Characterization of an Ultra-High Temperature Ceramic Composite

Stanley R. Levine, Elizabeth J. Opila, Raymond C. Robinson[a], and Jonathan A. Lorincz[b]

NASA Glenn Research Center
Cleveland, Ohio 44135

Ultra-high temperature ceramics (UHTC) are of interest for hypersonic vehicle leading edge applications. Monolithic UHTCs are of concern because of their low fracture toughness and brittle behavior. UHTC composites (UHTCC) are being investigated as a possible approach to overcome these deficiencies. In this study a small sample of a UHTCC was evaluated by limited mechanical property tests, furnace oxidation exposures, and oxidation exposures in a flowing environment. The composite was prepared from a carbon fiber perform using ceramic particulates and a preceramic polymer.

The as-received composite plate was non-uniform from front to back surface. Plate dimensions were 150 x 150 x 6 mm. The back surface had a fibrous, uniform appearance; XRD analysis revealed the presence of SiC and C. The front surface was smooth and non-uniform in appearance with evidence of a coarse grain structure produced by a liquid phase; XRD analysis revealed the presence of HfB_2. Microcracks were present throughout the thickness as one might expect from a carbon fiber reinforced composite with attendant large thermal expansion mismatch between the matrix phases and the fibers. The HfB_2 phase on the front surface was comparable in thickness to a fiber ply or about 0.6 mm, and surface microcracks were evident. Limited four point flexural tests were carried out at span to depth ratios of approximately 14 and 16 with markedly different results. Tests were run with the front or the back surface in tension. At the shorter span to depth failures occurred under a loading pin for both orientations. At a span to depth of 16 failures occurred in the center of the span with fracture clearly initiating from a tensile failure. Ultimate flexural strength, strain at ultimate stress, stress and strain at deviation from linear elastic behavior are reported. Strains at ultimate stress ranged from about 0.6 to 0.7 % for the back surface in tension, and 0.4 to 0.6 for the front surface in tension. At constant span to depth the strain at ultimate stress was about 0.2% greater for the back surface in tension and the ultimate strength was also higher. Strengths were in line with predictions from theory.

Furnace oxidation studies were carried out at 1627 and 1927°C in a static furnace environment using ten minute cycles and one, five, and ten cycles. Limited oxidation studies were also carried out in a flowing oxyacetylene torch environment. Specimens were photographed, and weight and dimensional changes were determined. XRD and SEM characterizations were performed. Weight losses were attributed primarily to carbon fiber oxidation. The composite survived the torch test with little visible distress. Further details will be determined once metallographic studies are completed.

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[a] QSS Group Inc.
[b] Ohio University

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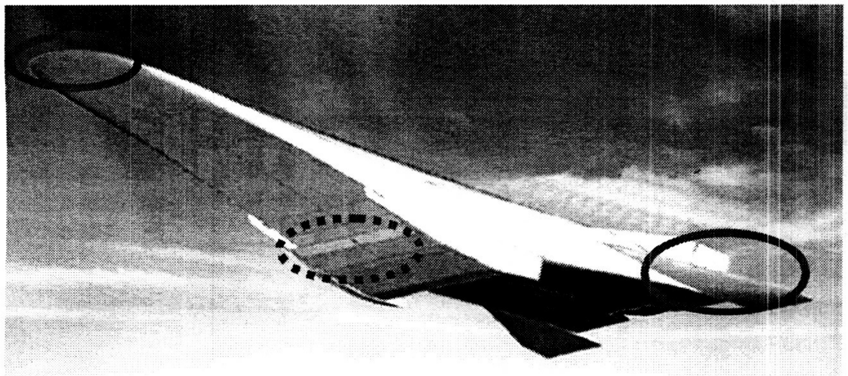
Characterization of an Ultra-High Temperature Ceramic Composite

Outline

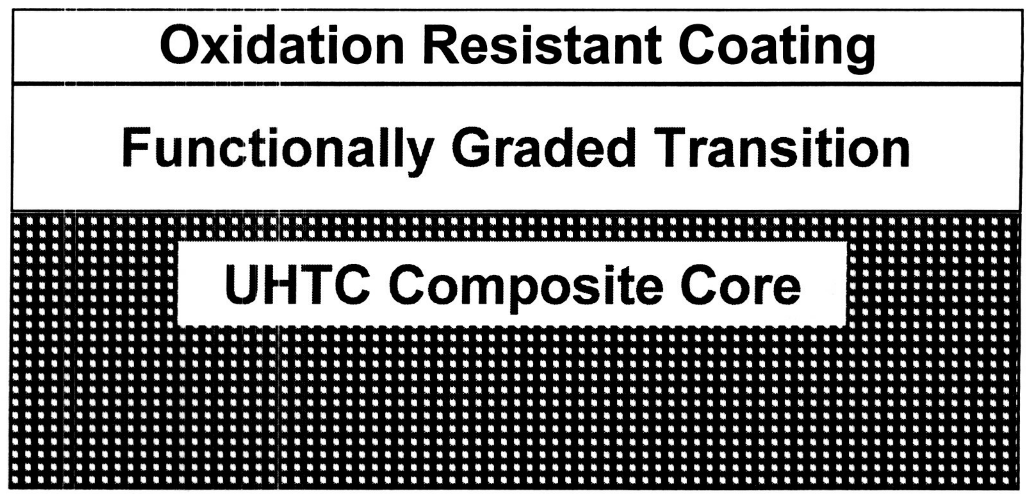
- Background
- Objectives
- UHTCC Description
- Results
  - Flexural tests
  - Furnace oxidation
  - Torch tests
- Concluding Remarks

Ultra High Temperature Ceramic Composite (UHTCC) Leading Edge



Key Issues

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



Characterization of an Ultra-High Temperature Ceramic Composite

- Objectives
  - Characterize a UHTC composite plate fabricated by Starfire
    - 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

UHTCC Processing by Starfire

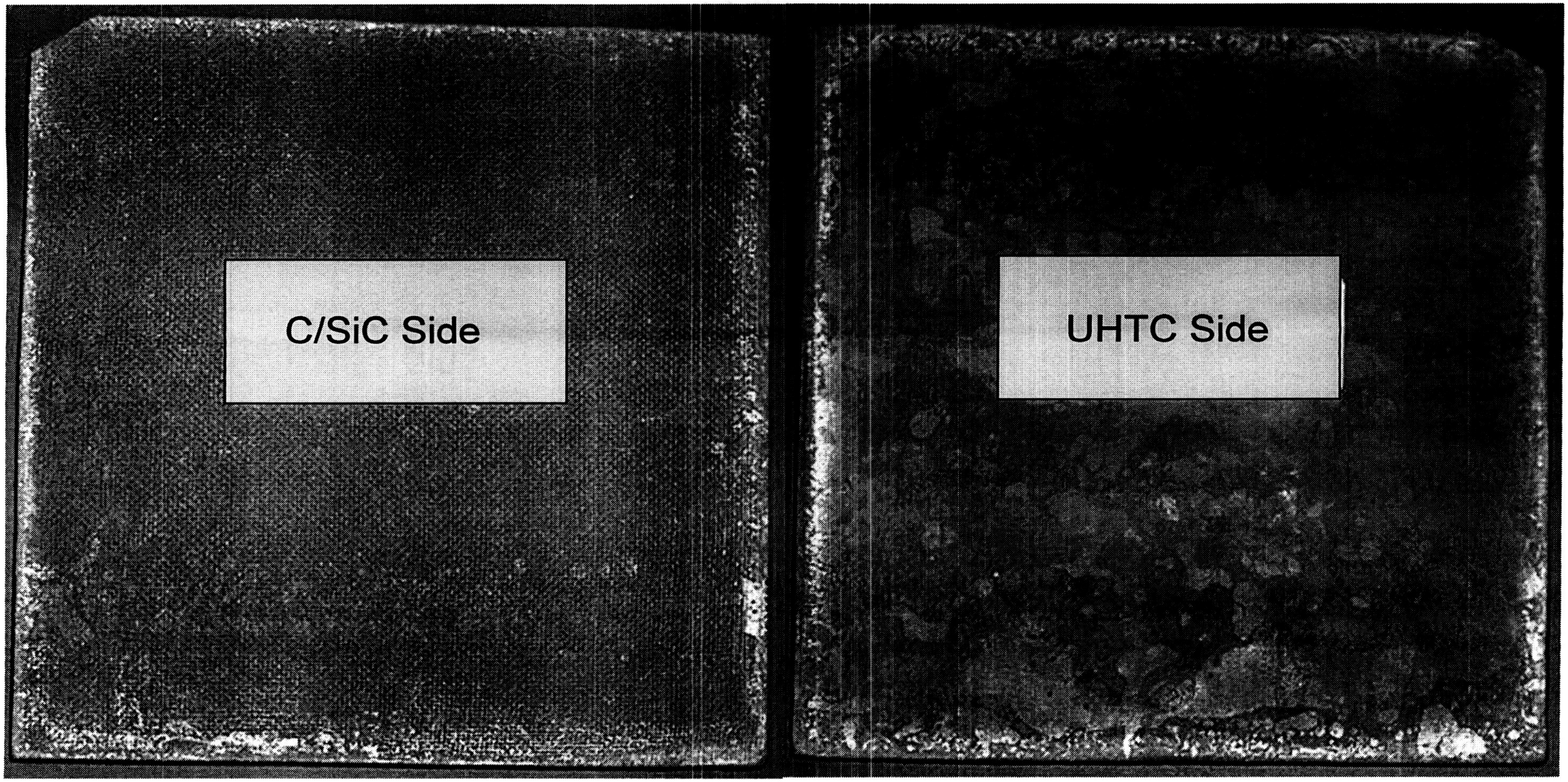
Constituents

- **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:**
  - Zoltek cloth is cut into ~6"x6" pieces. **11 plies** used
  - 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**.
  - The cloth is put into an Al mold and pressed to ~1800lbs. The mold is clamped and cured under inert gas to 400°C.
  - The plate is removed from the mold and clamped between graphite plates 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.**
  - Clamp and 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.

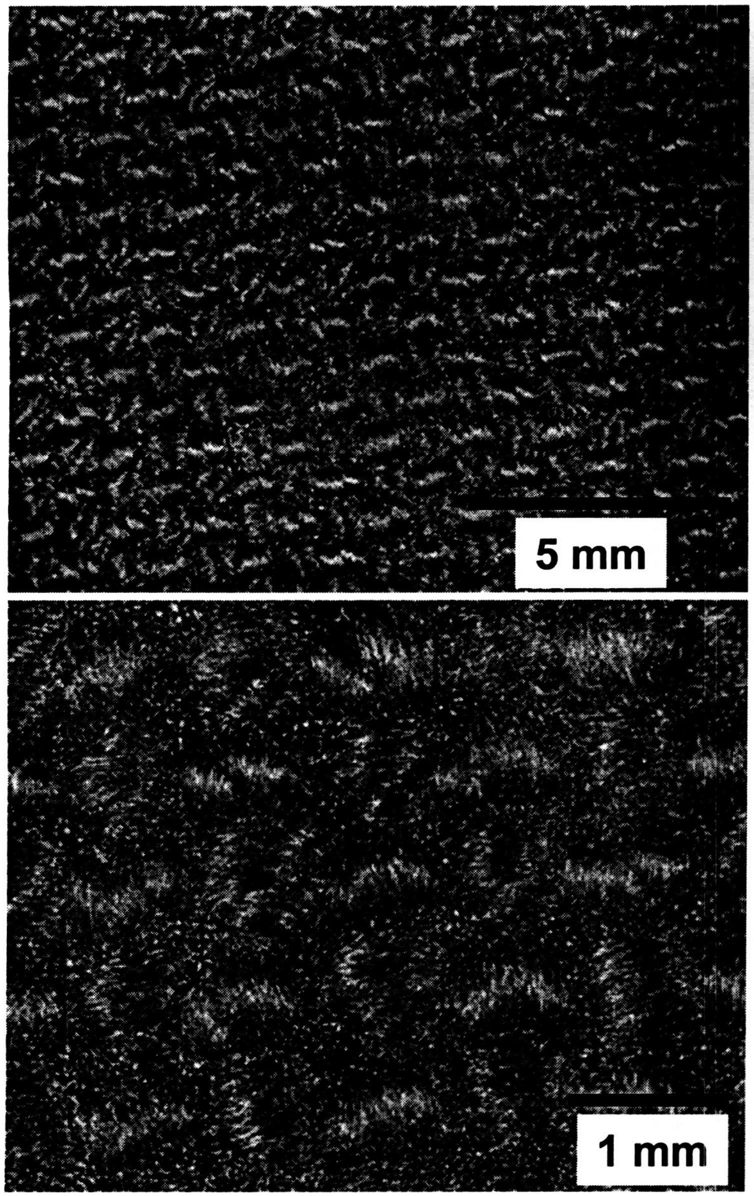
As-Received UHTCC Plate



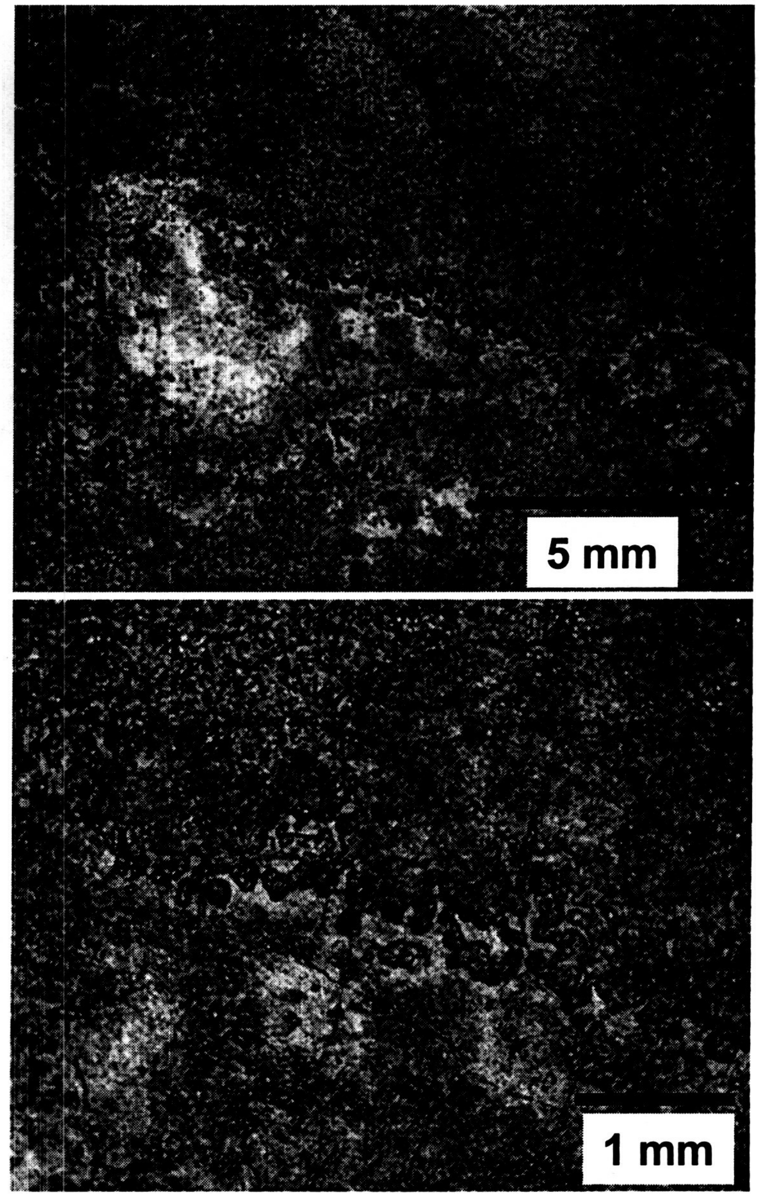
150 mm

Macros of UHTCC Plate

C/SiC Side

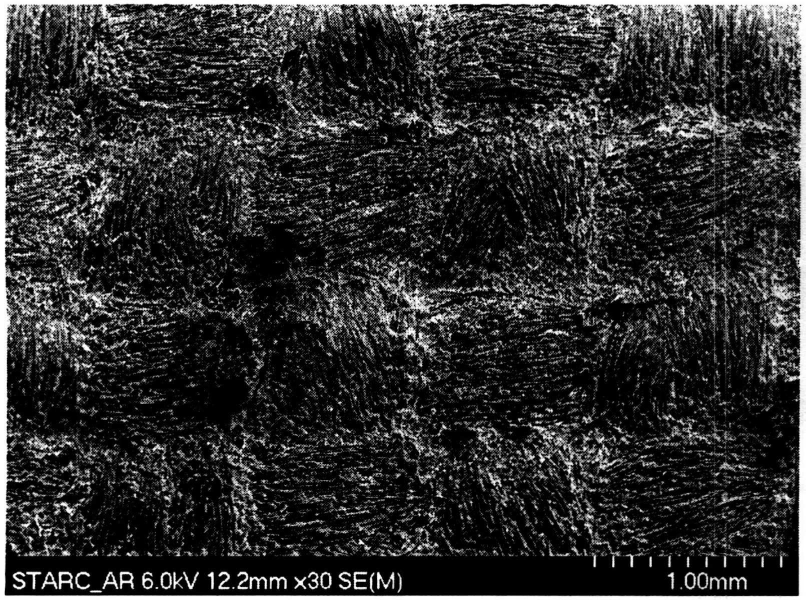


UHTC Side

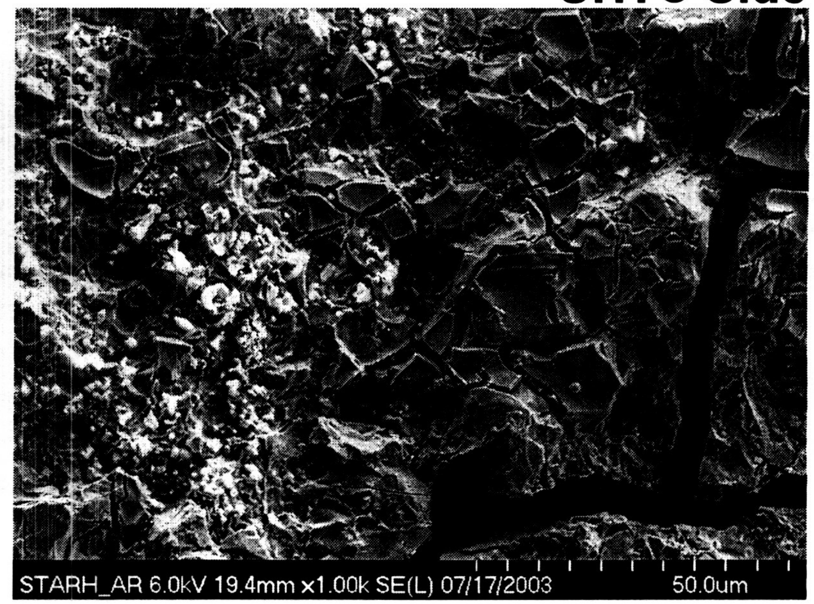


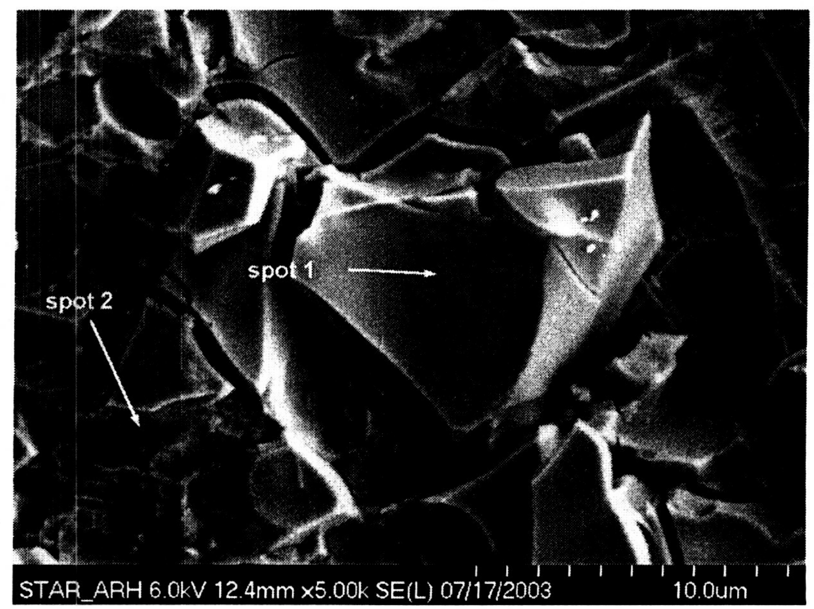
As -Received UHTCC

C/SiC Side

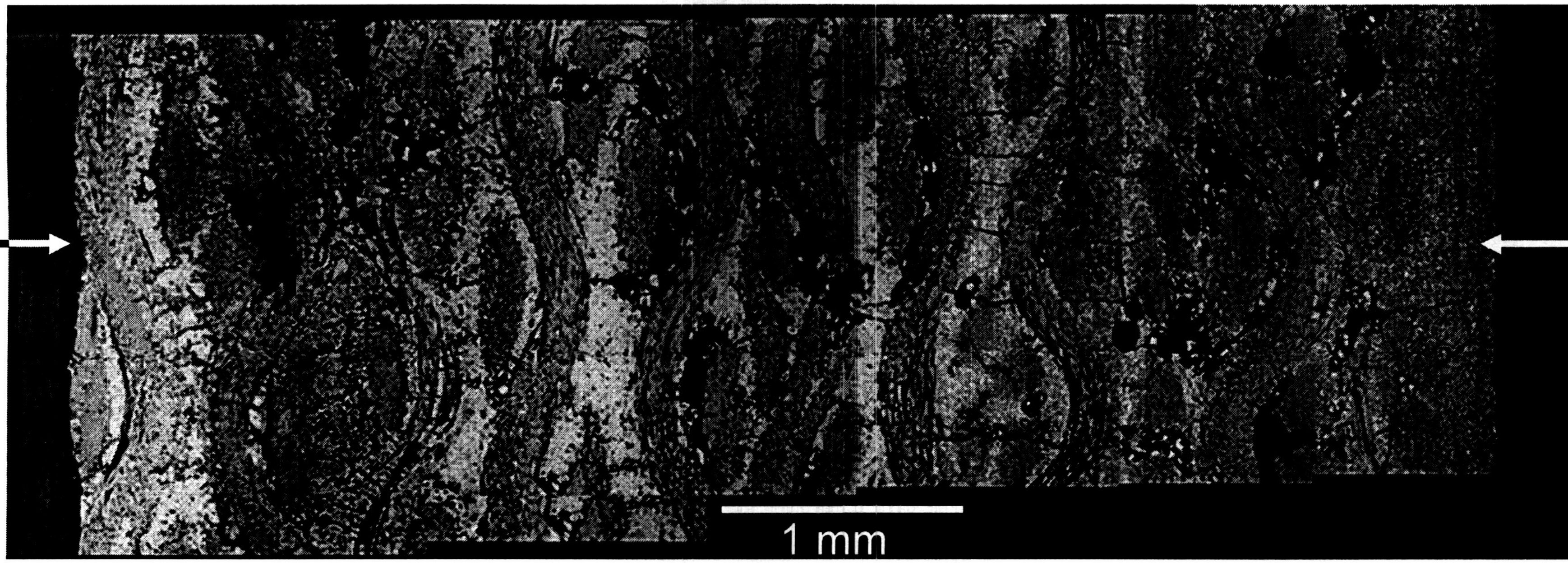


UHTC Side





UHTCC Cross-section

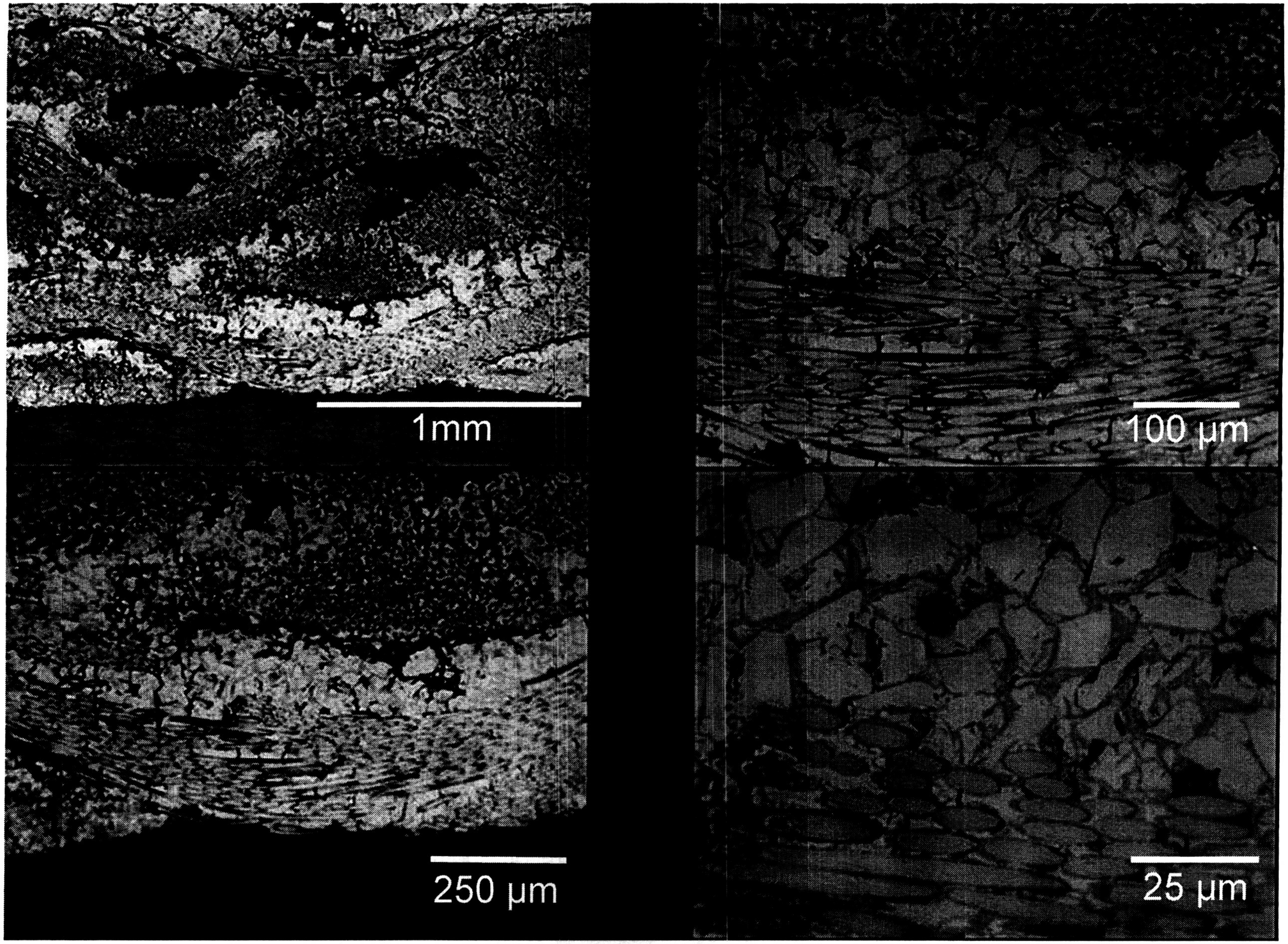


SiC
C

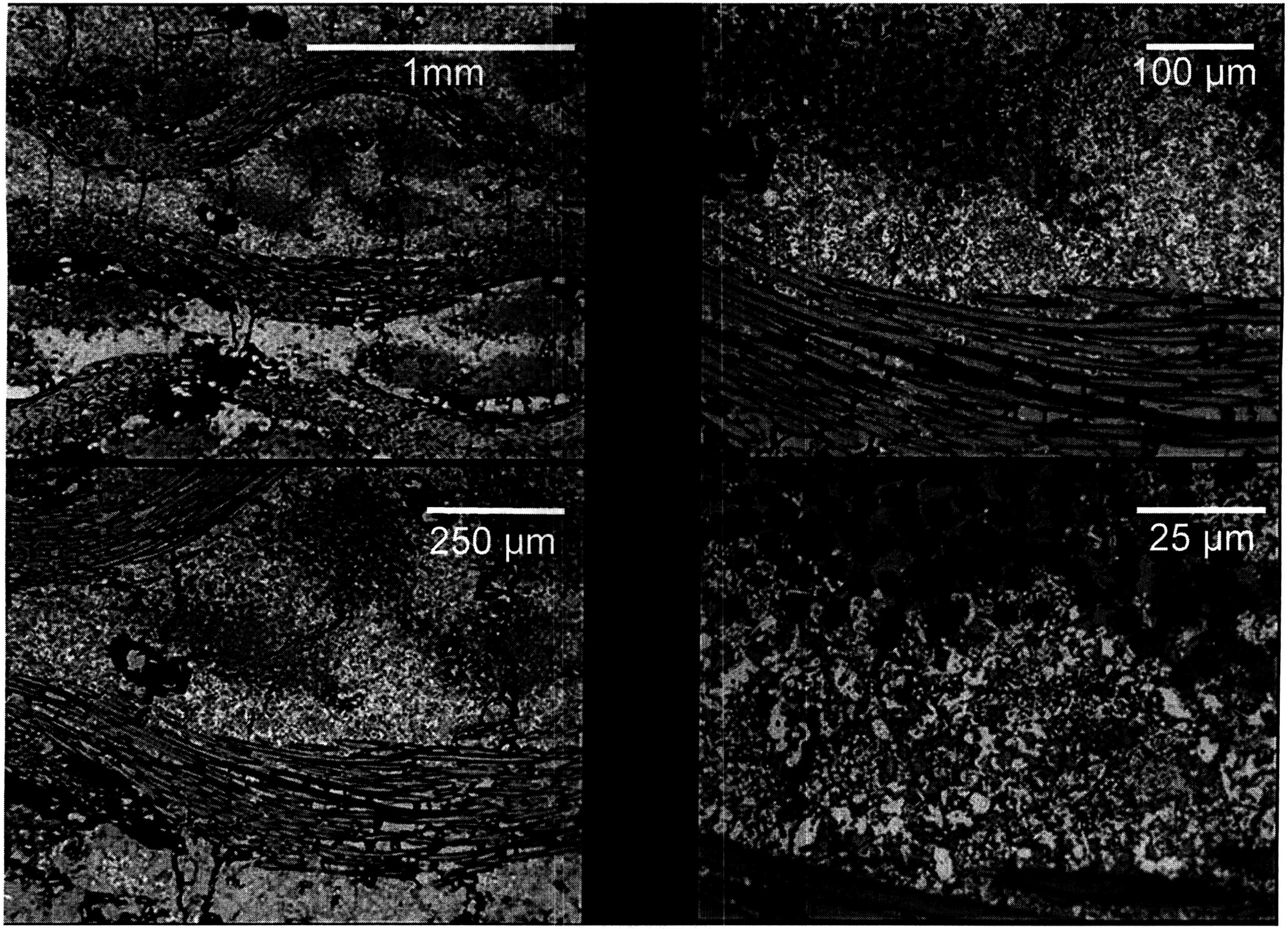
Phases Detected by XRD

HfB_2

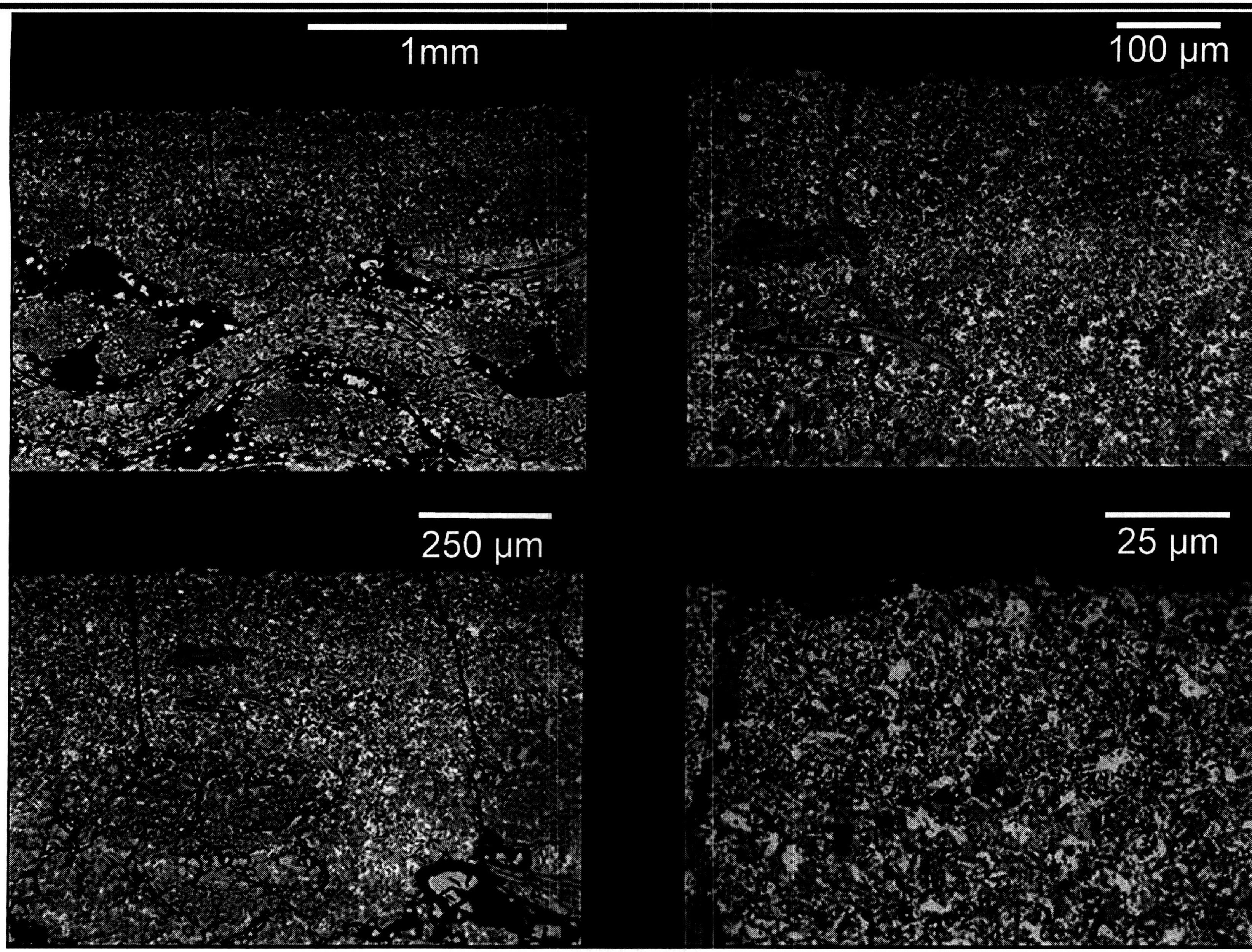
C/SiC Side of UHTCC



Center of UHTCC

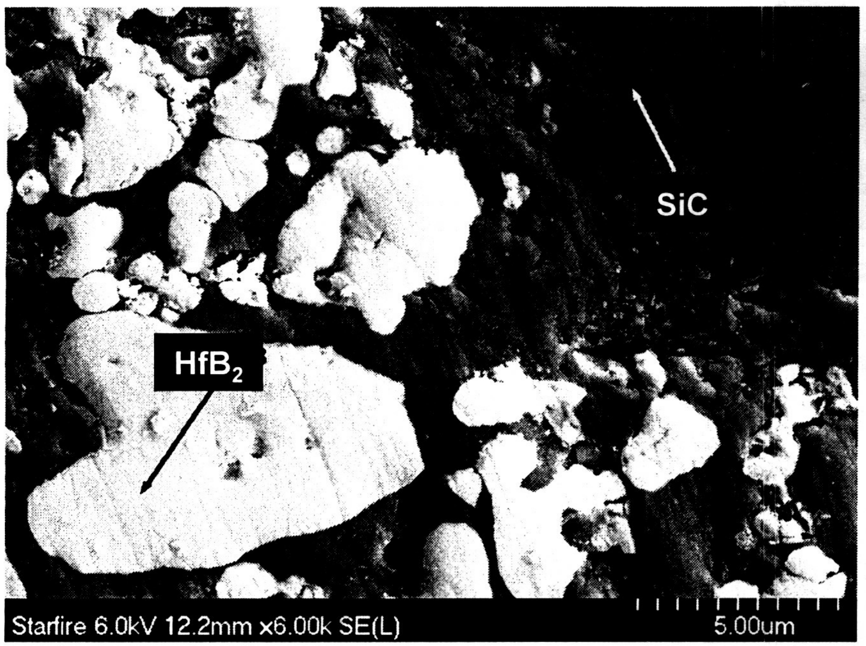


HfB_2–rich Side of UHTCC

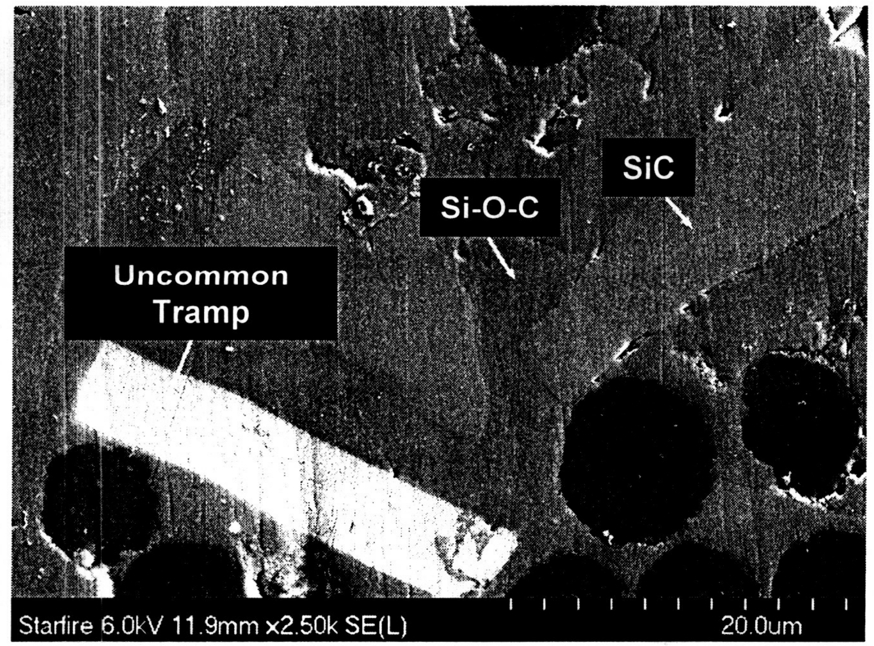


Constituents in As-Received UHTCC

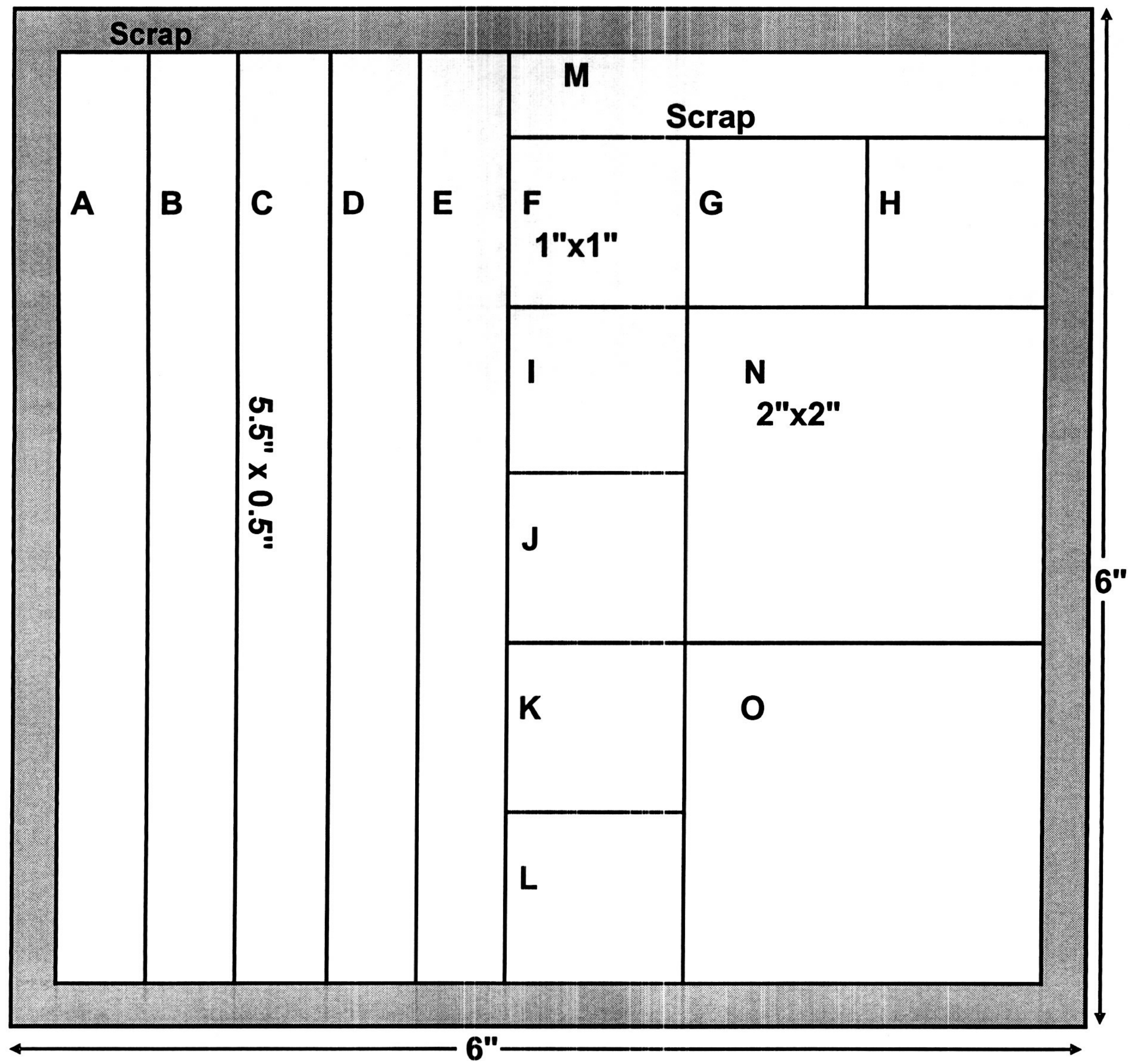
HfB_2 Coating Layer



Matrix on C/SiC Side



UHTCC Specimen Layout



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

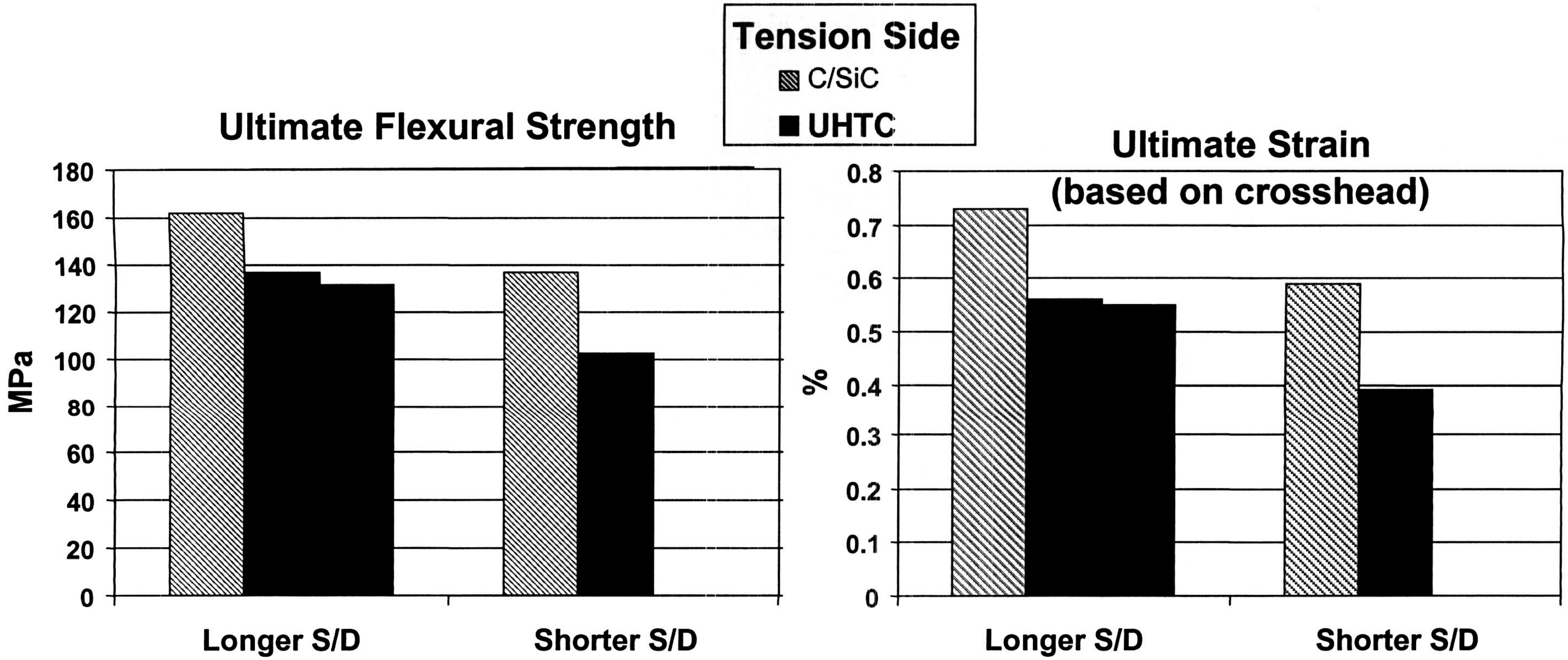
•Panex 30 minimum property: E = 193 GPa

•Rule of mixtures with no matrix contribution

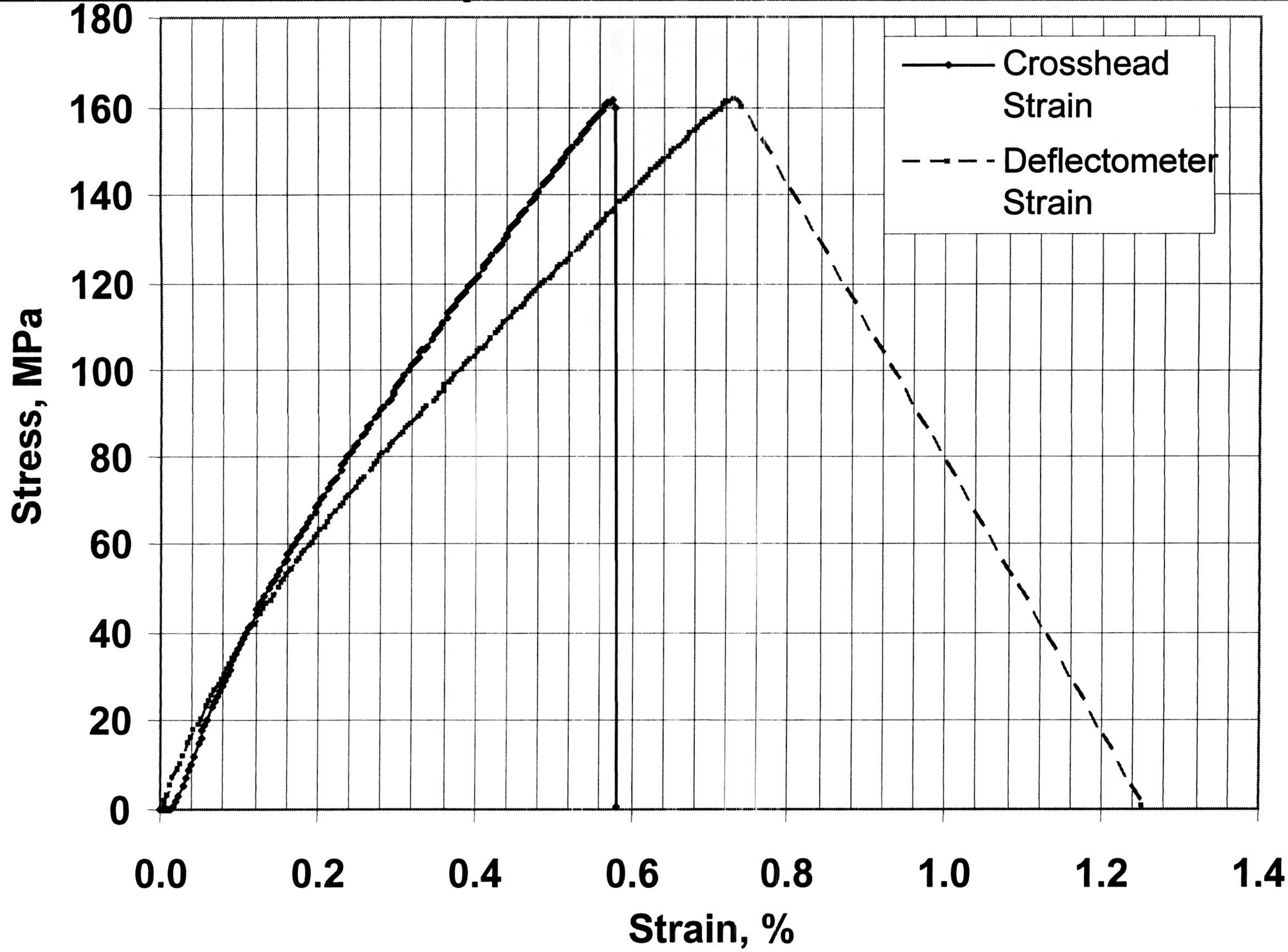
Flexural Strength Results

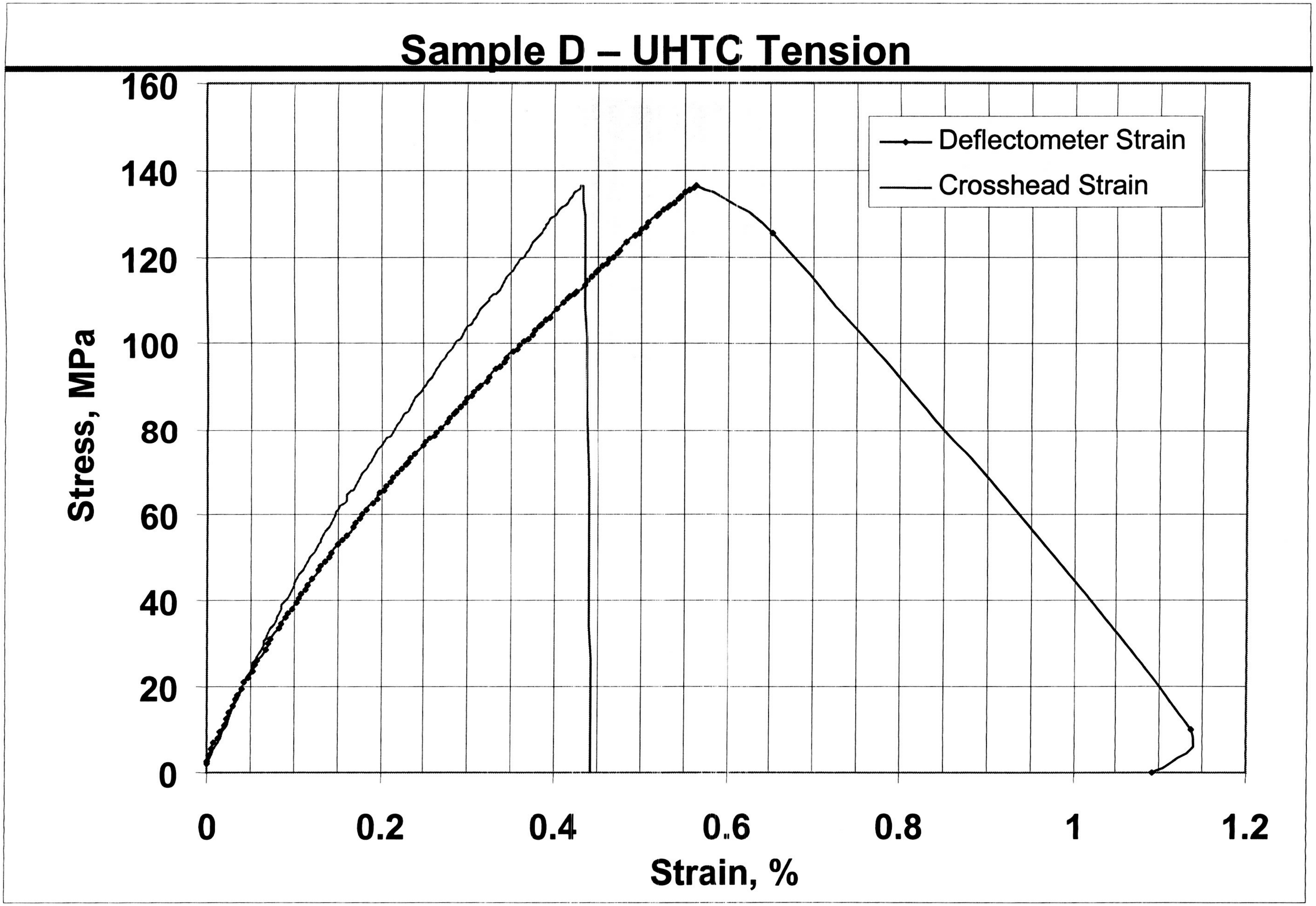
Test			Results					
ID	~ Span / Depth	Tensile Side	ultimate flexural strength	ultimate strain (crossh'd)	deviation from linearity	strain at dfl	deviation from linearity	strain at dfl
					crosshead strain		deflectometer	
			MPa	%	MPa	%	MPa	%
A	14	C/SiC	137.0	0.59	26.4	0.105		
B	14	UHTC	102.3	0.39	31.4	0.113		
C	16	C/SiC	161.8	0.73	28.2	0.078	23.0	0.058
D	16	UHTC	136.7	0.56	24.7	0.056	26.0	0.059
E	16	UHTC	131.8	0.55	26.1	0.090	26.1	0.063

UHTCC Flexural Strength Results



Sample C – C/SiC Tension

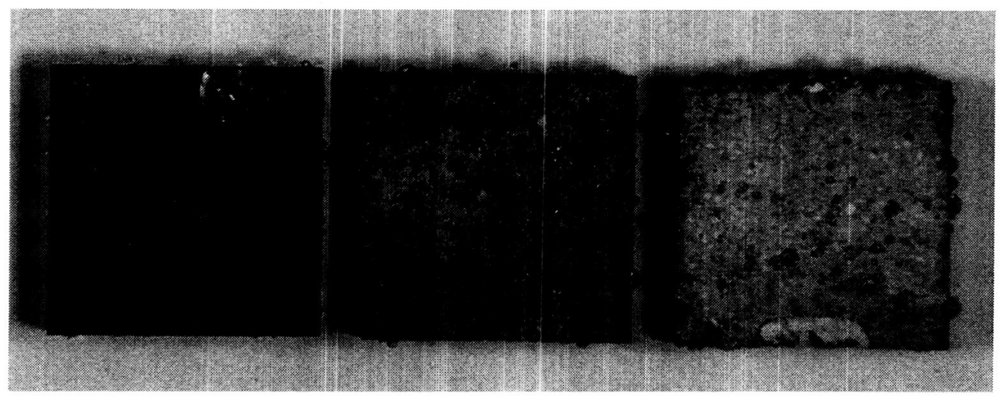



Sample D – UHTC Tension
Stress, MPa
160
140
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
1.2
Strain, %
Deflectometer Strain
Crosshead Strain

UHTCC After 1627°C Furnace Oxidation

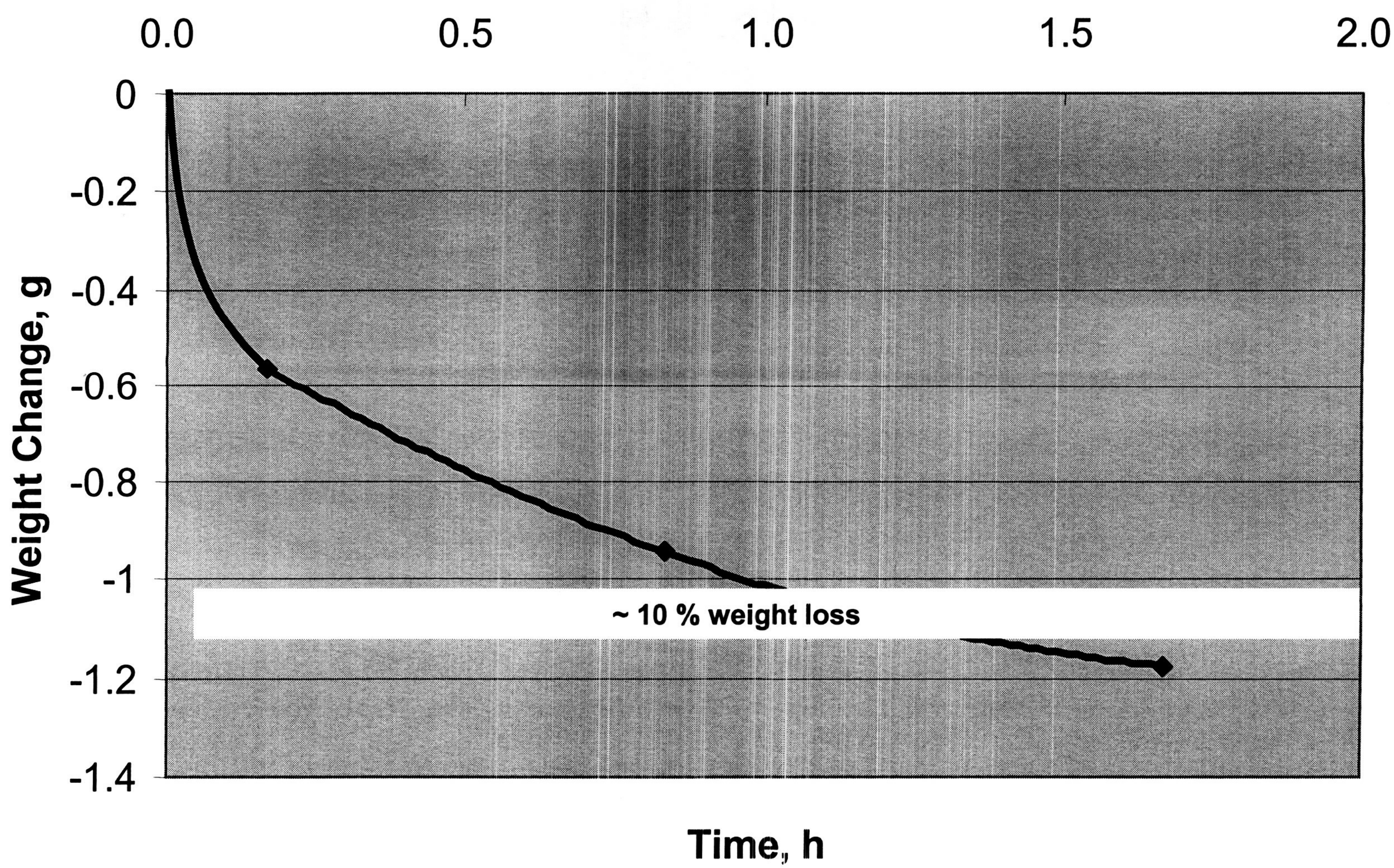
C/SiC Side

HfB_2 Side



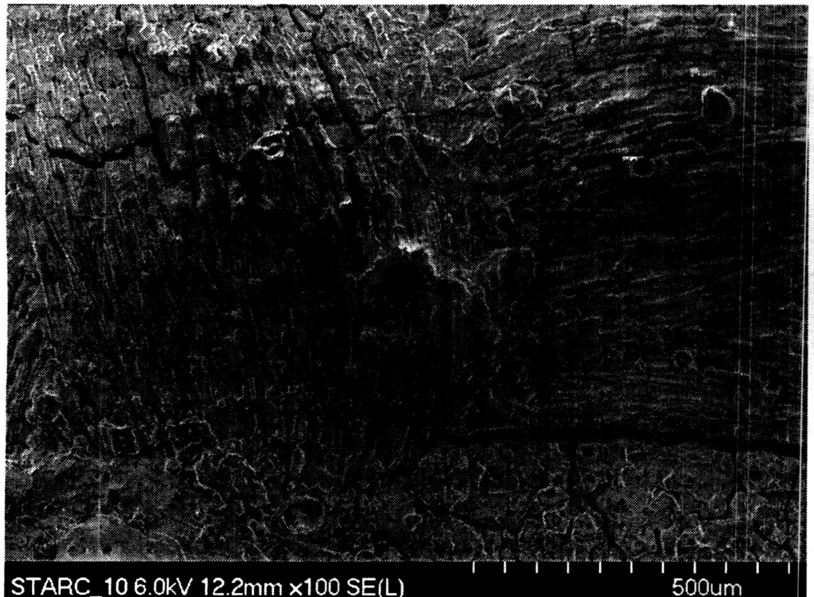
Cycles	1	5	10
Hours	0.167	0.833	1.667

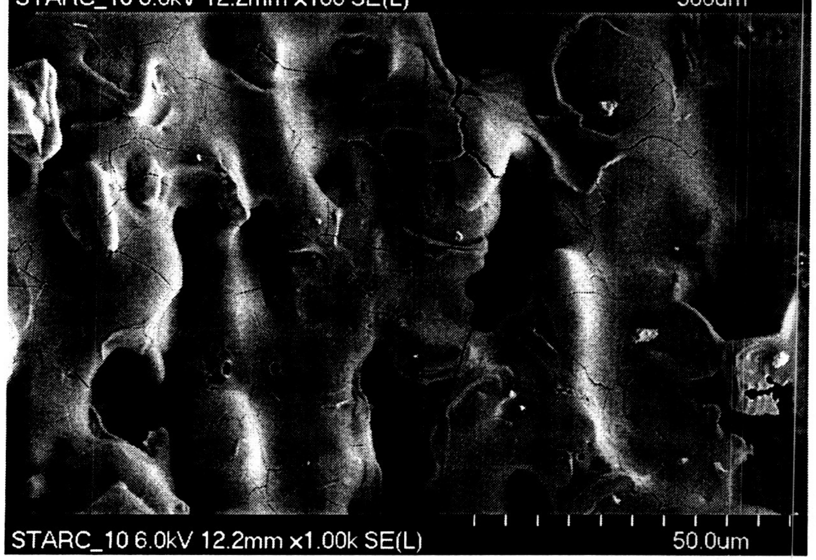
Furnace Oxidation of UHTCC at 1627°C



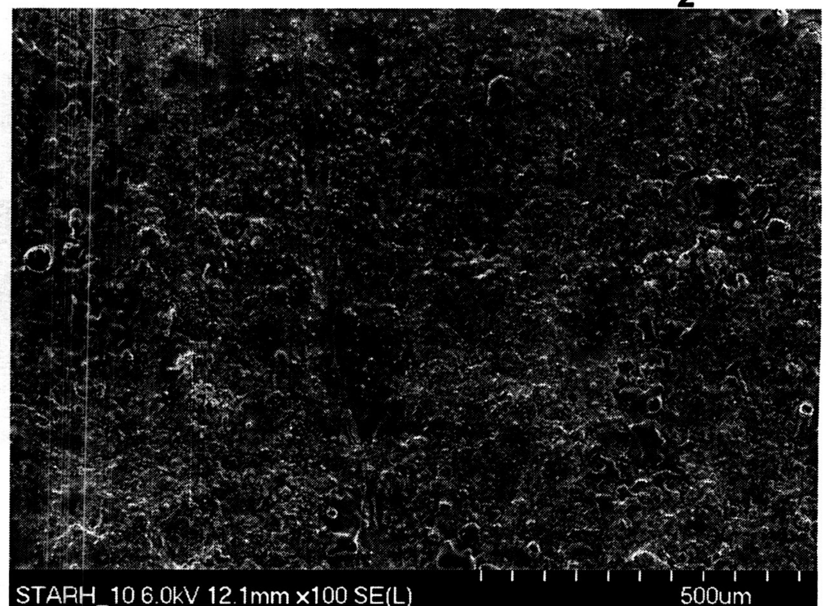
UHTCC After 10 Ten-minute Cycles in Air at 1627°C

C/SiC Side





HfB_2 Side

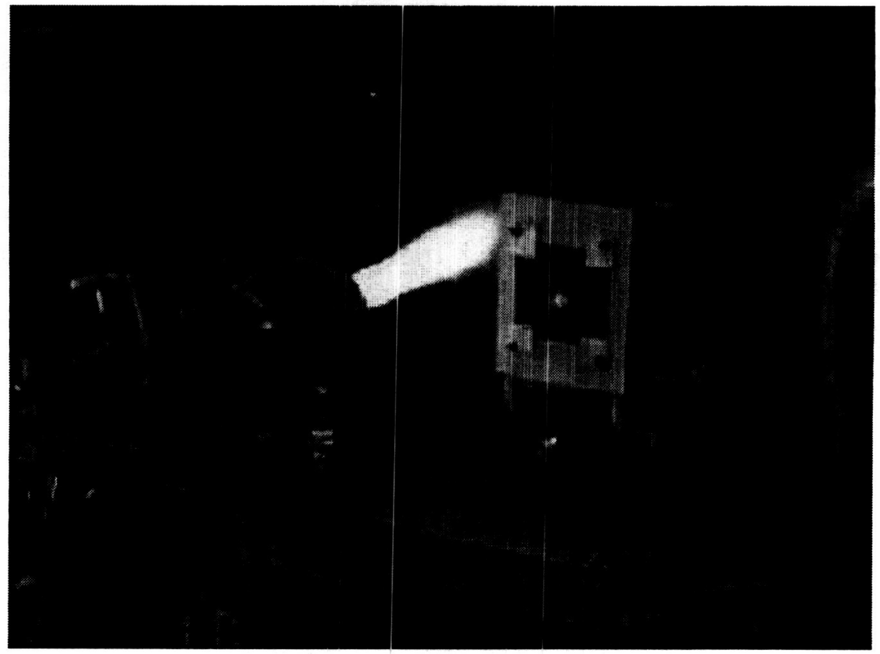


UHTCC Oxy-Acetylene Torch Test

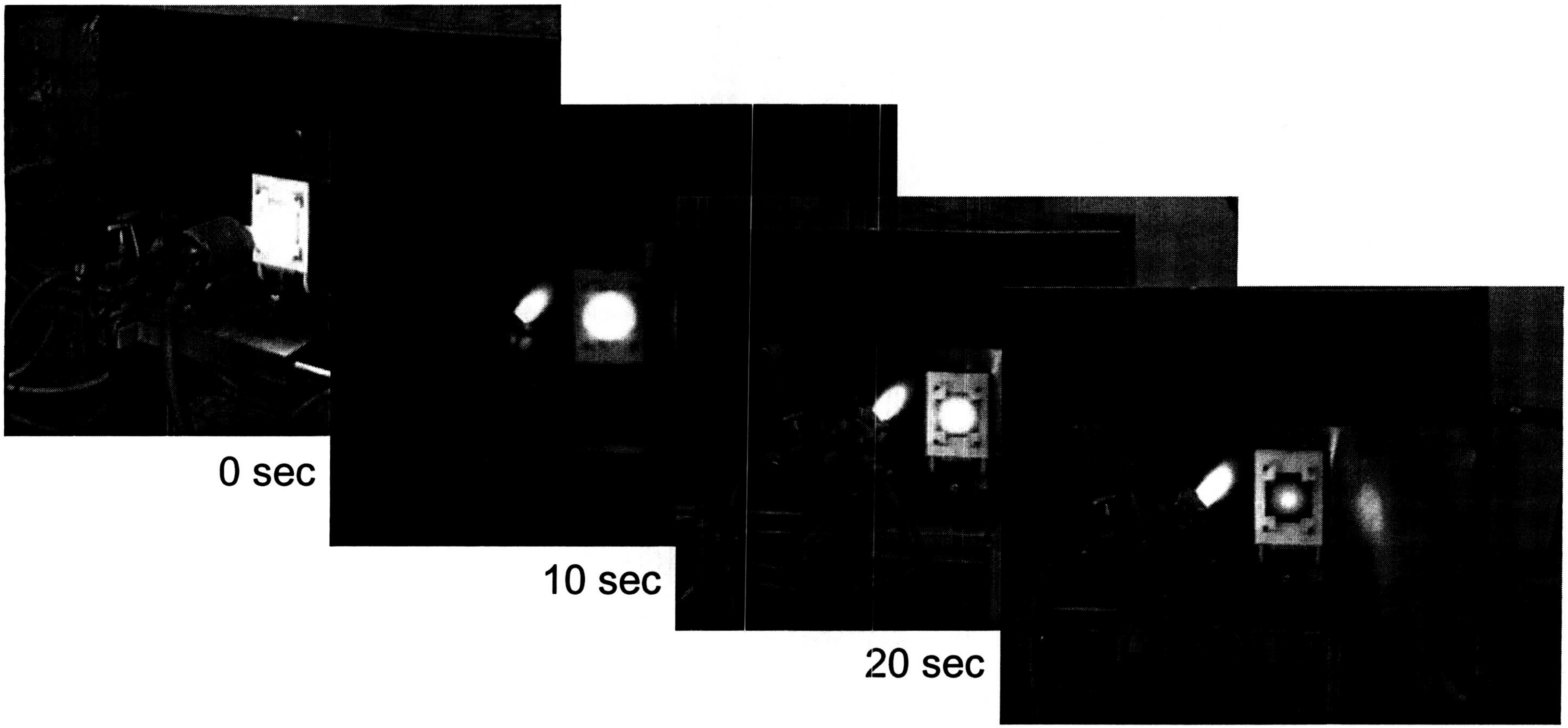
- Sample O: One 4 min. cycle to 1805°C
  - Photos on cool down
  - Temps with Ircon 2 color pyrometer, 980-1760°C range
  - Weight change
    - Initial weight 41.66 g
    - Final weight 40. 87 g
    - Weight loss 0.79 g, or 1.9%
- Sample N: Three ~4 min. cycles
  - Cycle 1 max temp 1815°C
  - Cycle 2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

UHTCC Torch Test Video



UHTCC Torch Test Cool Down



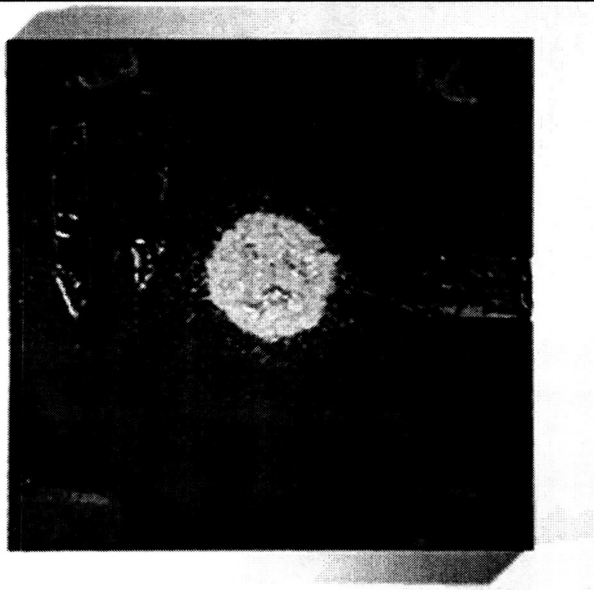
0 sec

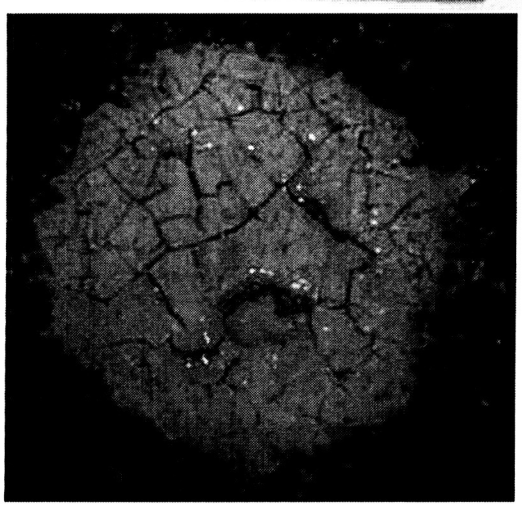
10 sec

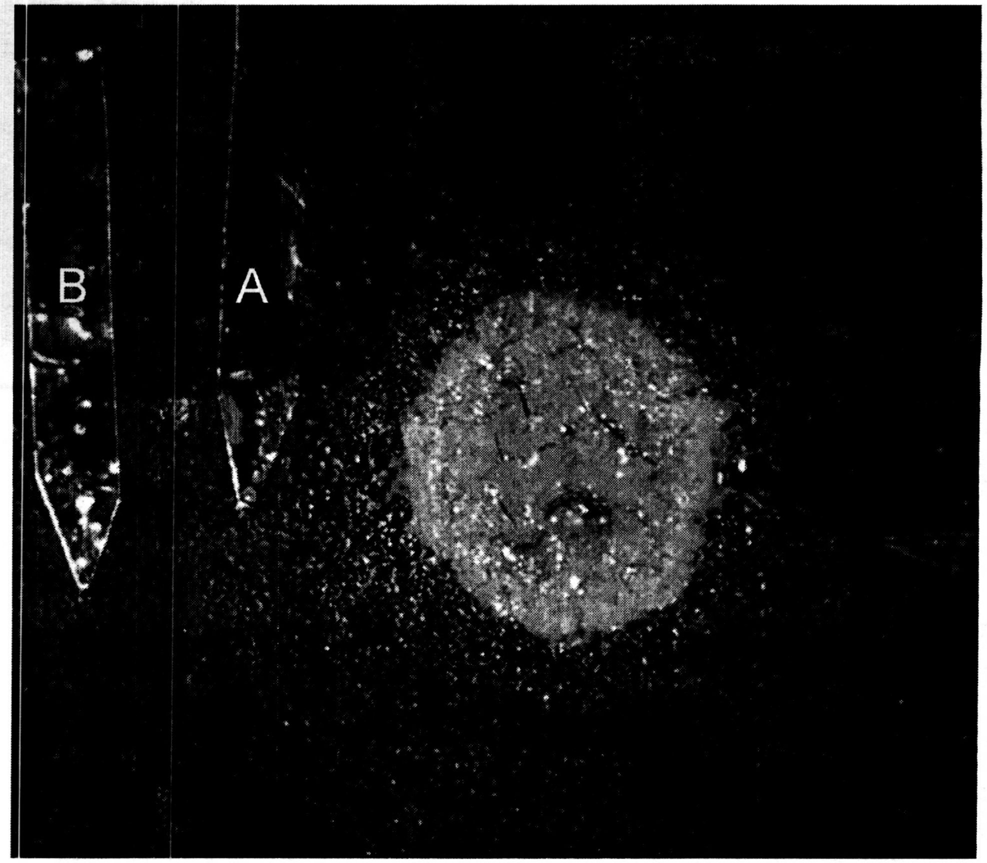
20 sec

30 sec

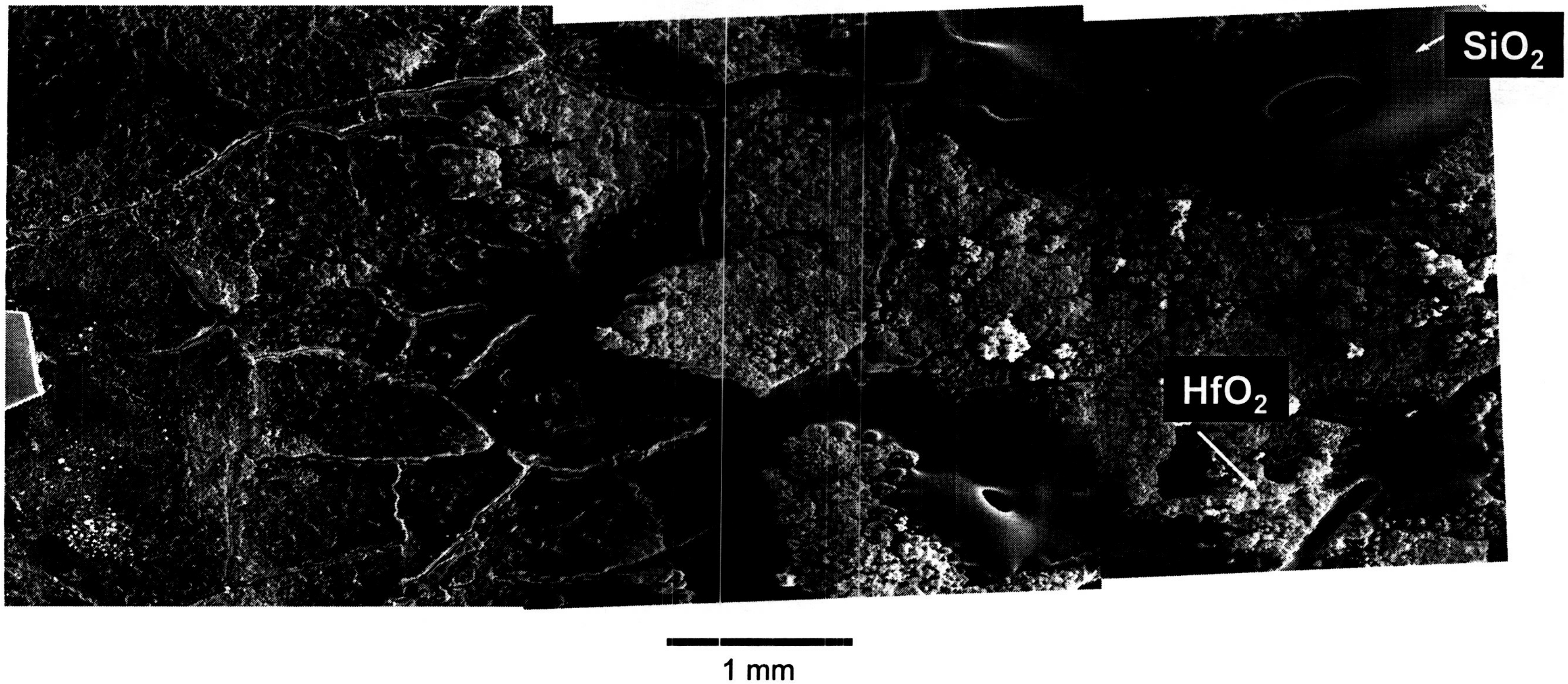
UHTC Surface After Three 4-Minute Torch Cycles to 1815 to 2025°C



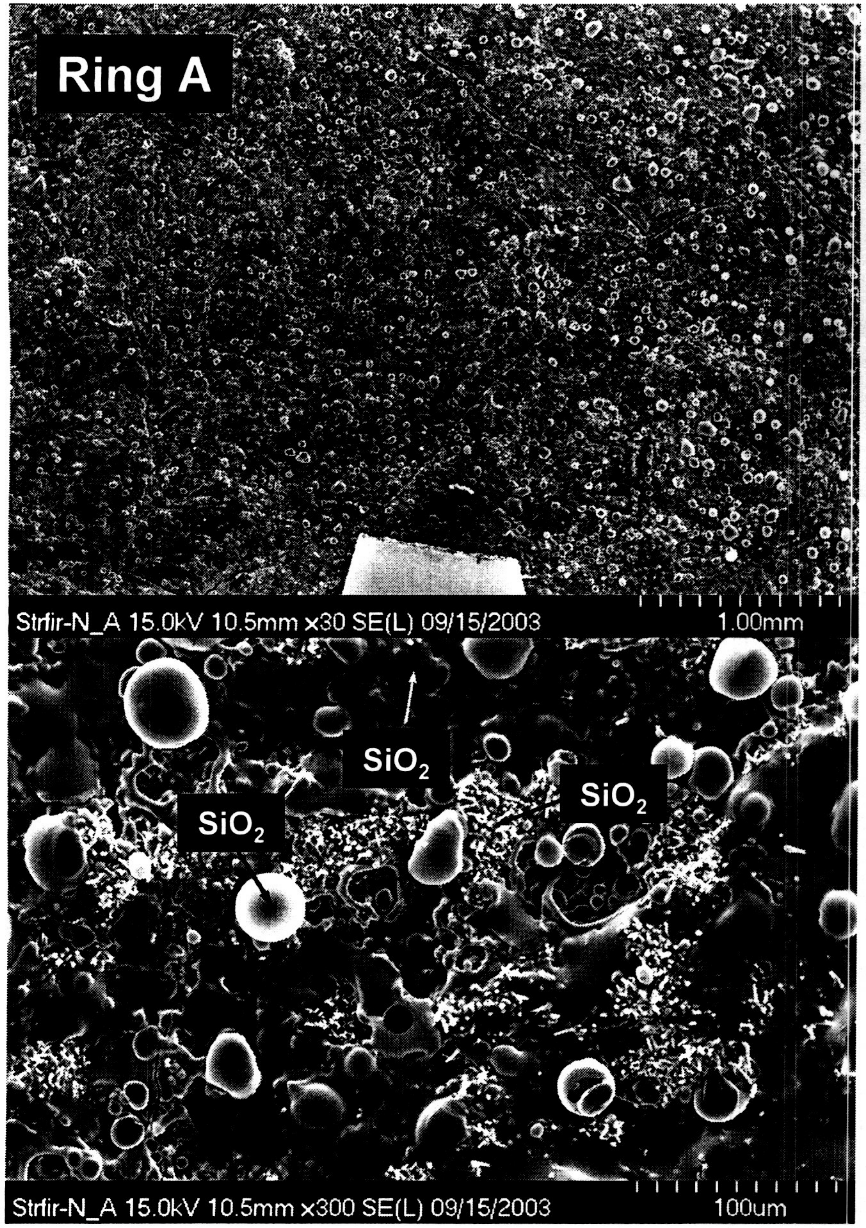


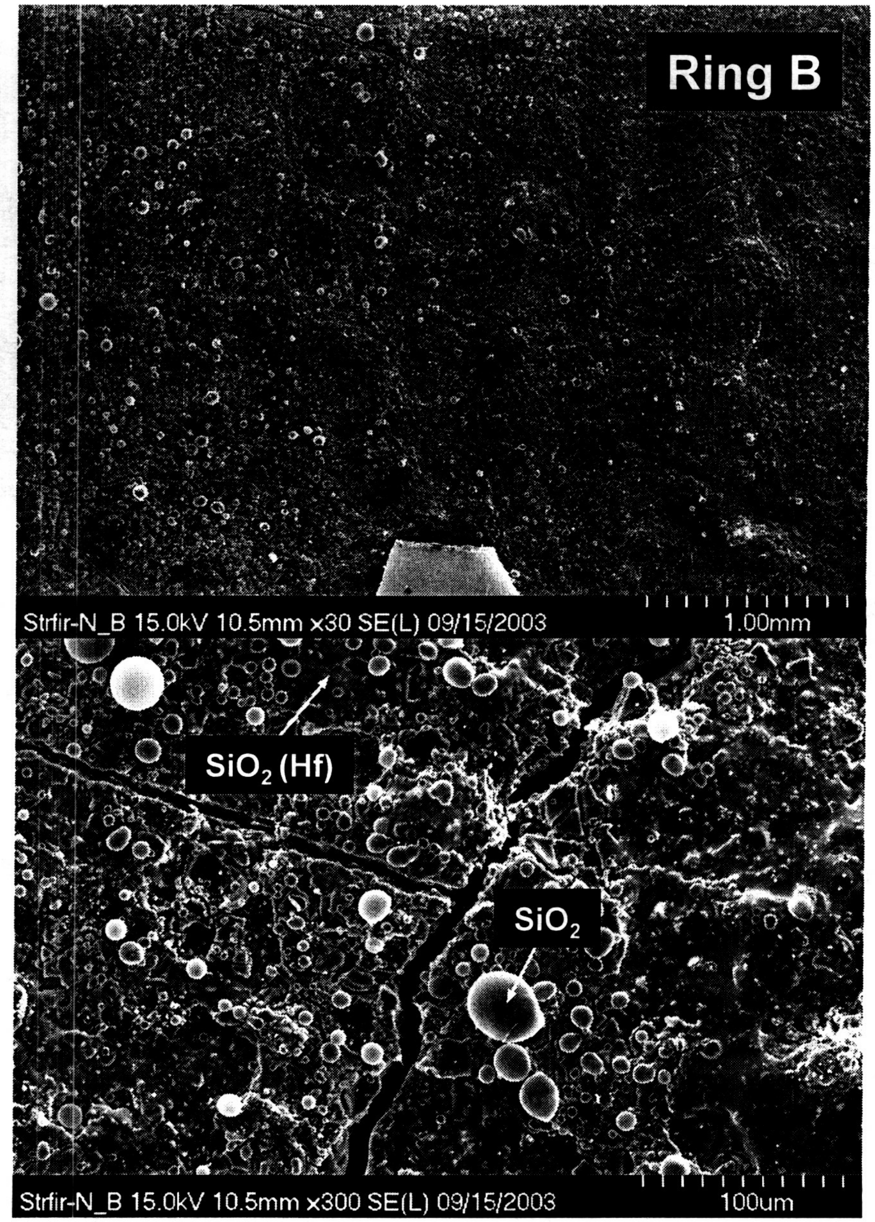


SEM of Center of UHTC Surface After Three Torch Cycles



SEM of UHTC Surface, Three Torch Cycles





Conclusions

- **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

- The thermal stress response of this 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

- Continue UHTCC development
- Continue UHTCC evaluation
  - Complete metallography on Starfire specimens
  - Evaluate other NASA and industry developed materials

Acknowledgements

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- Thanks to Walt Sherwood of Starfire Inc. for providing processing details and for permission to present this study.