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Fabrication, properties, and arc-jet testing of ZrB2-based composites Containing short SiC fibers

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DIAS

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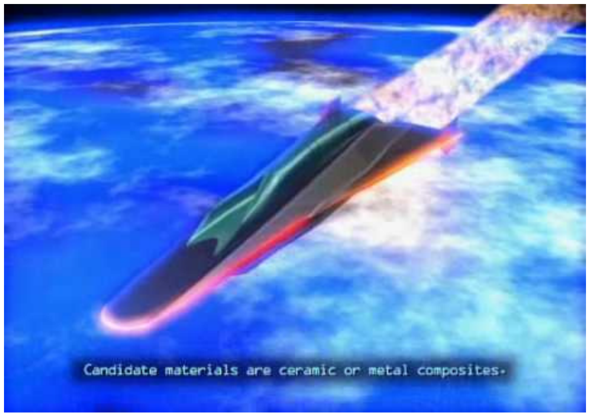
Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications II
May 14th 2012, Hernstein (Austria)

Re-entry flight trajectories



To re-enter Earth's atmosphere in an alternative way, flying with lower aerodynamic drag, larger cross range and better maneuverability along more gentle trajectories slender vehicles with sharp edges flying at moderate angles of attack are necessary.

The reduced leading edge's curvature radius implies surface temperature higher than that of the actual blunt vehicles and that could not be withstood by the conventional thermal protection system materials.

Refractory and oxidation resistant aero-surfaces (with **sharp profile**)

ARE REQUIRED

Ultra-high temperature ceramics

Melting point range of UHTCs (nitrides, borides and carbides of Zr, Hf, Ta)

UHTCs are currently investigated as TPS of fuselage nosecone and wing leading edges istec

Key requisites for materials

Mechanical requisites: high resistance to thermal shock, high fracture toughness

Thermal requisites: high thermal conductivity, high emittance, low catalytic efficiency, high resistance to oxidation

MB_2 (M=Zr, Hf) ceramics alone possess

- **high temperature capabilities and high thermal conductivity**
- poor oxidation resistance
- low fracture toughness

} Add SiC (particle, whiskers, fibers)

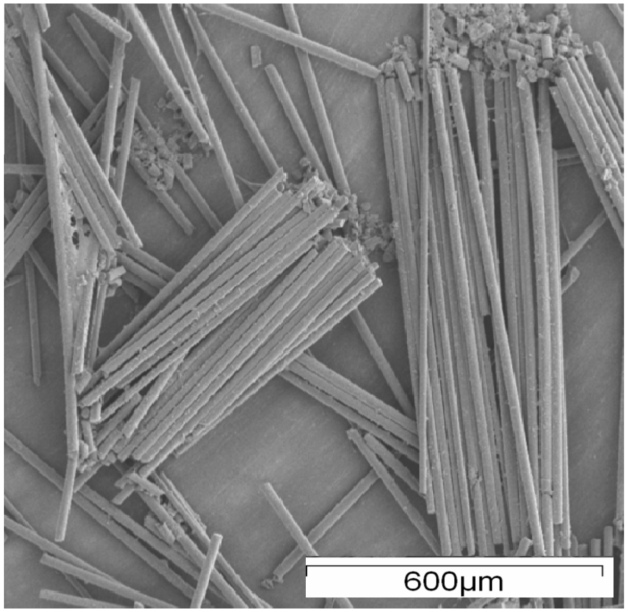
Aim of this work

Study of the effects of SiC chopped fibers on ZrB_2–based massive ceramic

- properties
- resistance to oxidation under static conditions
- stability under aerothermal heating

Raw materials

- **ZrB_2** - (H.C. Starck) grade B
- **Si_3N_4** – Baysind



- **SiC** – HI Nicalon (COI Ceramics)
  - length: 0.5-1 mm + debris
  - density: 2.74 g/cm^3
  - composition: 55% β-SiC crystallites (2 nm), 5% C, embedded in 40% Si-C-O intergranular phase

Production of ZrB_2-15%SiC_F

✓ Starting composition (vol%): **ZrB_2 + 15% SiC_{Fiber} + 5 % Si_3N_4 (s.a)**

✓ Material processing

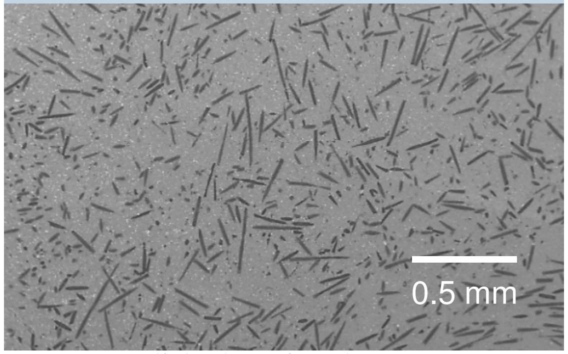
1) Batching of powders → 2) Homogenization of the slurry in EtOH → 3) Drying and de-agglomeration → 4) Cold linear pressing → 5) Debonding in Ar → 6) Hot-pressing →

Fully dense pellet ϕ 40 mm

5.3 g/cm^3

ZrB_2-15 SiC_F: microstructure and properties

View plan ⊥ applied P



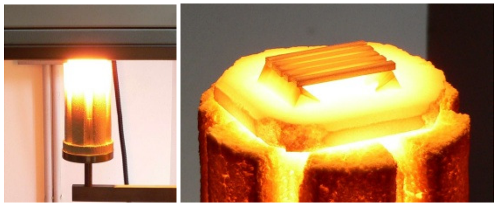
Polished section, by SEM

max fiber length: ~ 0.3 mm

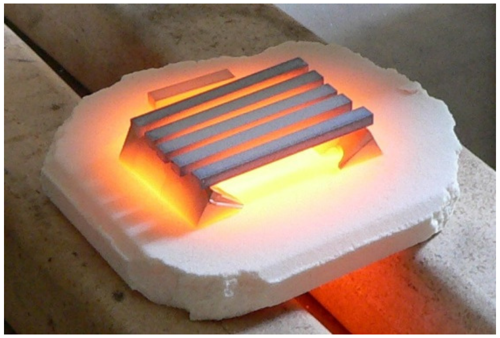
Property	Method	Specimen size	Notes	Mean value (±1s.d)
Elastic modulus	Resonance frequency	30 x 8 x 0.8 mm	RT	402 GPa
Flexure strength	4-pt bending	25 x 2.5 x 2 mm	RT	**(453± 19)** MPa
Flexure strength	4-pt bending	25 x 2.5 x 2 mm	1200°C air	(336 ± 29) MPa
Fracture toughness	Chevron notched beam	25 x 2.5 x 2 mm	RT	**(5.3±0.05)** MPa√m (ΔK_{Ic} 50%)
Thermal shock resistance	Water quenching method	25 x 2.5 x 2 mm	RT	400-500°C (in progress)
Thermal conductivity	Laser flash	Φ 12.7 mm	RT - 1500°C	**65 - 50 W/m K**

Resistance to oxidation in static air

Iso-thermal run for 30 min at 1700°C



Bottom-up loading furnace



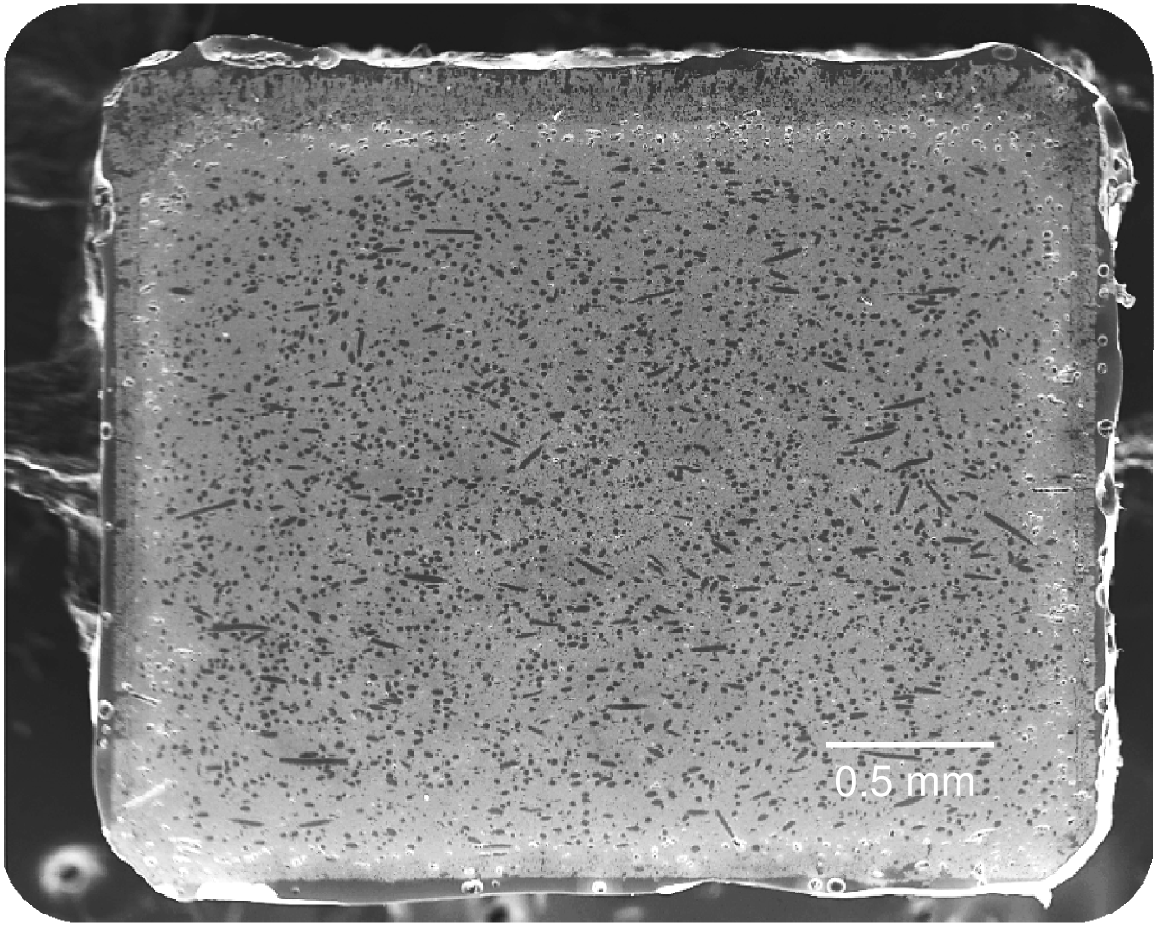
Visual appearance before oxidation

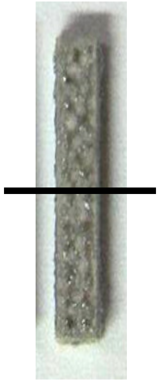
Visual appearance after oxidation

Specific mass change (w/S)
(7.5 ±0.1) mg/cm^2

Resistance to oxidation in static air

<u>Iso-thermal run</u> for 30 min at 1700°C

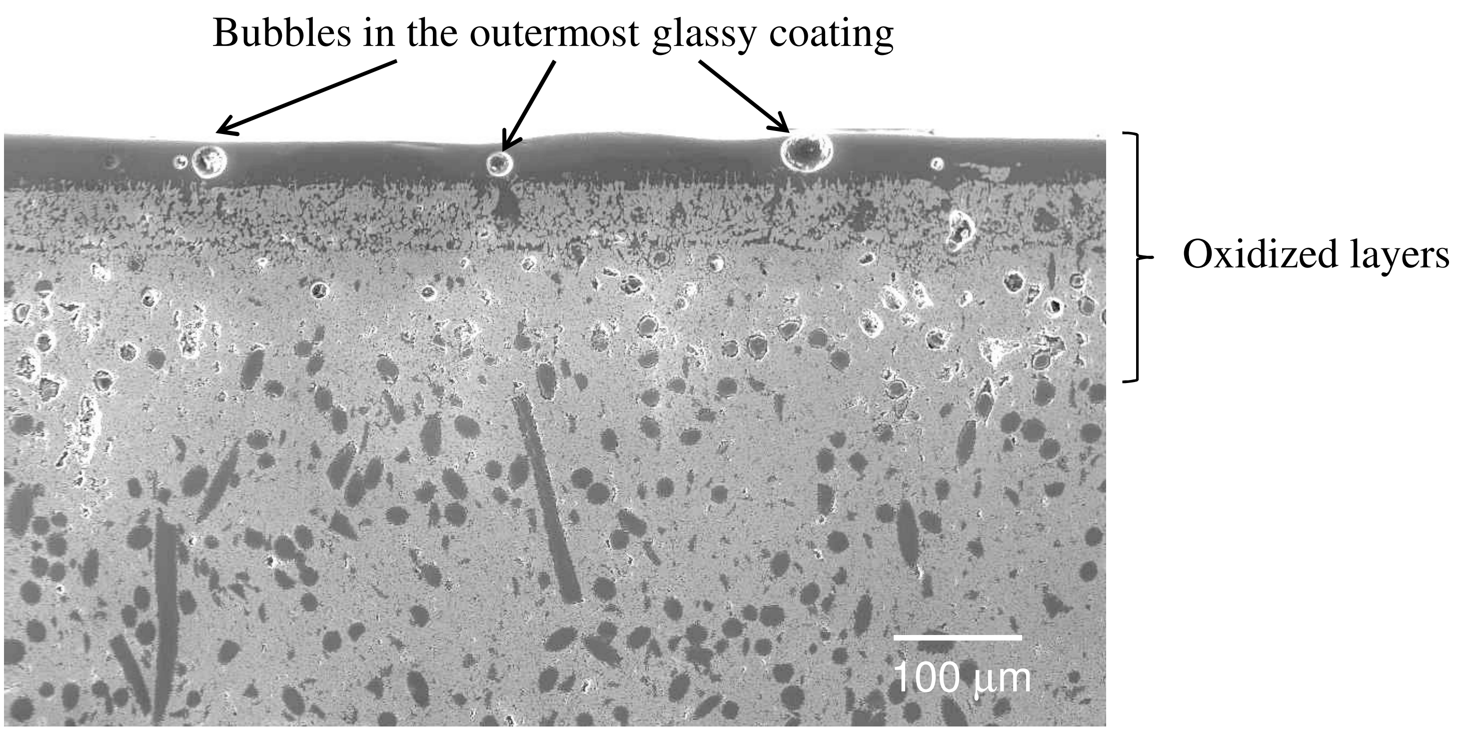




Polished cross-section of oxidized bar (SEM micrograph)

Resistance to oxidation in static air

Iso-thermal run for 30 min at 1700°C

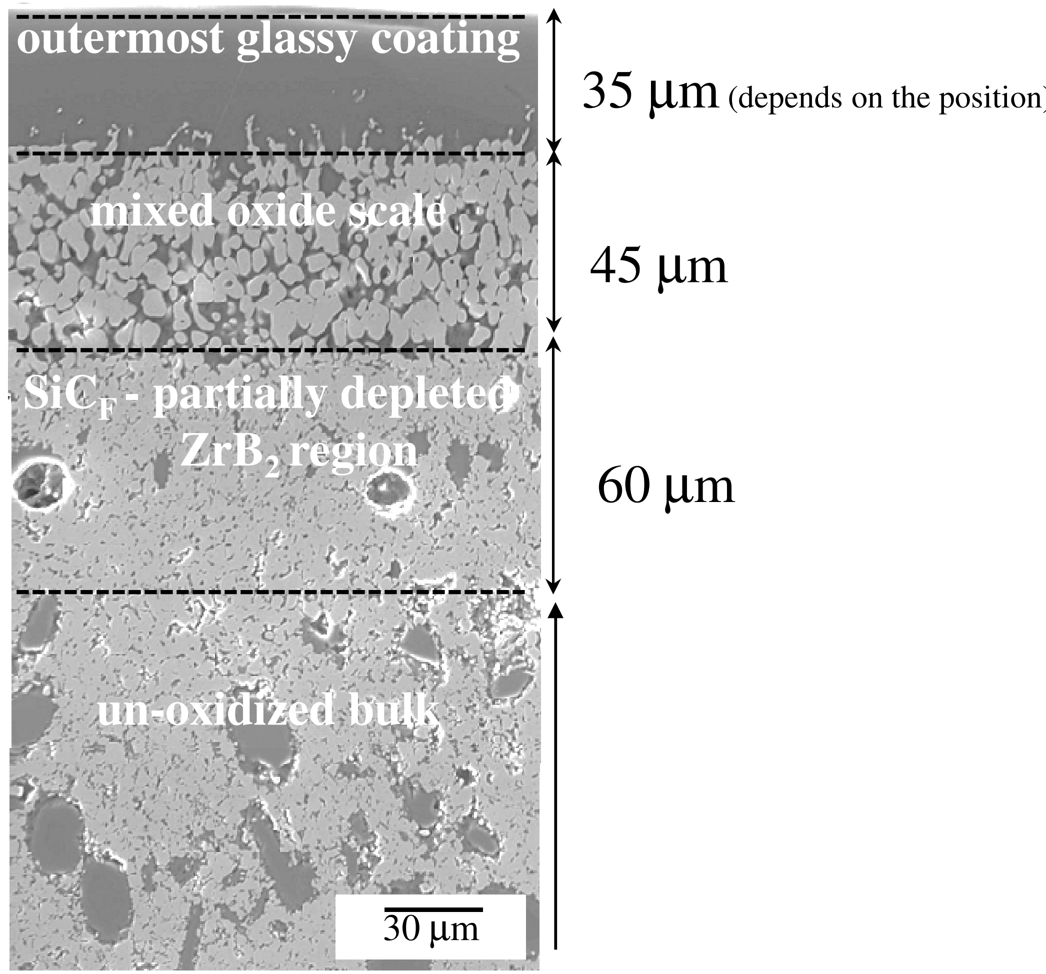


Polished cross-section: details of the external oxide scale

(SEM micrograph)

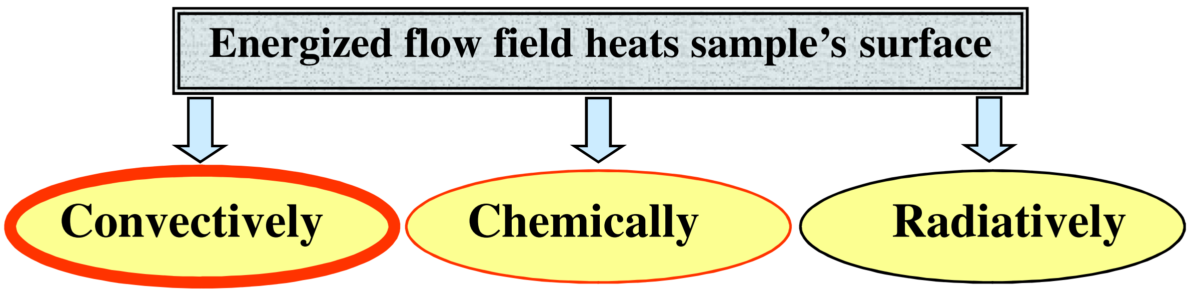
Resistance to oxidation in static air

<u>Iso-thermal run</u> for 30 min at 1700°C



Arc-jet testing

- Simulate re-entry conditions in a ground-based facility
- Heat a test gas (air) to plasma temperature by an electric arc, then accelerate into a pressure-controlled chamber, and onto a stationary test article



In a re-entry environment:

- Oxygen and Nitrogen may be dissociated, thus their recombination adds to surface heating
- stagnation pressure may be below 1 atm, thus active oxidation of SiC plays an important role

Arc-jet testing in high enthalpy supersonic flows

<u>S</u>mall <u>P</u>lanetary <u>E</u>ntry <u>Simulator</u>

Dept. of Aerospace Engineering - University of Naples "Federico II", Italy

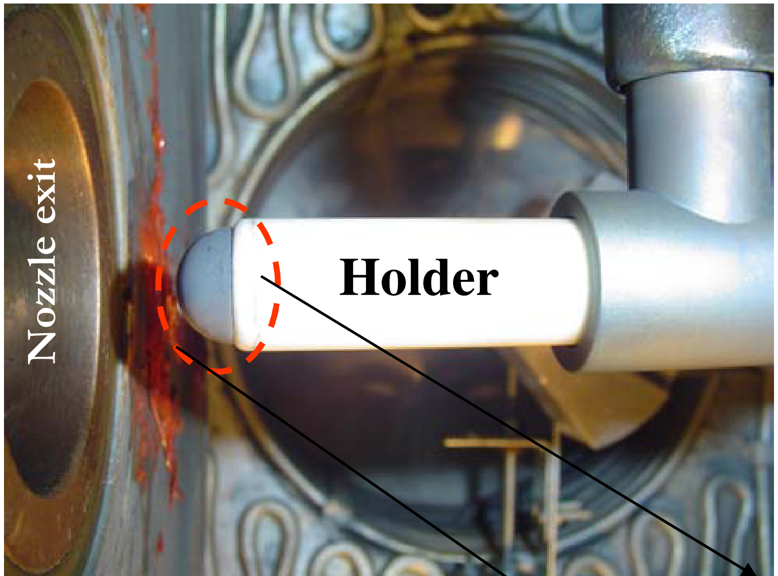
Main Technical Specifications

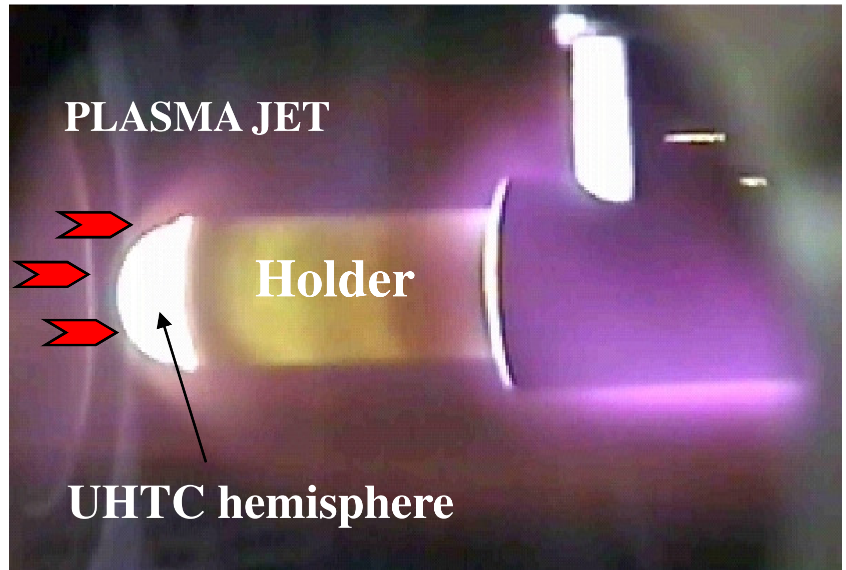
- Mean free stream total enthalpy (MJ/kg)	3 - 35
- Stagnation-point pressure (Pa)	500 – 10000
- Mach number	up to 5
- Mass flow rate (g/s)	0.5 - 5
- Gas mixtures	**air**, Ar, N_2, CO_2
- Nozzle exit diameter (mm)	22, 60
- Model size (mm)	up to 40

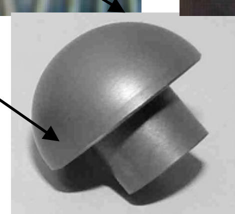
Main Measurement Techniques

- Total enthalpy	**energy balance**
- Stagnation-point pressure	water-cooled Pitot probe
- Stagnation-point heat flux	Gardon gauges and slug calorimeters
- Pressures	precision vacuum transducers
- Mass flowthermal	mass flowmeters
- Surface temperatures	**IR thermography, pyrometer**

Arc-jet testing_setup







Two UHTC hemispheres (nominal R= 5 mm) were machined

- M ≈ 3 (supersonic regime)
- 1 g/s of 80%N_2+ 20% O_2 (air)
- static chamber pressure ≈ 200 Pa
- maximum stagnation point pressure 8.5-10 kPa

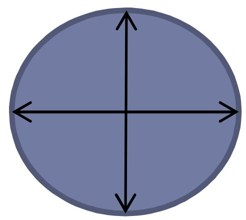
Two arc-jet tests were executed

1st test: max H_0= 13 MJ/kg for 350 s

2nd test: max H_0= 17 MJ/kg for 270 s

Arc-jet testing_setup

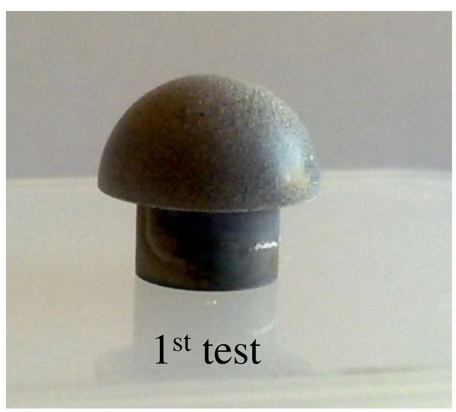
- After conventional machining, UHTC hemispheres were cleaned, and weighed before and after arc-jet testing (precision 10^{-4} g)
- The profile of the curved surface was measured before and after arc-jet test using an contact-stylus profilometer



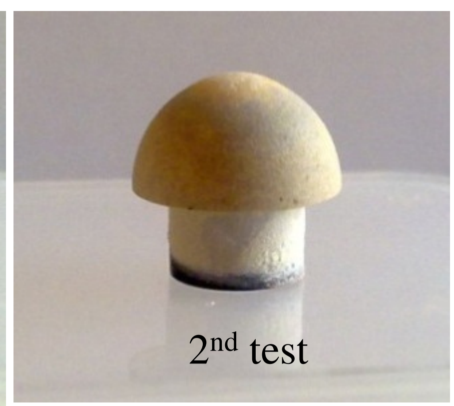
- Best fitted R* was estimated along two orthogonal directions

Visual appearance of hemispheres after

As-machined



1st test



2nd test

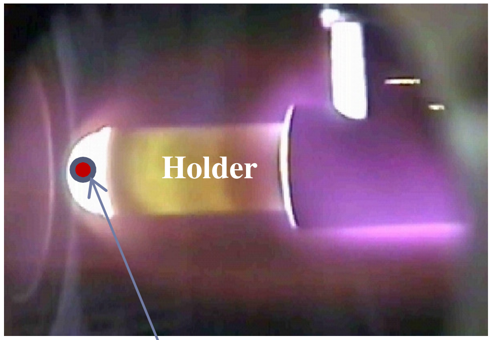
1^{st} arc-jet test_results

- Max H_0: 13 MJ/kg, duration (t): 350 s
- Equilibrium temperature (by two-color pyrometer)

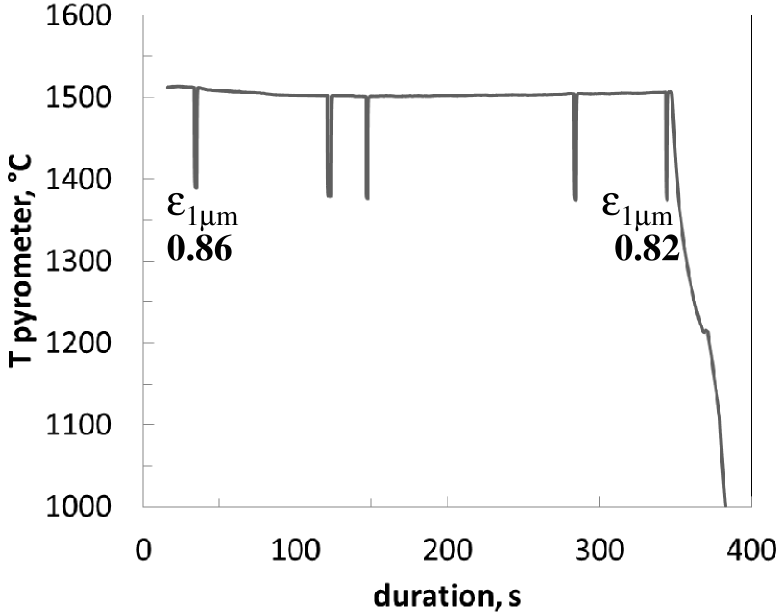
1500°C at t_{0s} 1505 °C at t_{350s}

- Spectral emissivity at 1 µm ($\varepsilon_{1\mu m}$)

t_{0s}= 0.86 , t_{350s} = 0.82



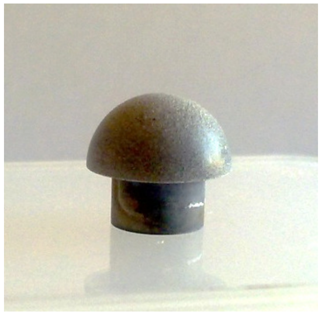
Two-color pyrometer



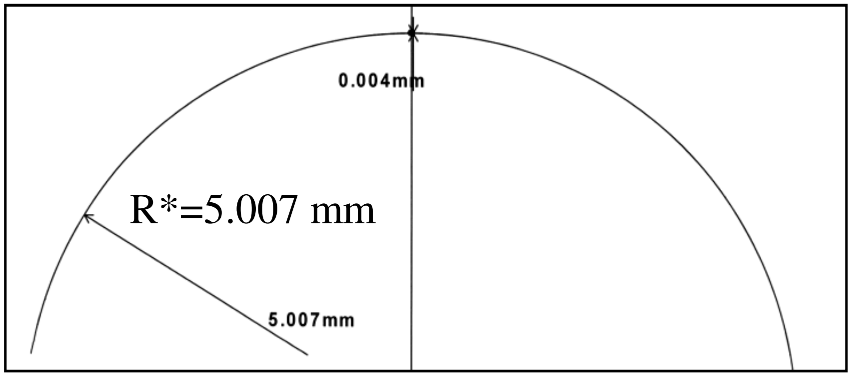

As-cut cross section of the hemisphere, by OM

1^{st} arc-jet test_results

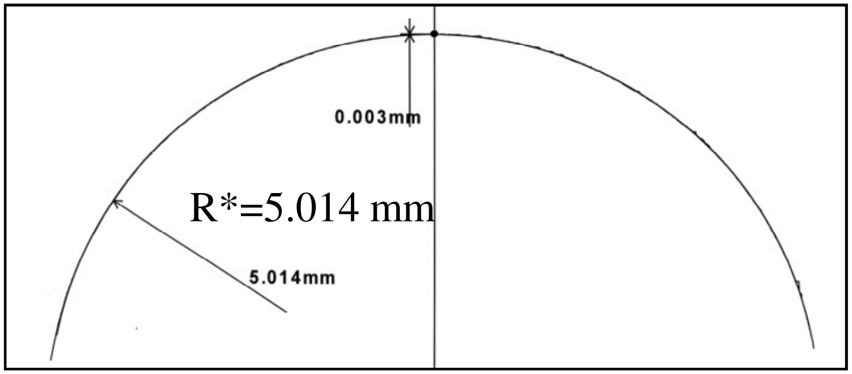
- Mass change ($\Delta m/m_0$): 0.4% (all modifications upon the curved surface)
- R* (best fitted radius of curvature) change: + 0.007 mm (profilometer)



Profile of the round hemispheric surface



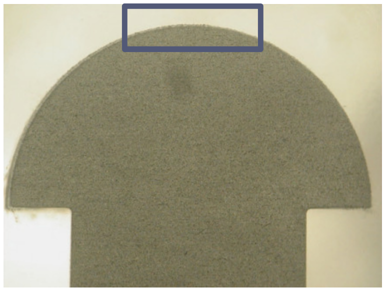
before arc-jet

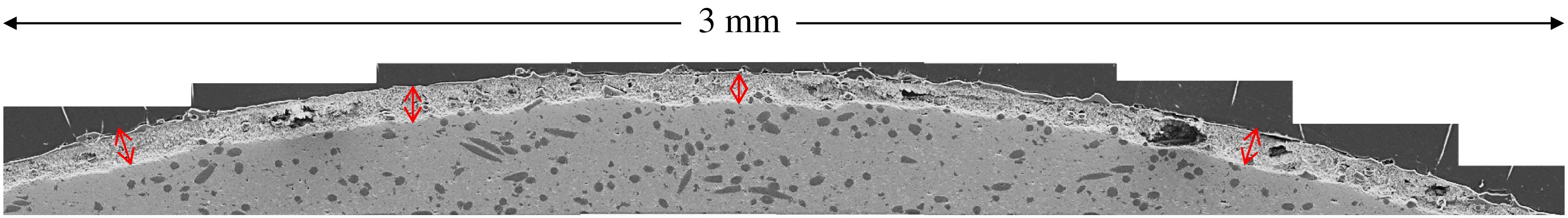


after arc-jet test

1st arc-jet test_results

- **Max H_0: 13 MJ/kg, duration: 350 s**
- **Equilibrium temperature range (by two-color pyrometer): 1500 - 1505 °C**



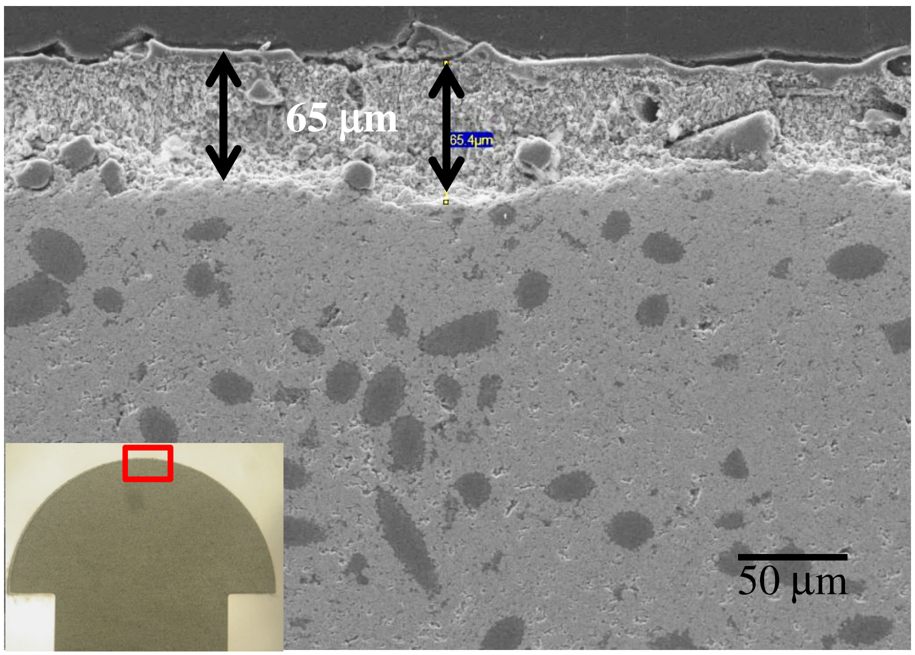


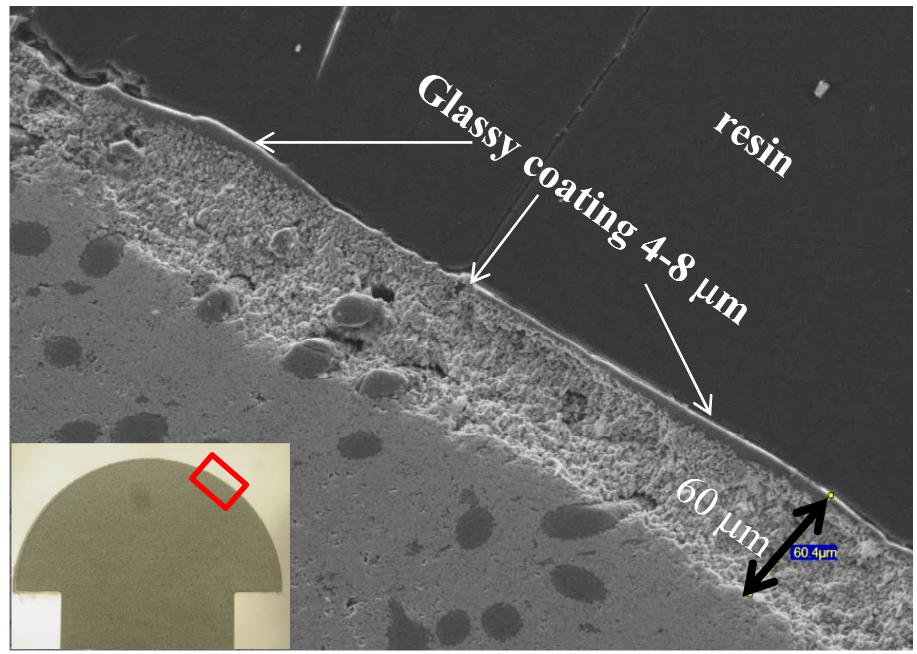
Polished cross section, by SEM, near the stagnation point

oxide scale thickness 60-65 μm

1^{st} arc-jet test_results

- **Max H_0: 13 MJ/kg, duration: 350 s**
- **Equilibrium temperature range (by two-color pyrometer): 1500 - 1505 °C**



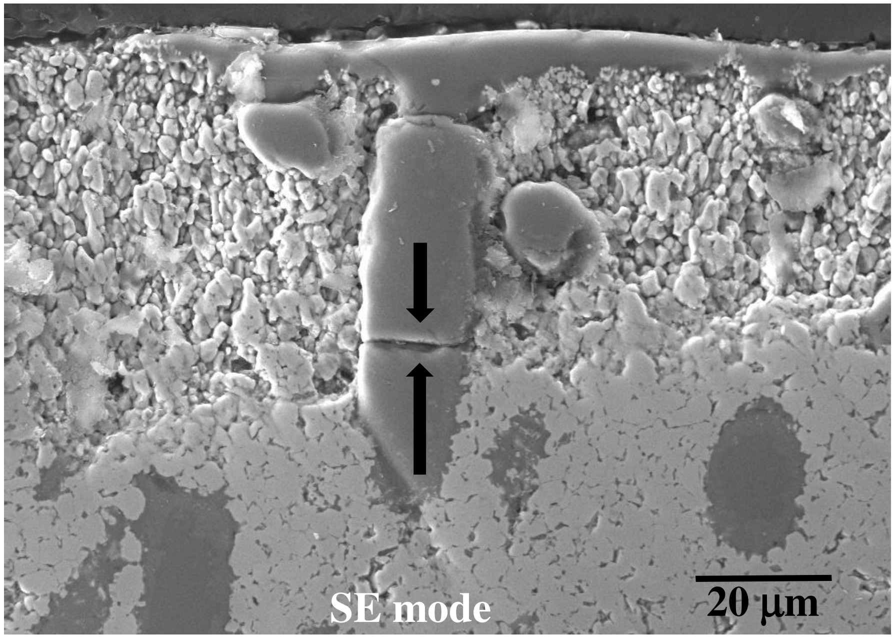


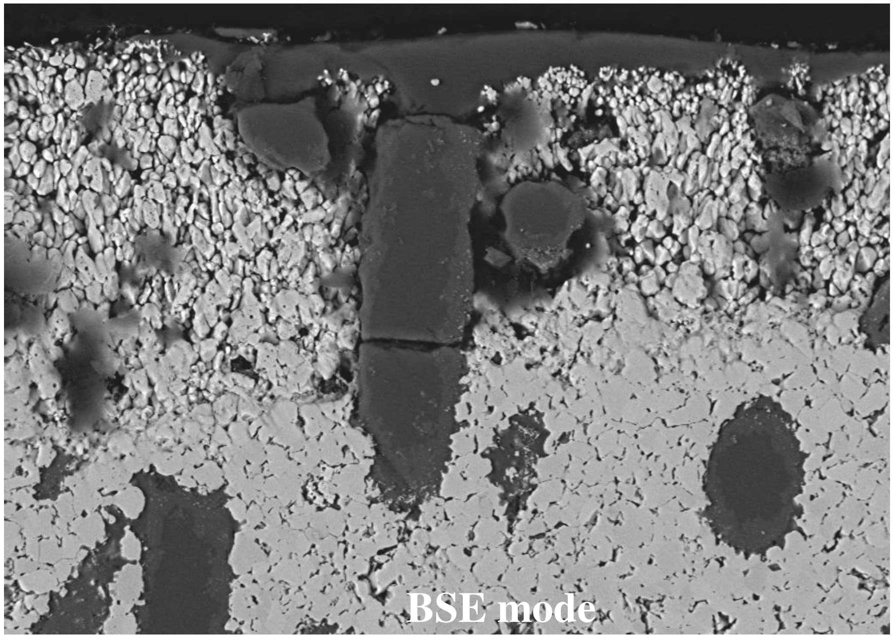
Polished cross section, by SEM: the external oxide layers

thickness of zirconia scale 60-65 µm; thickness of glassy coating 4-8 µm

1^{st} arc-jet test_results

- **Max H_0: 13 MJ/kg, duration: 350 s**
- **Equilibrium temperature range (by two-color pyrometer): 1500 - 1505 °C**



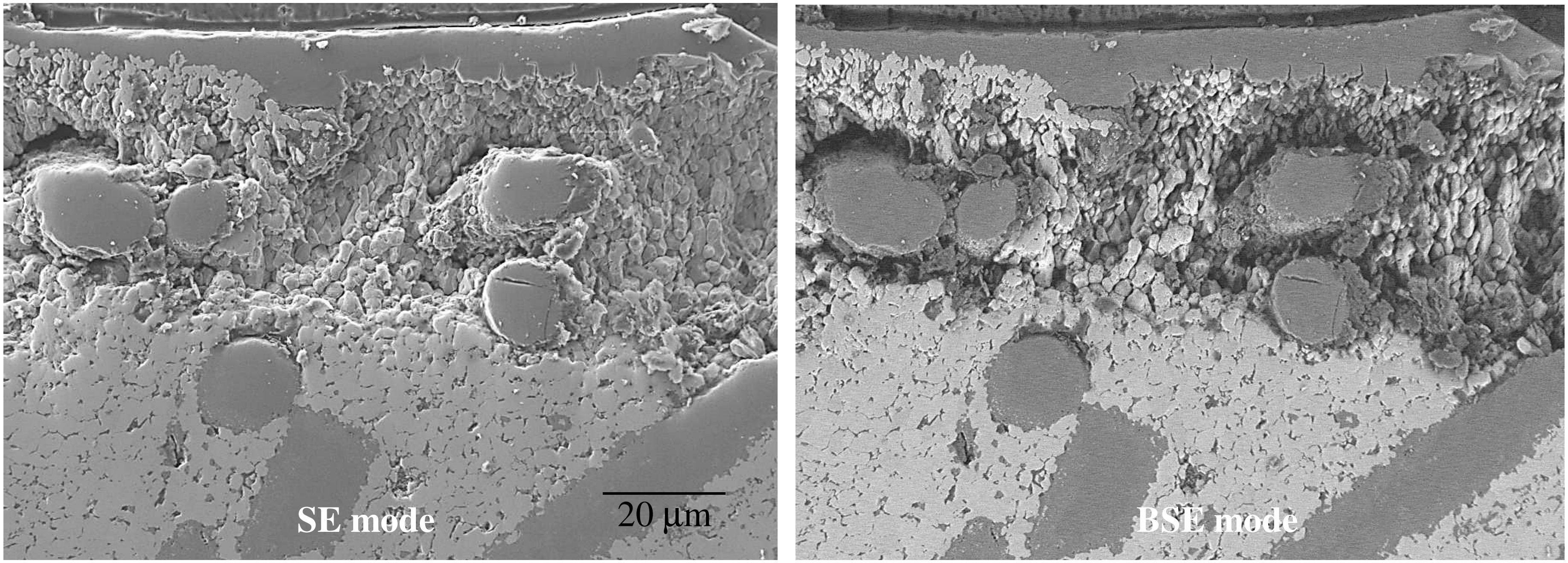


Polished cross section, by SEM: details on the fibers inside the oxide scale

SE: secondary electron, BSE: backscattered electron

1^{st} arc-jet test_results

- **Max H_0: 13 MJ/kg, duration: 350 s**
- **Equilibrium temperature range (by two-color pyrometer): 1500 - 1505 °C**



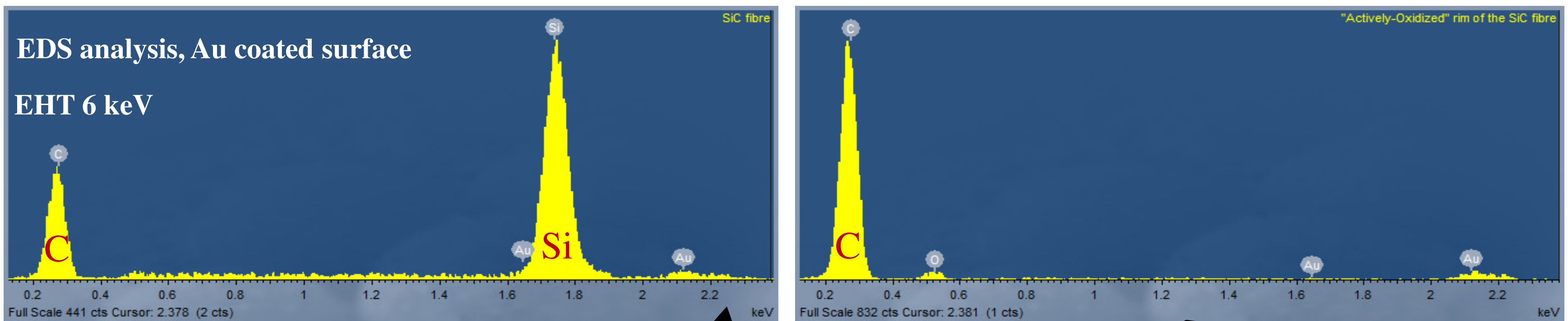
Polished cross section, by SEM: details on the fibers inside the oxide scale

The partially –consumed SiC fibers via mechanism of active oxidation

SE: secondary electron, BSE: backscattered electron

1^{st} arc-jet test_results

- **Max H_0: 13 MJ/kg, duration: 350 s**
- **Equilibrium temperature range (by two-color pyrometer): 1500 - 1505 °C**

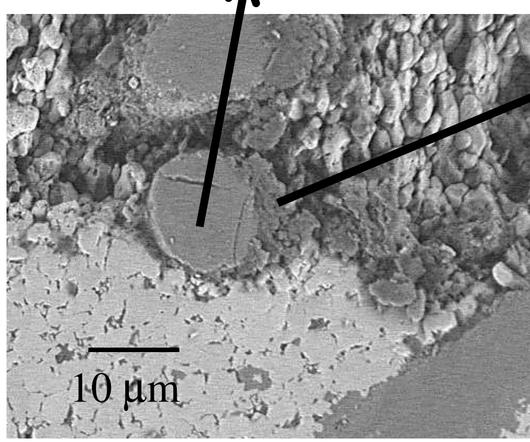


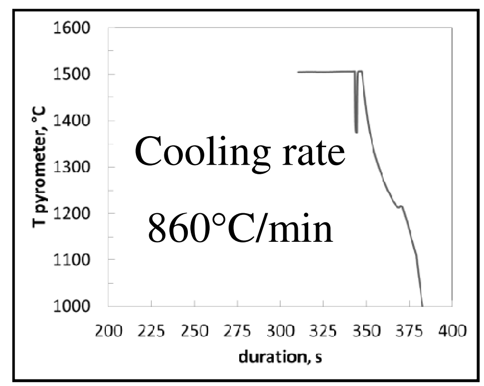
$SiC + ½ O_2(g) = C(s) + SiO(g)$

$SiC + O(g) = C(s) + SiO(g)$

$SiC + O_2(g) = SiO(g) + CO(g)$

$SiC + 2O(g) = SiO(g) + CO(g)$





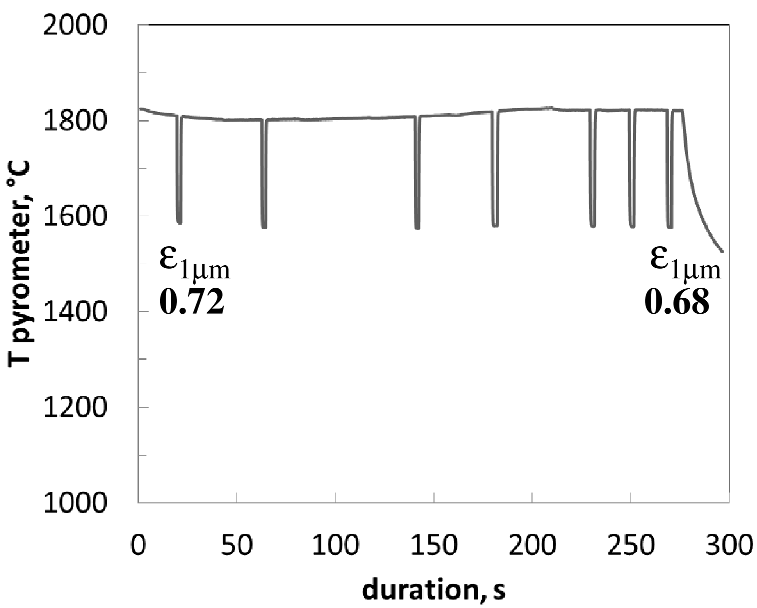
Detail of a partially oxidized SiC fiber, by BSE-SEM

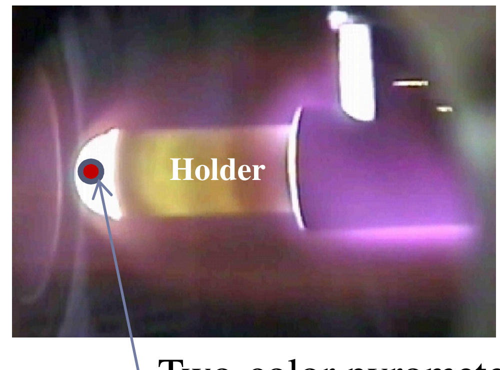
2^{nd} arc-jet test_results

- Max H_0: 17 MJ/kg, duration: 270 s
- **Equilibrium temperature (by two-color pyrometer)**

  $t_{0\text{-}360}$ = (1800-1820)°C
- **Spectral emissivity at 1 µm**

  t_0= 0.72 , t_{270s} = 0.68





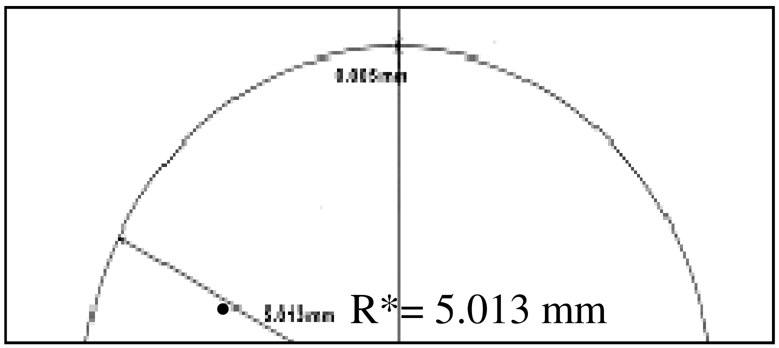
Two-color pyrometer

As-cut cross section of the hemisphere, by OM

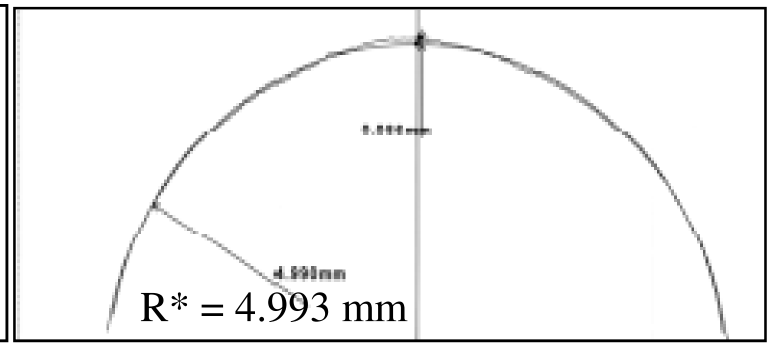
2^{nd} arc-jet test_results

- Mass change ($\Delta m/m_0$): + 0.145 % (all modifications upon the curved surface)
- R* (best fitted radius of curvature) change: - 0.02 mm (profilometer)

before arc-jet



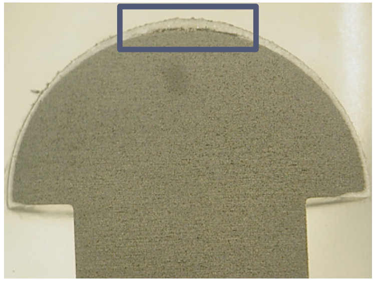
after 2^{nd} arc-jet test

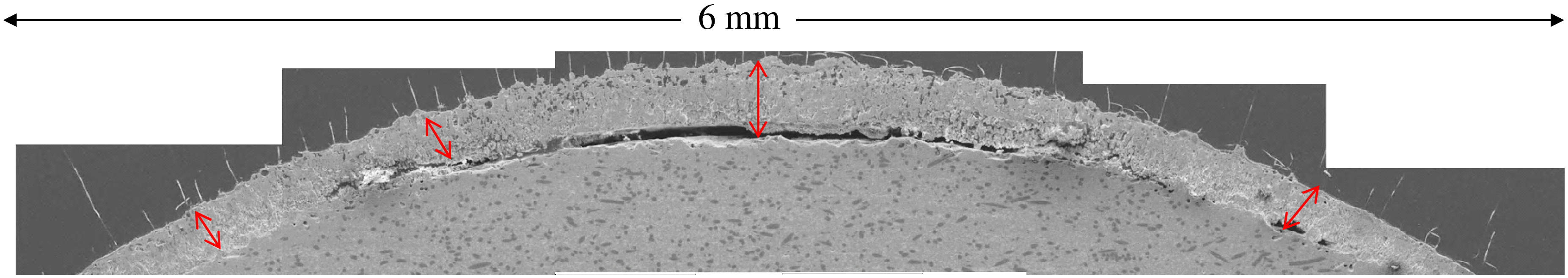


Profile of the round hemispheric surface

2^{nd} arc-jet test_results

- Max H_0: 17 MJ/kg, duration: 270 s
- **Equilibrium temperature range (by two-color pyrometer): 1800-1820 °C**



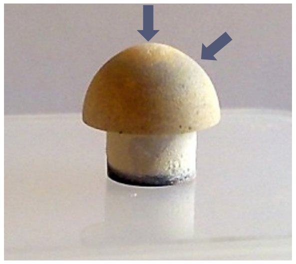


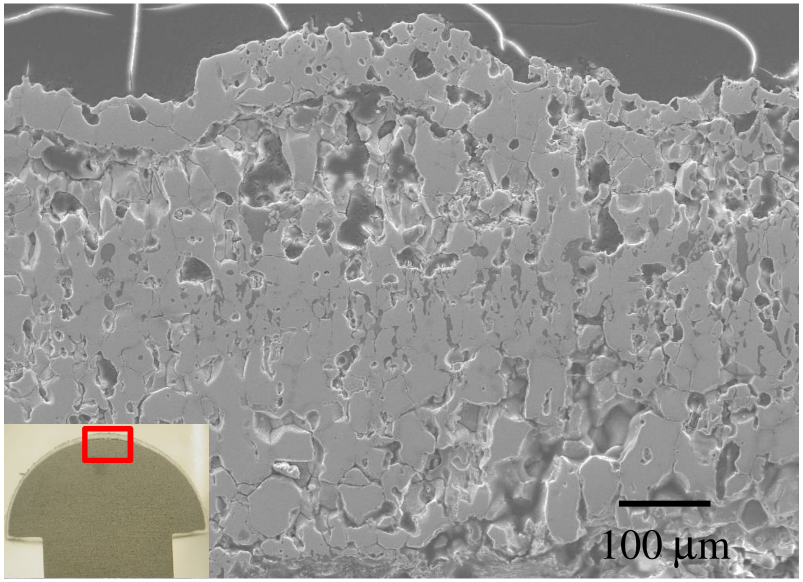
Polished cross section, by SEM, near the stagnation point

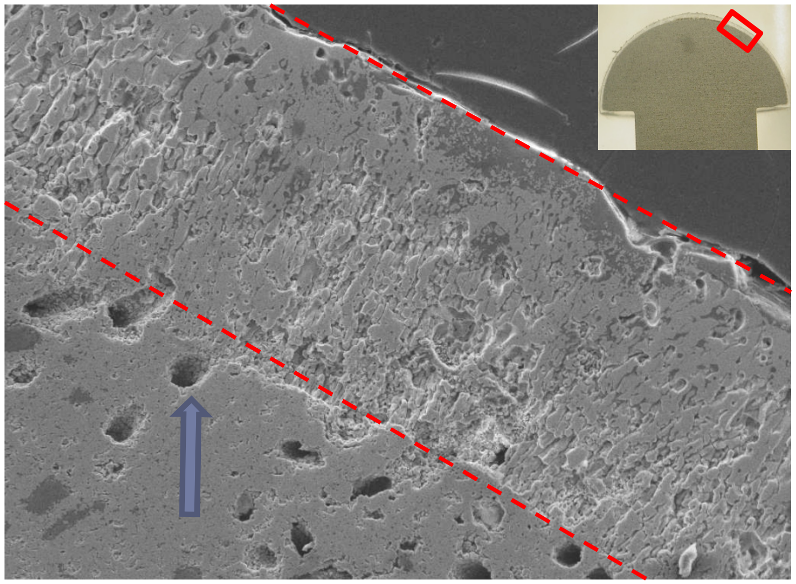
oxide scale thickness 280-170 μm ; no external glassy coating was observed

2nd arc-jet test_results

- Max H_0: 17 MJ/kg, duration: 270 s
- **Equilibrium temperature range (by two-color pyrometer): 1800-1820 °C**





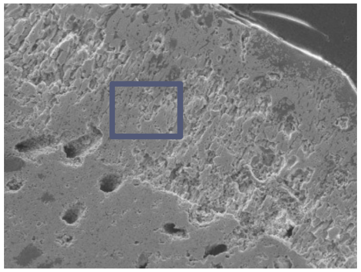


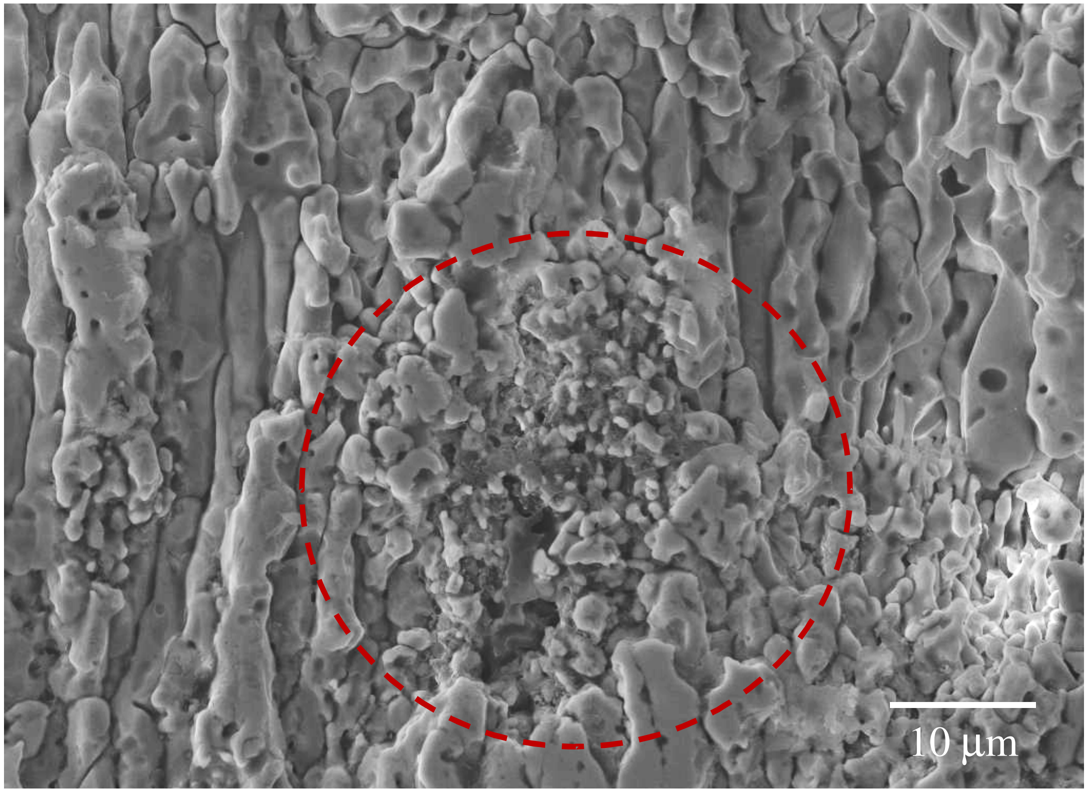
Zoomed views near (left) and far (right) from the stagnation point

(polished cross section, by SE-SEM)

2^{nd} arc-jet test_results

- Max H_0: 17 MJ/kg, duration: 270 s
- **Equilibrium temperature range (by two-color pyrometer): 1800-1820 °C**



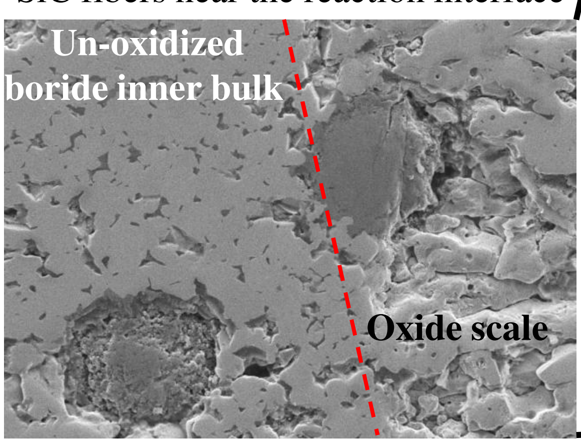


Residue of the SiC fiber inside the zirconia scale
(polished cross section, by SE-SEM)

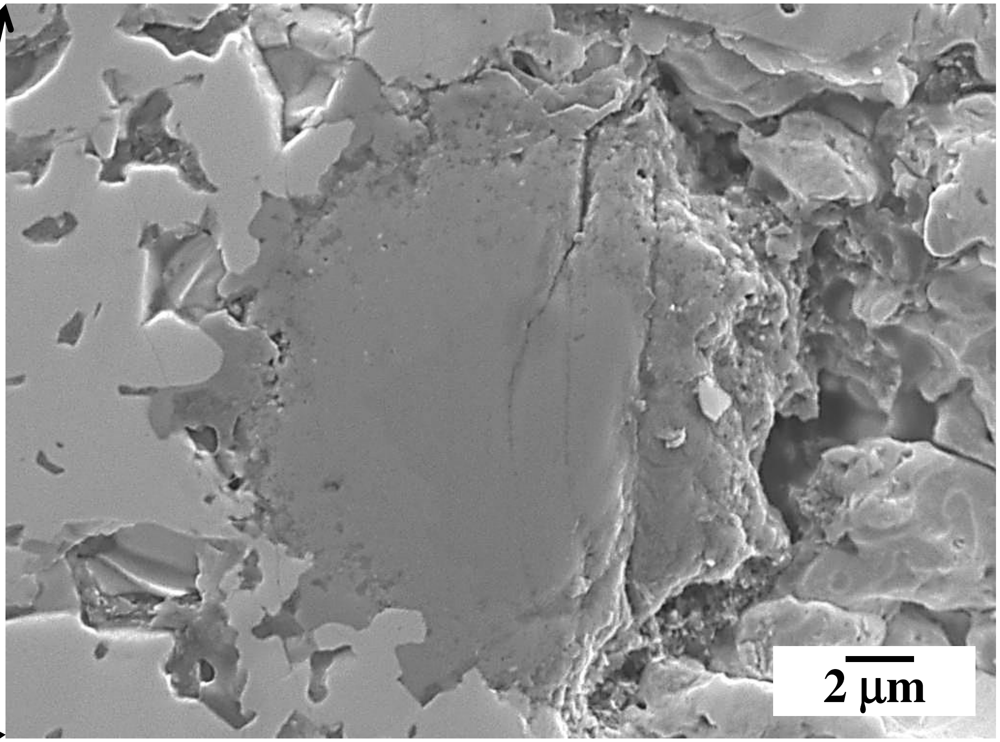
2^{nd} arc-jet test_results

- Max H_0: 17 MJ/kg, duration: 270 s
- **Equilibrium temperature range (by two-color pyrometer): 1800-1820 °C**

SiC fibers near the reaction interface



Polished cross section, by SE-SEM



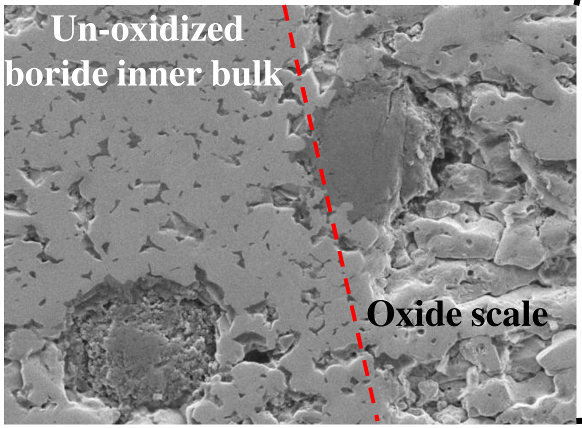
EXTERIOR

SiC fiber across the reaction interface (polished cross section, by SE-SEM)

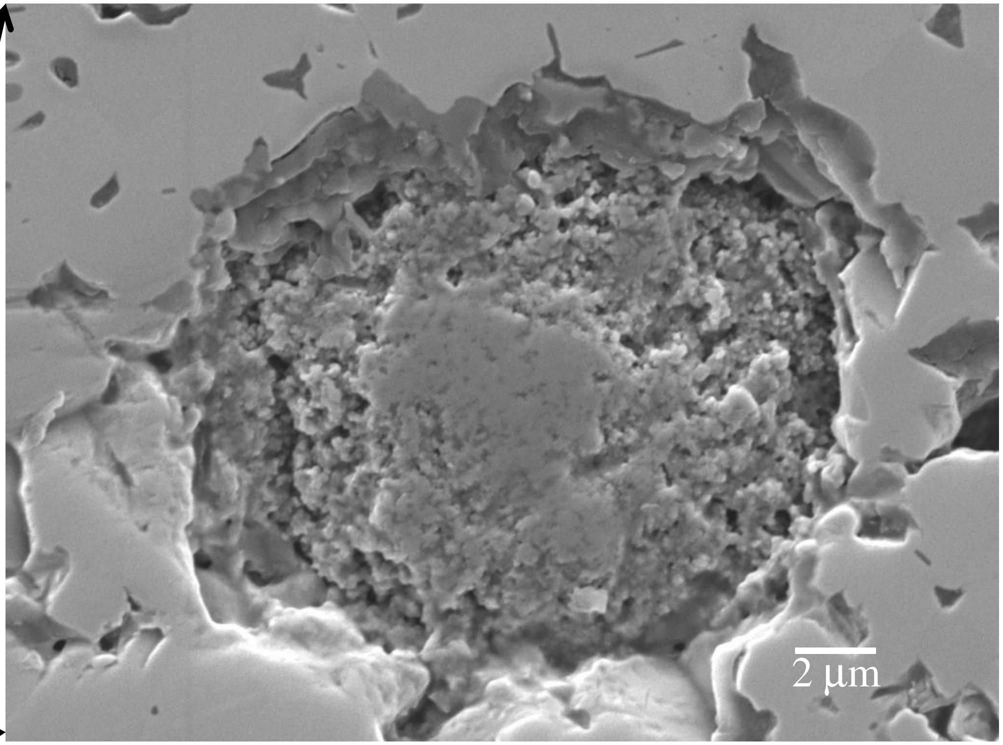
2^{nd} arc-jet test_results

- Max H_0: 17 MJ/kg, duration: 270 s
- **Equilibrium temperature range (by two-color pyrometer): 1800-1820 °C**

SiC fibers near the reaction interface

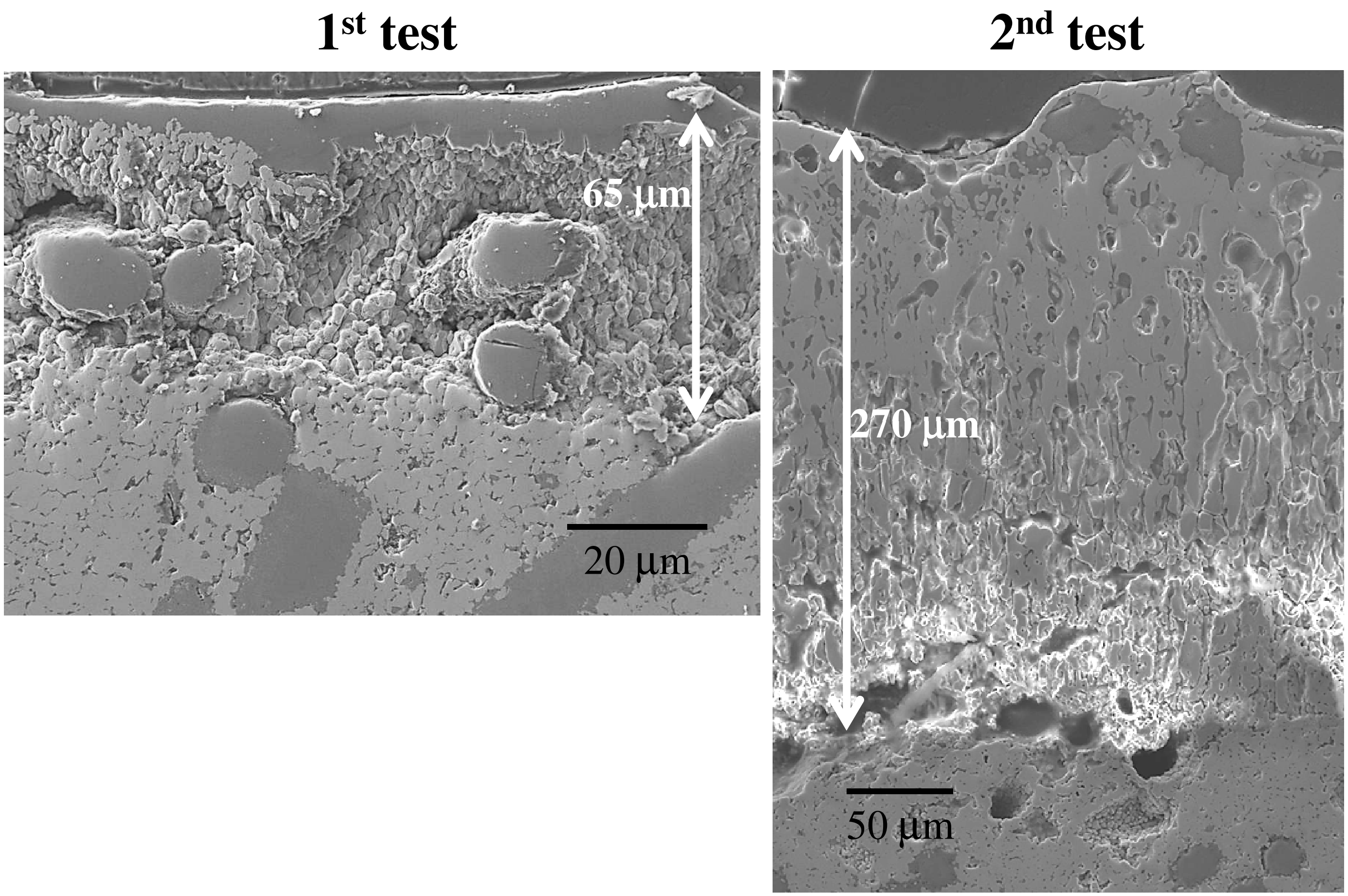


Polished cross section, by SE-SEM



SiC fiber just below the reaction interface
(polished cross section, by SE-SEM)

Arc-jet test_comparison



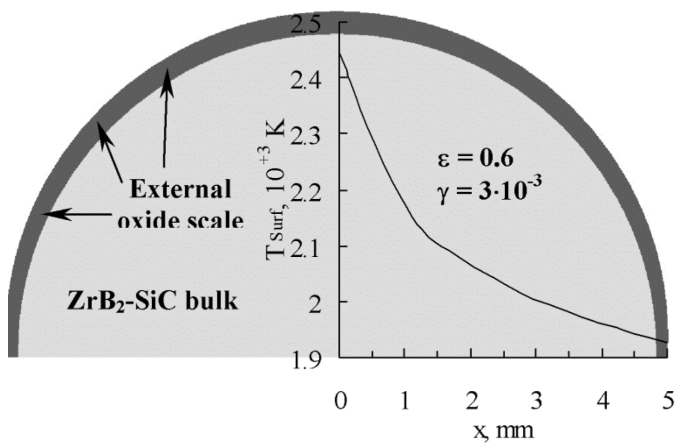
Comparison of the external oxide scale (by SE-SEM) near the stagnation point

Summary

- ZrB_2-15% SiC_F were fully densified by hot pressing and characterized
- In simulated aero-thermal heating the material withstood rather well the severe environment
- The chopped SiC_F behaved differently depending on the temperature regimes: in all cases provided a significant benefit to the overall resistance to oxidation

Work in progress

- Use more stable SiC fibers
- Optimize the max SiC fiber length
- CFD modeling to calculate equilibrium temperature map upon the surface (and inside the bulk)



F. Monteverde, R. Savino, Dynamic oxidation of ultra-high temperature ZrB_2–SiC under high enthalpy supersonic flows, *Corrosion Science* **53** (2011) 922