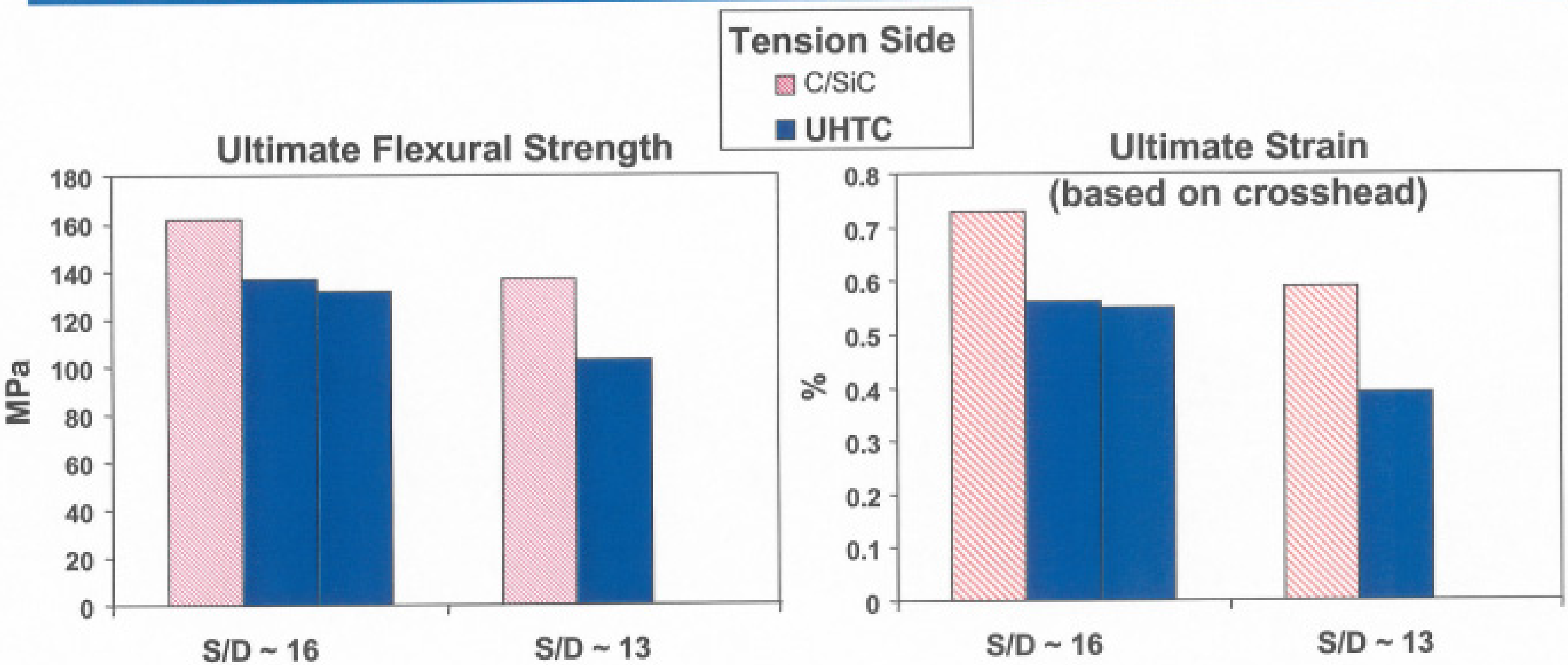
Flexural Strength Tests

Specimen			Test Fixture			Orientation		Ultimate Load	Calculated Load Based on Beam Theory*
ID	width	thickness	inner span	outer span	span/ depth	fracture	side down		
	mm	mm	mm	mm				N	N
A	12.7	5.79	40	80	13.8	under pin	C/SiC	972	1120
B	12.7	5.92	40	80	13.5	under pin	UHTC	757	
C	12.7	6.04	48	96	15.9	center	C/SiC	1025	1000
D	12.7	6.06	48	96	15.8	center	UHTC	811	
E	12.7	6.07	48	96	15.8	center	UHTC	855	

- Sample B remained intact. All other samples fractured into 2 pieces
- Samples B, D, and E retained an obvious permanent set

- *Calculated load at 0.7% strain
- Panex 30 minimum property: E = 193 GPa
- Rule of mixtures with no matrix contribution

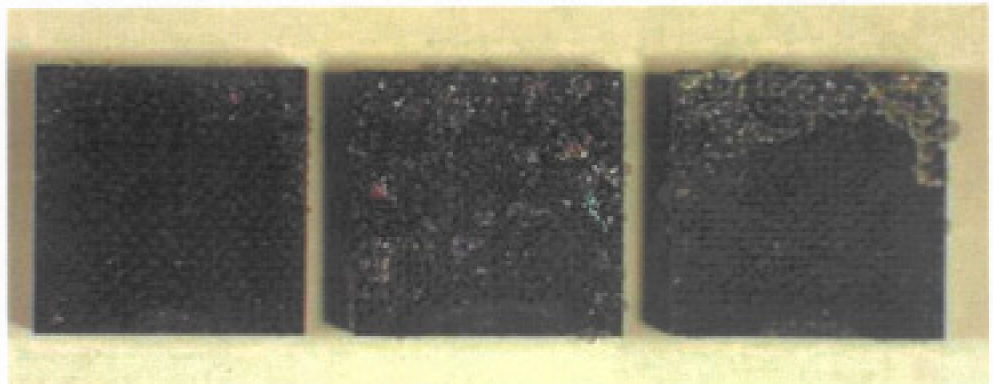
UHTCC Flexural Strength Results



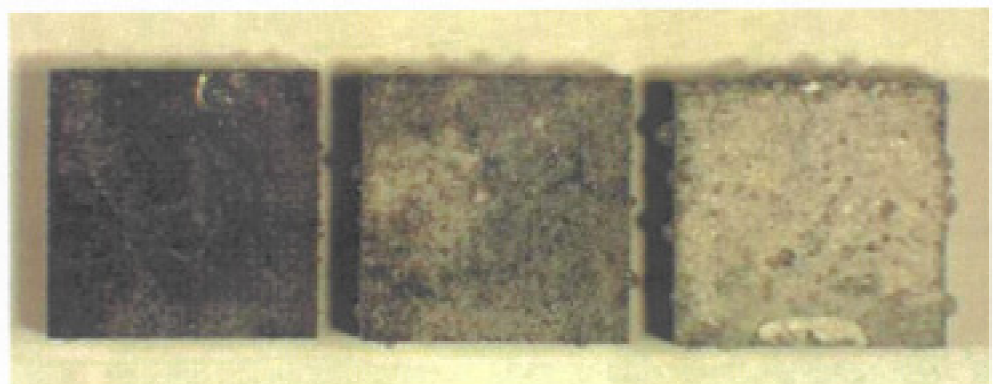
Note: S/D > 30 necessary for valid 4 point flexural test

UHTCC After 1627°C Furnace Oxidation

C/SiC Side

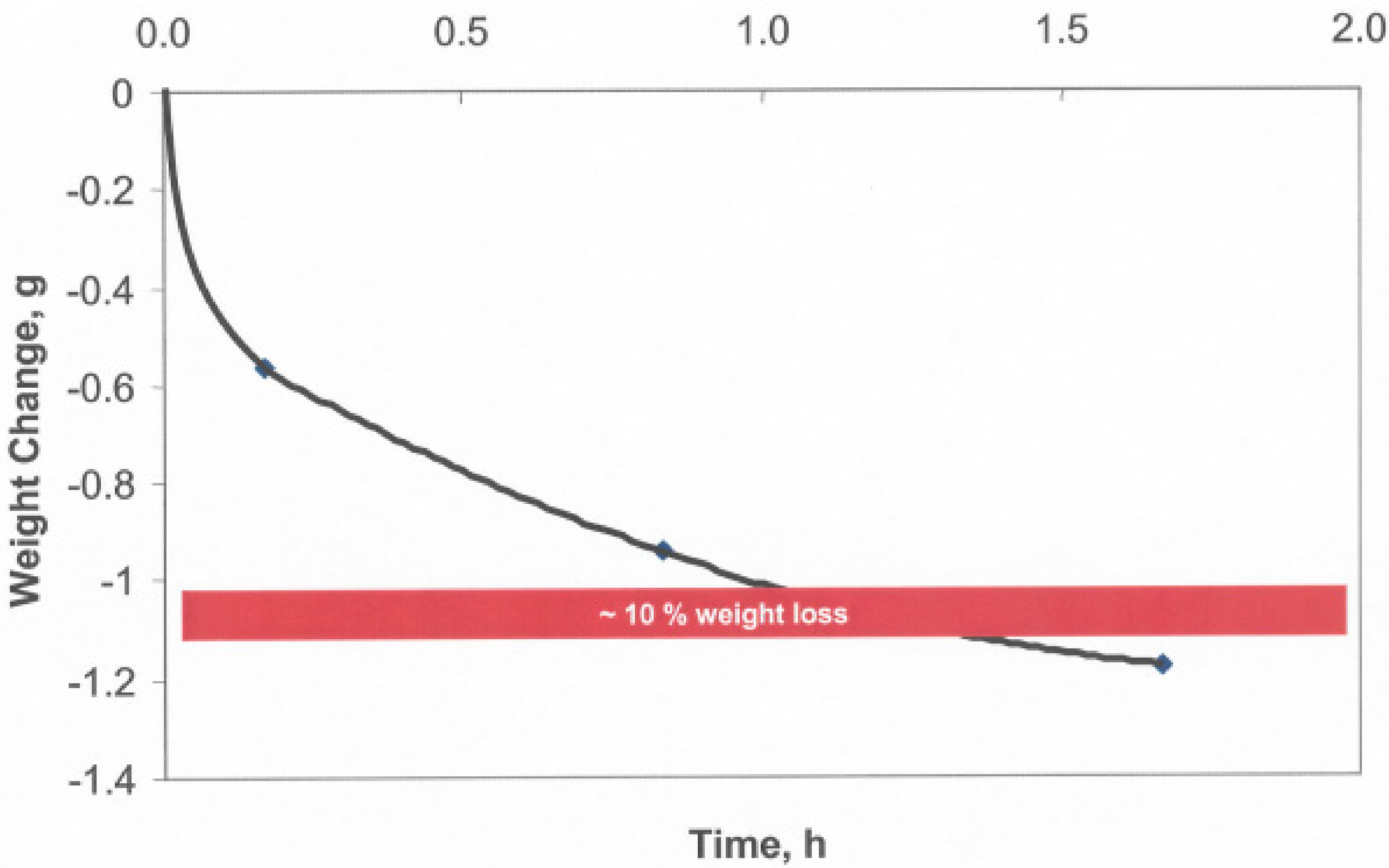


HfB_2 Side



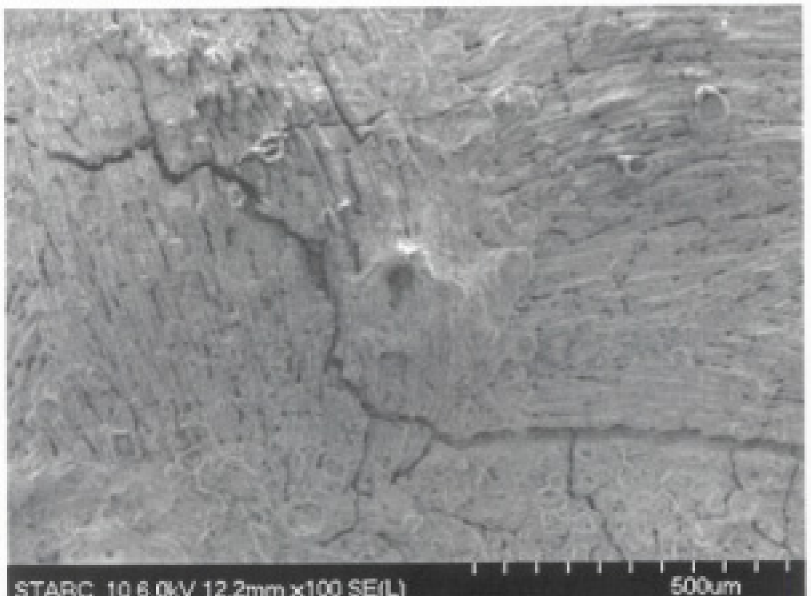
Cycles	1	5	10
Hours	0.167	0.833	1.667

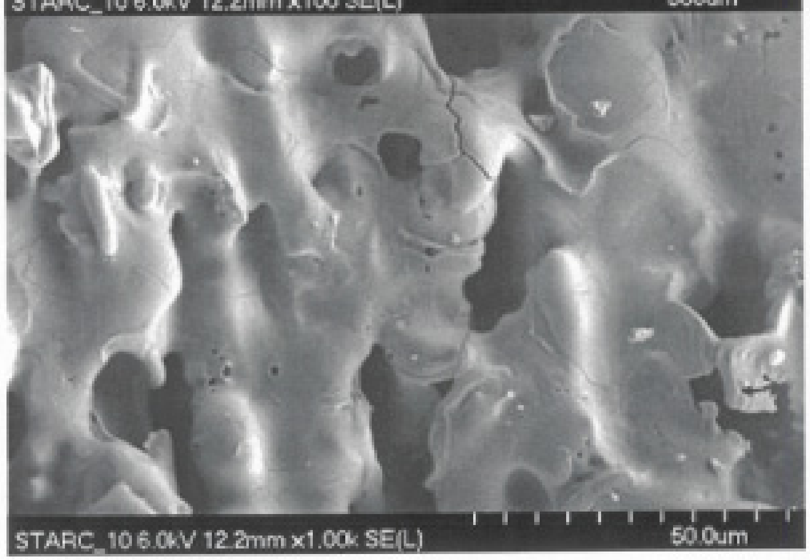
Furnace Oxidation of UHTCC at 1627°C



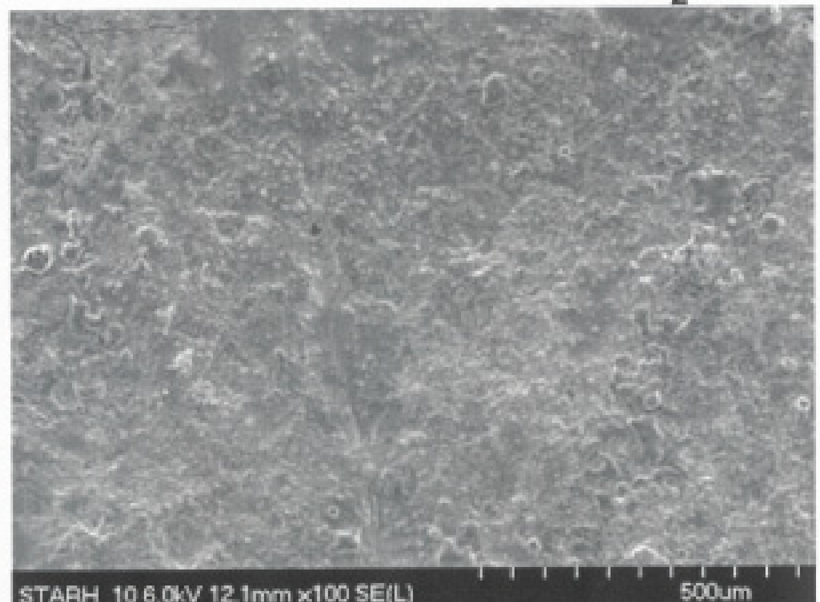
UHTCC After 10 Ten-minute Cycles in Air at 1627°C

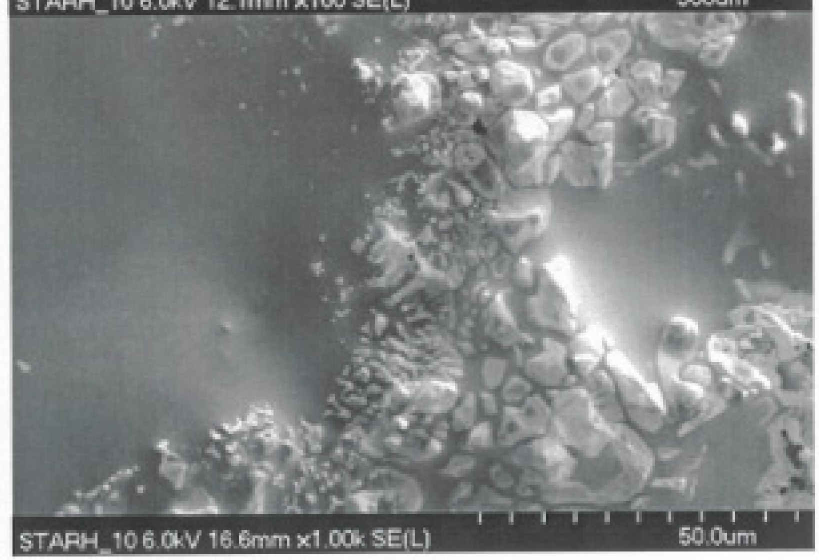
C/SiC Side





HfB_2 Side



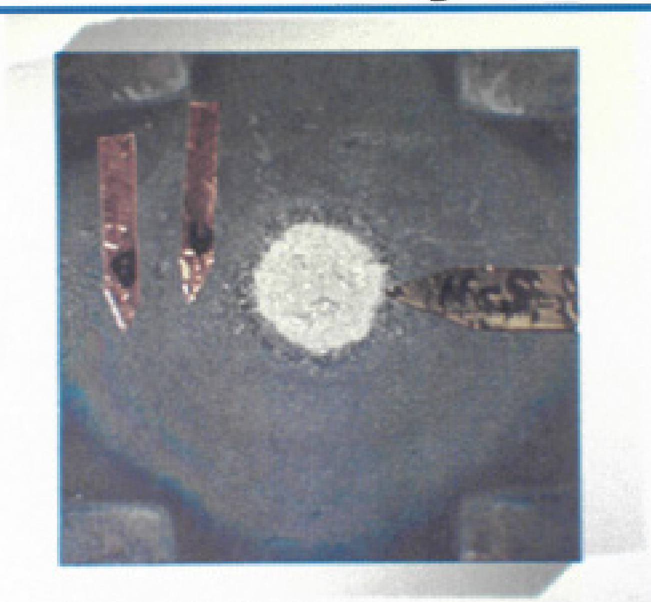


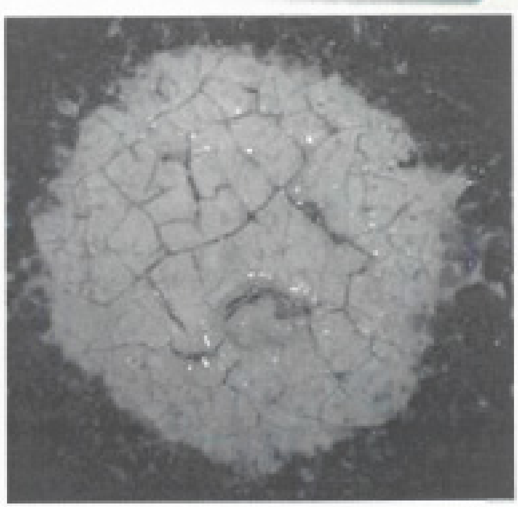
UHTCC Oxy-Acetylene Torch Test

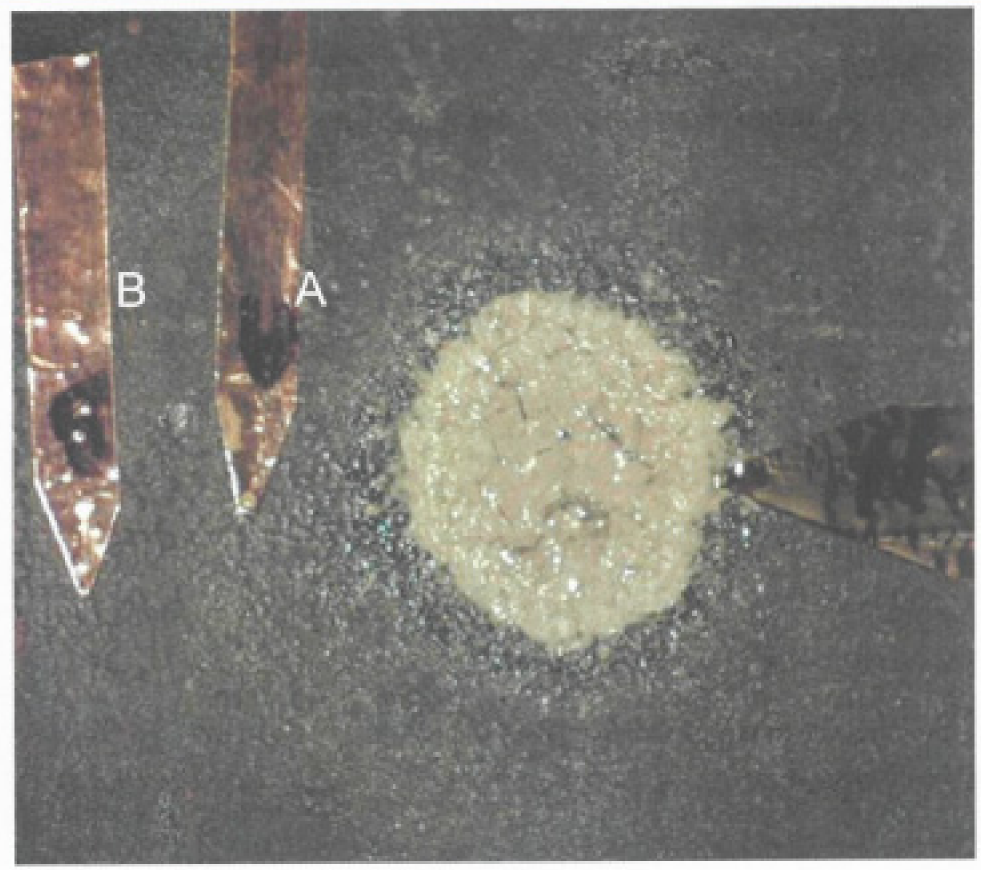
- Sample O: One 4 min. cycle to 1805°C
  - Photos on cool down
  - Temps with Ircon 2 color pyrometer, 980-1760°C range
  - Weight change
    - Initial weight 41.66 g
    - Final weight 40. 87 g
    - Weight loss 0.79 g, or 1.9%
- Sample N: Three ~4 min. cycles
  - Cycle 1 max temp 1815°C
  - Cycle 2 max temp 1915°C
  - Cycle 3 max temp 2015°C
    - Photos on heat up
  - Weight change
    - Initial weight 41.99
    - Final weight 40.04
    - 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

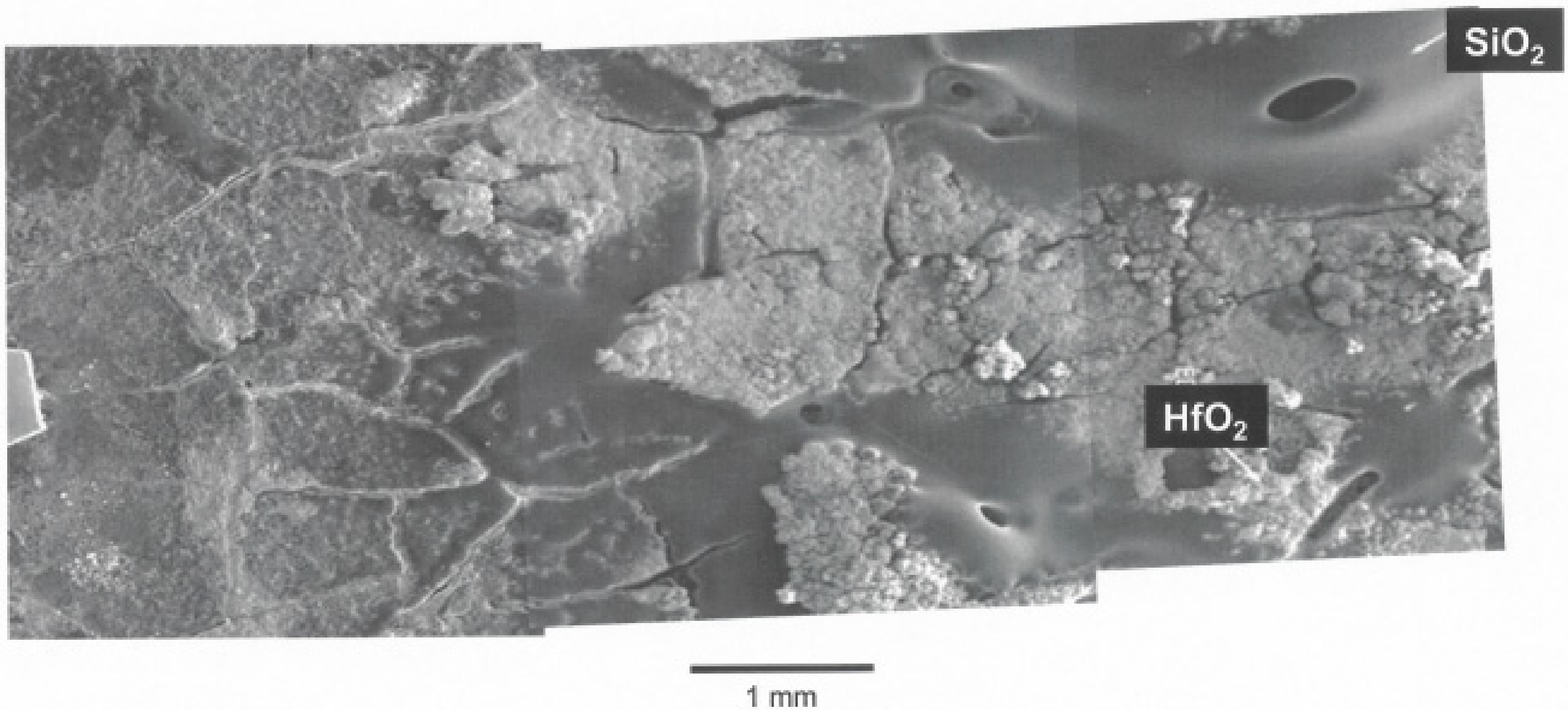
UHTC Surface After Three 4-Minute Torch Cycles to 1815 to 2015°C







SEM of Center of UHTC Surface After Three Torch Cycles



Conclusions

- **$TaSi_2$ Additions**
  - Good results at 1627°C, but oxide scale too fluid at > ~ 1800°C
- **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**
    - Based on weight loss, carbon fiber oxidation occurred rapidly
  - **Torch Test**
    - Material withstood ~2000°C (~3600°F), severe heat-up and thermal gradients with no major visible distress
    - Based on observed temperature spikes during test, adherence of the HfO_2-rich scale is an area of concern

Recommendations

- Lower levels of Ta addition to achieve doping without low melting phase formation should be investigated
- The thermal stress response of early UHTCC makes the concept worthy of further study
- 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

Future Work

- Complete oxidation studies focused on Ta additions
- Continue UHTCC development
- Continue UHTCC evaluation
  - Complete metallography on Starfire specimens
  - Evaluate other NASA and industry developed materials

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