Spring 4-15-2015

UHTC Composites: Processing, Performance and Future

Jon Binner
University of Birmingham

Ultra-High Temperature Ceramics:
Processing, Properties and Applications

Jon Binner

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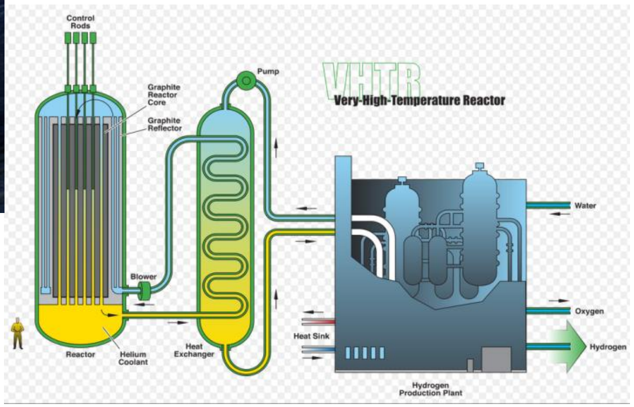
Applications

- Potential future advanced aerospace vehicles
  - Hypersonic aviation
  - Re-usable atmospheric re-entry vehicles
  - Air-breathing hypersonic missile systems
- Nuclear
  - Advanced reactor designs
- Other niche applications
  - High temperature electrodes
  - Molten metal handling

Require new materials with >2000°C capability

X-43B Hypersonic Concept
Image Courtesy of NASA

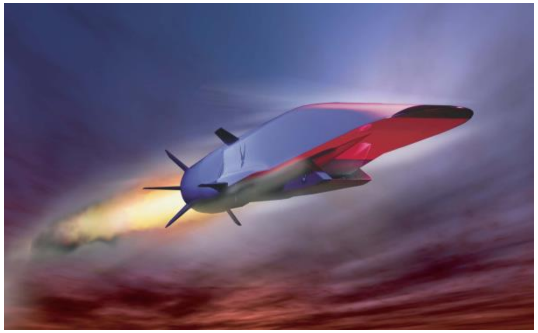
Hypersonic scramjet concept missile



Very high temperature nuclear reactor (VHTR)

Key Issues for Implementation

- **Performance:** Can improvements be made to resistance to oxidation, ablation, thermal shock, thermal cycling and creep?
- **Properties:** Is component behaviour representative of the inherent material properties?
- **Fabrication:** Can parts be made to near net shape at reasonable cost?



X-51 Concept
Image Courtesy of NASA

X-51 Test Vehicle
Image Courtesy of NASA

Can we move from concept to an operational hypersonic flight vehicle?

Materials Systems for Extreme Environments

XMat

Jon Binner, University of Birmingham

Bill Lee, Imperial College London

Mike Finnis, Imperial College London

Mike Reece, Queen Mary London

EPSRC Engineering and Physical Sciences Research Council

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Imperial College London

Queen Mary University of London

Background

The overall objective is to establish in the UK the capability to discover and understand new materials (not just UHTCs) that can operate under increasingly extreme conditions, thus enabling a wide range of new technologies.

The vision is to develop the required understanding of how the processing, microstructures and properties of materials systems operating in extreme environments interact to the point where materials with the required performance can be designed and then manufactured.

Funding is provided by EPSRC via the Programme Grant scheme and is valued at £4.2M (A$8.1M) over 5 years. It formally started on the 1st February 2013.

Partners

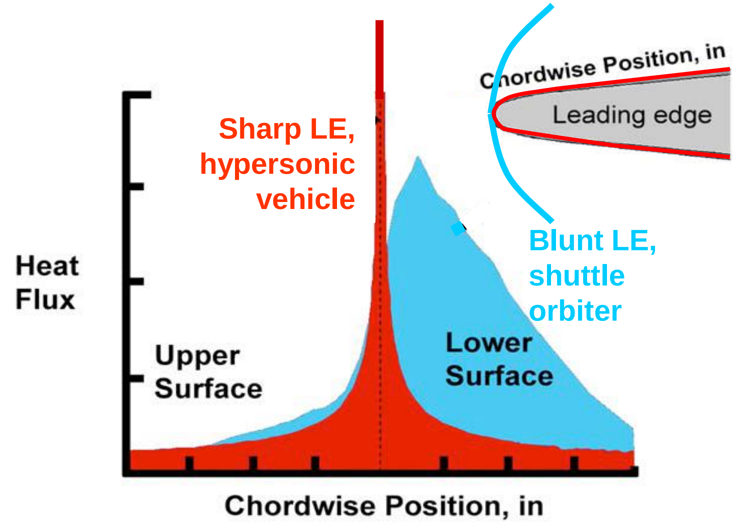
AFRL	Morgan Ceramics
AWE	NASA
CERAM	NNL
Culham	NPL
DSTL	Powders
ESA	Reaction Engines
FCT	Sintec
ISTEC	Teledyne
Kerneos	Tokamak
Limoges	TWI
Missouri S&T	Vesuvius

Additional programmes to date valued at nearly £500k (A$960k).

Materials for Sharp Leading Edges

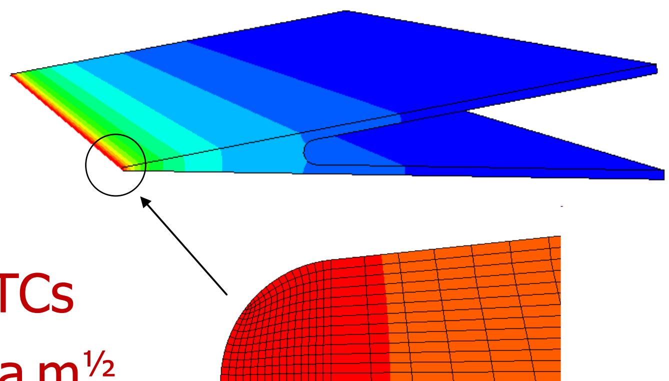
Materials need to withstand:

- Very high heat fluxes over small areas
- Very high temperatures, oxidation & erosion
- Very high temperature gradients



ZrB_2/HfB_2-based ceramics offer:

- Ultra-high temperature capability
- High thermal conductivity
- Some oxidation resistance – best of the UHTCs
- Low fracture toughness – typically 3 – 4 MPa m$^{1/2}$



Steep temperature gradient with high temperature at tip

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Carbon-Carbon Based Composites for UHTC Applications

Advantages of CC composites

- Excellent high temperature strength
- Light weight
- Low coefficient of thermal expansion
- Good ablation resistance

Disadvantages

- Poor oxidation resistance above 500°C

The original goal of the project was to produce UHTC powder impregnated C_f-based composites that would withstand as high a temperature as possible for as long as possible.

Composite Manufacture

Surface Transforms

2.5 D Cf preform → Vacuum impregnation

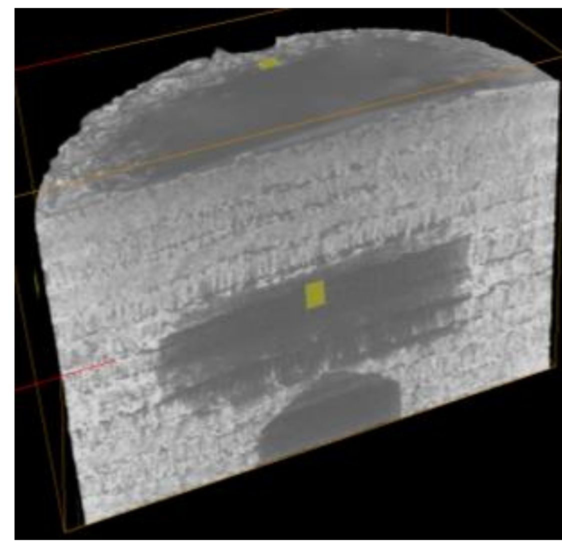
UHTC - phenolic slurry → Vacuum impregnation → Drying → Curing → Pyrolysis → C-CVI

- ZrB_2
- HfC
- HfB_2
- ZrB_2+20vol%SiC
- ZrB_2+20vol%SiC+ 10vol%LaB_6

Preform 2.5D

Impregnation & curing

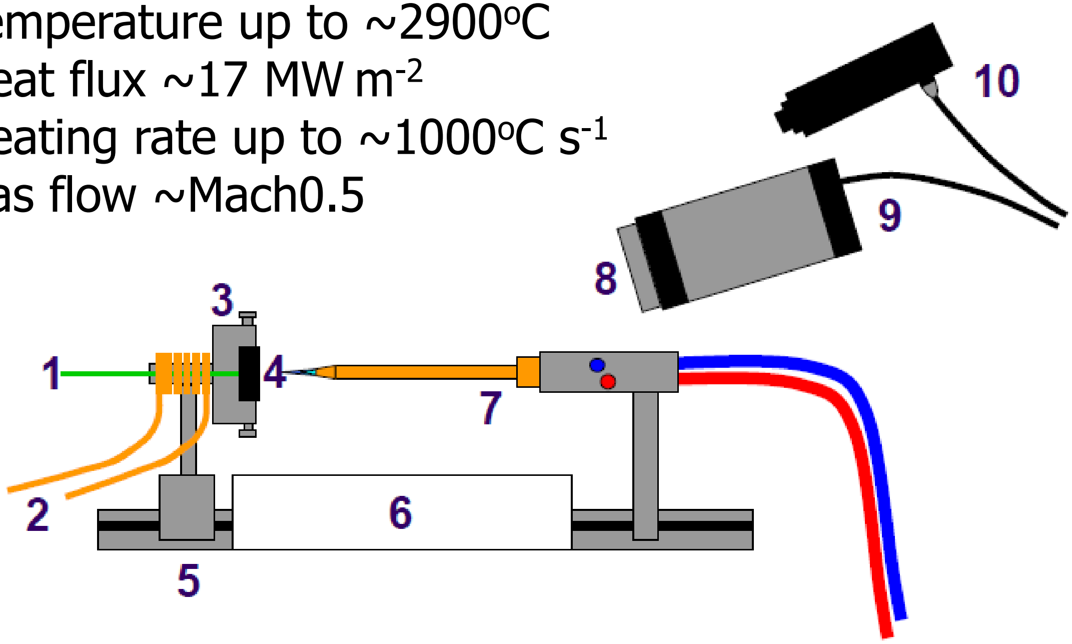
Pyrolysis



Impregnated carbon preform

Oxyacetylene Torch Testing (OAT)

Sample typically 10 mm from flame tip
Temperature up to ~2900°C
Heat flux ~17 MW m^{-2}
Heating rate up to ~1000°C s^{-1}
Gas flow ~Mach0.5



1. Back face thermocouple
2. Water cooling
3. Graphite sample holder
4. Sample
5. Guide rail
6. Protective insulation
7. Oxyacetylene torch
8. Neutral density filter
9. Thermal imaging camera
10. Two colour pyrometer

Ability to measure front face temperature, temperature distribution and back face temperature.

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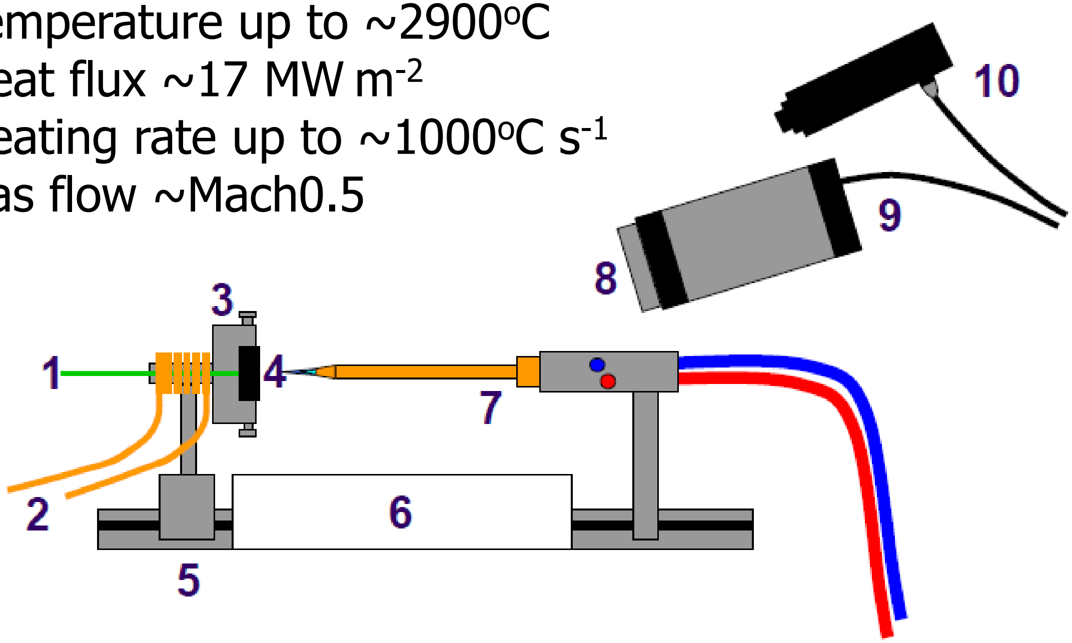

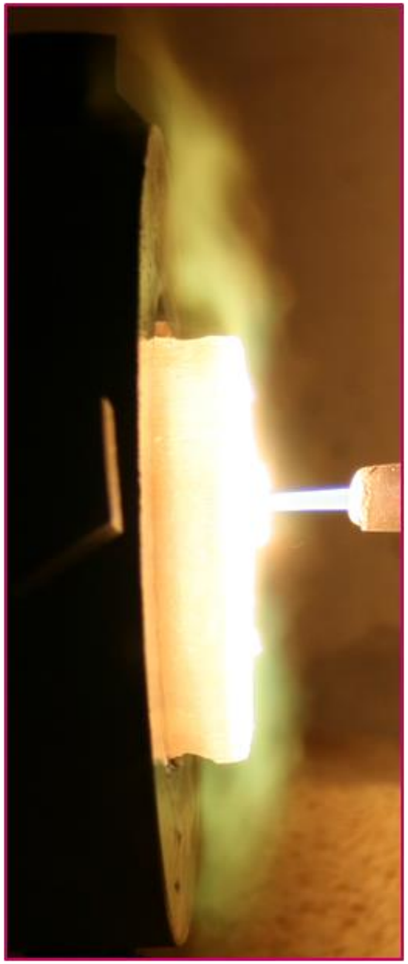

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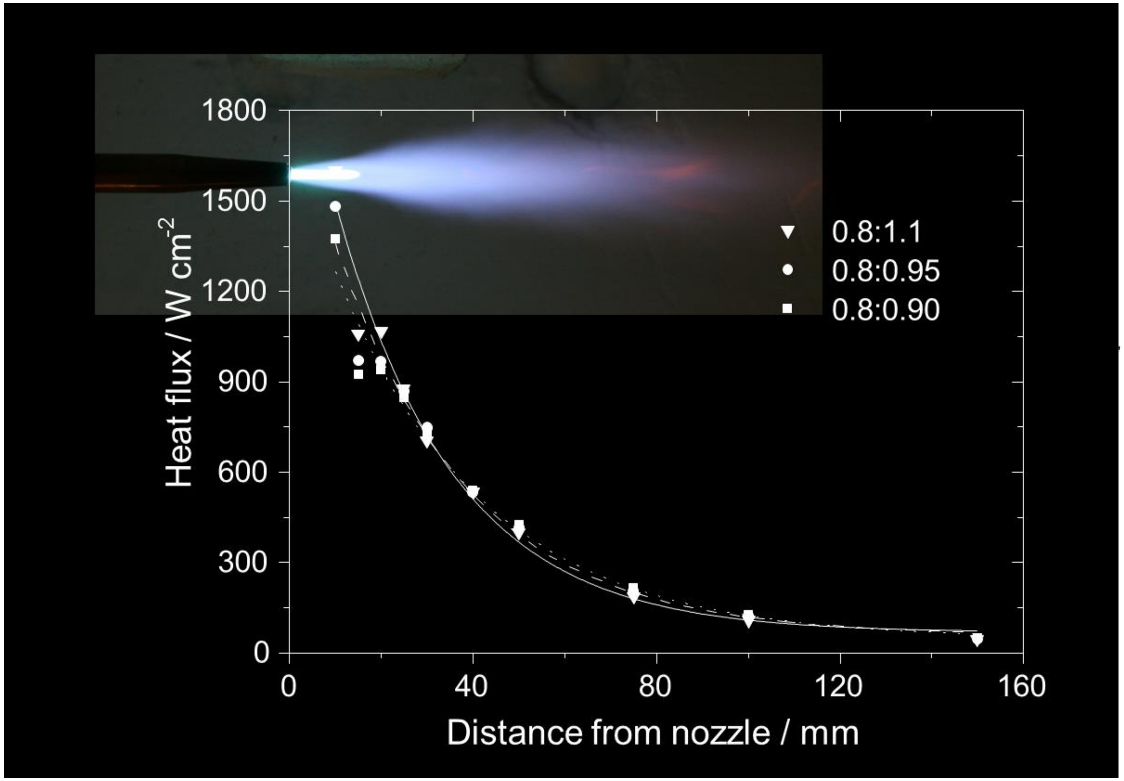
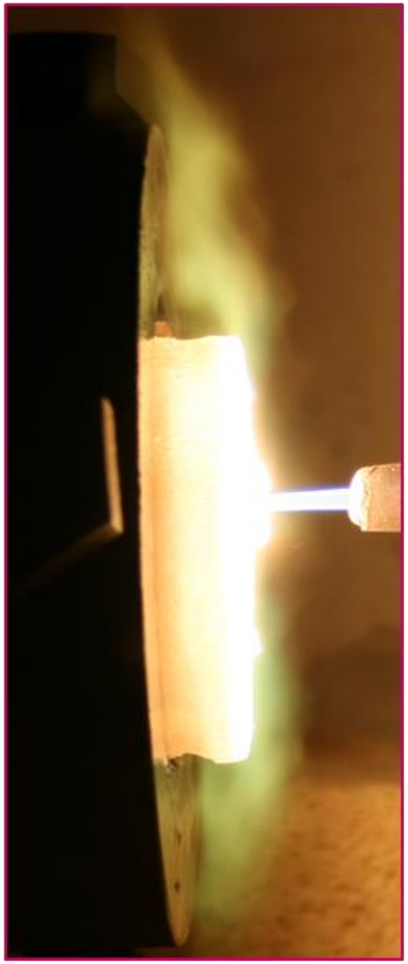
Oxyacetylene Torch Testing (OAT)





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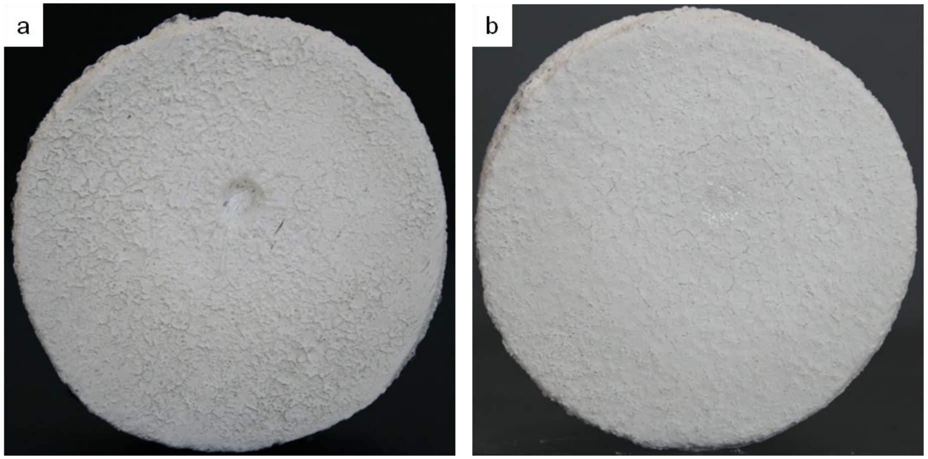
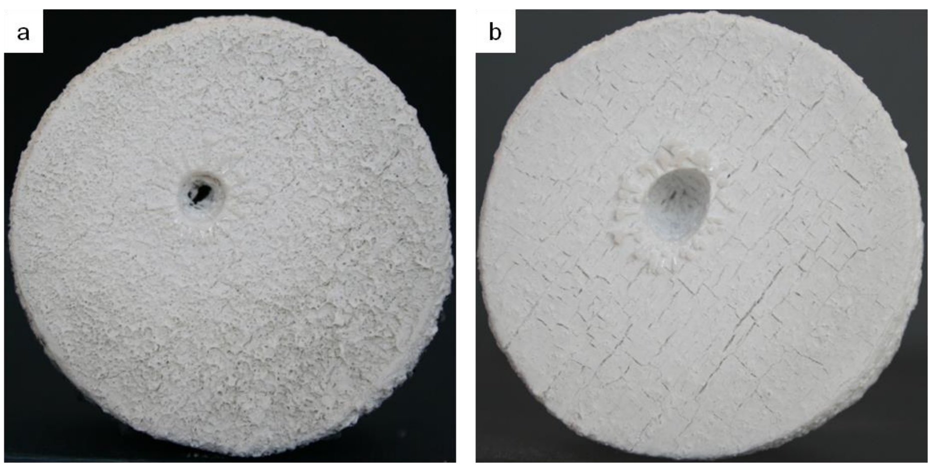
Effect of HfB_2 Particle Size



UHTC composites after 60 s OA testing @ 2700^{o}C a) Cf-fine HfB_2 and b) Cf-coarse HfB_2.

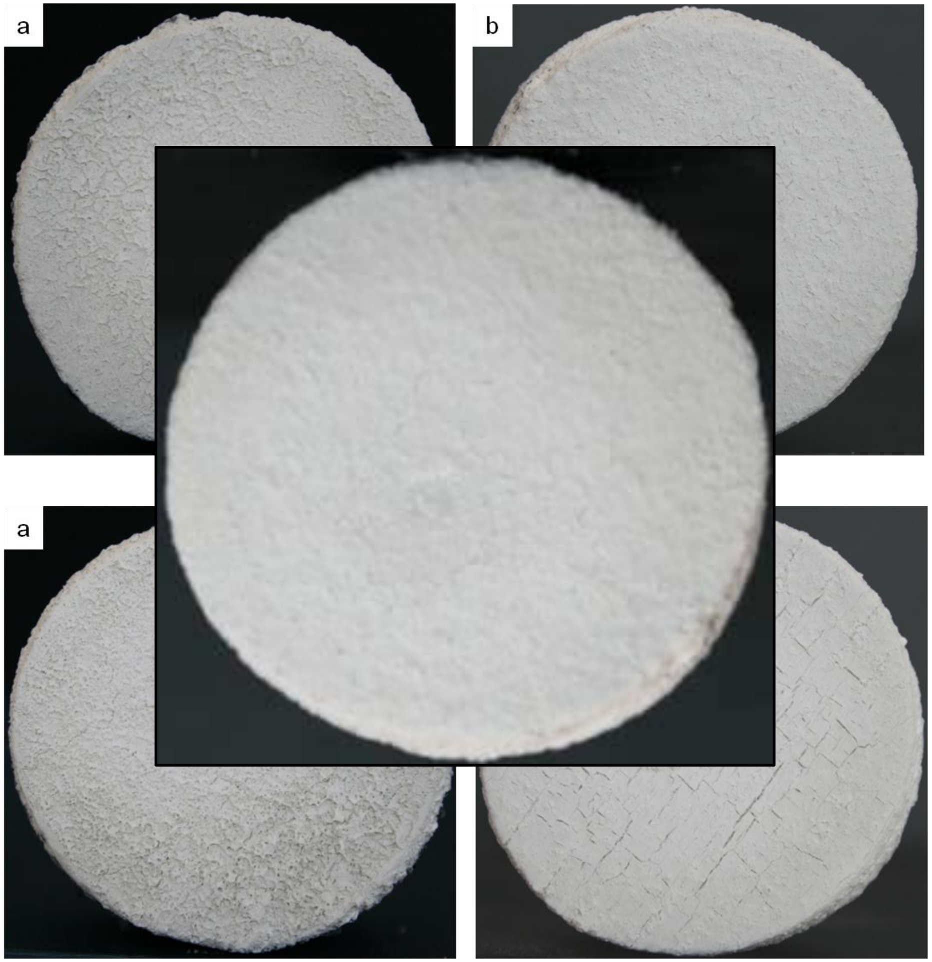
Coarse is better.



UHTC composites after 140 s OA testing @ 2700^{o}C a) Cf-fine HfB_2 and b) Cf-coarse HfB_2.

Fine is better.

Effect of HfB_2 Particle Size



UHTC composites after 60 s OA testing @ 2700ºC a) Cf-fine HfB_2 and b) Cf-coarse HfB_2.

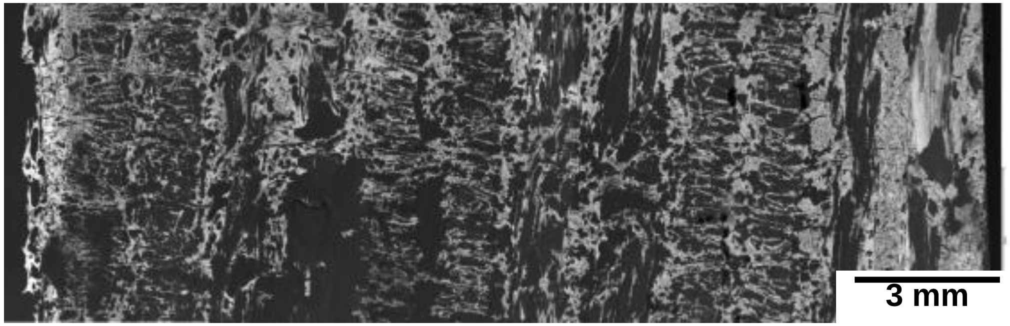
Coarse is better.

The combination is best

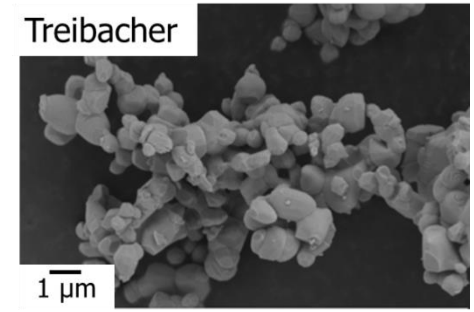
UHTC composites after 140 s OA testing @ 2700ºC a) Cf-fine HfB_2 and b) Cf-coarse HfB_2.

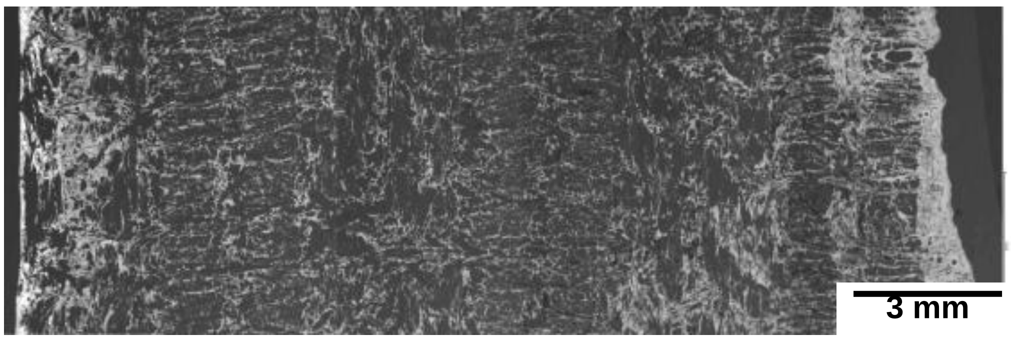
Fine is better.

Effect of HfB_2 Particle Size

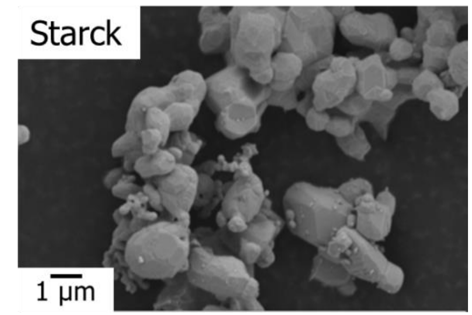


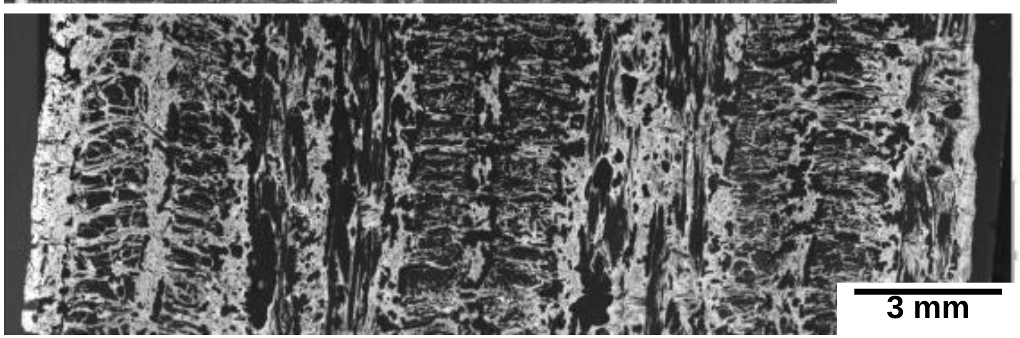
HfB_2 Fine





HfB_2 Coarse





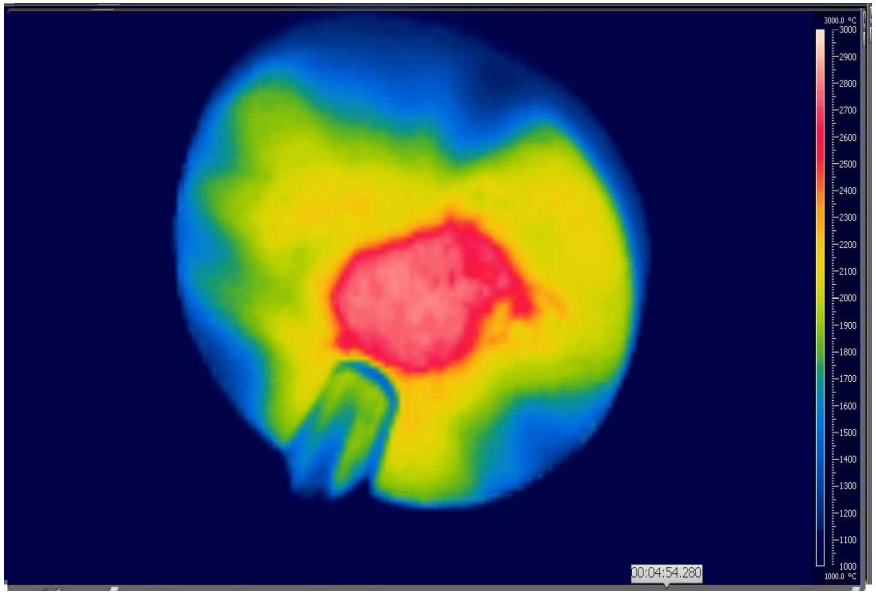
HfB_2 30% fine & 70% coarse

Oxyacetylene Torch (OAT) Test

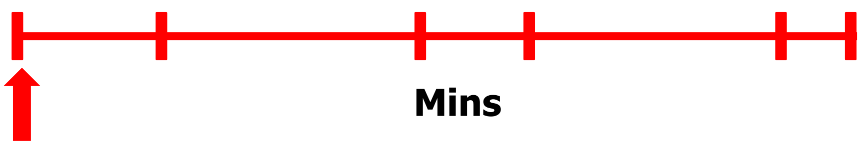
Duration: 300 s

C_2H_2/O_2 0.8 : 1.1 $m^3 h^{-1}$

Heat flux >17 MW m^{-2}



At the end of OAT



Thermal imaging videos of C_f-HfB_2 samples (edited time frame)

Sample after
300 s OAT @ ~2900°C

Mass loss: 2.1 g

Erosion depth:
~5 mm

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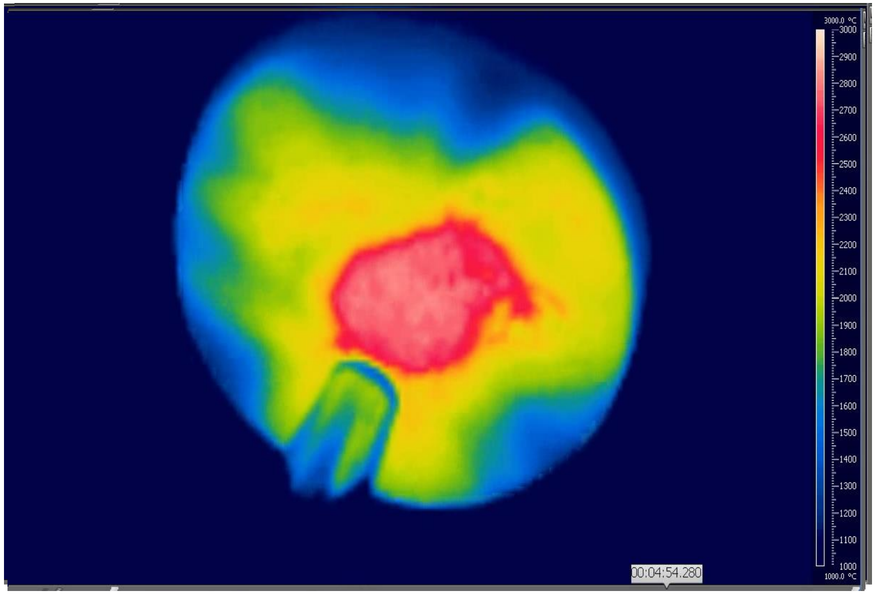
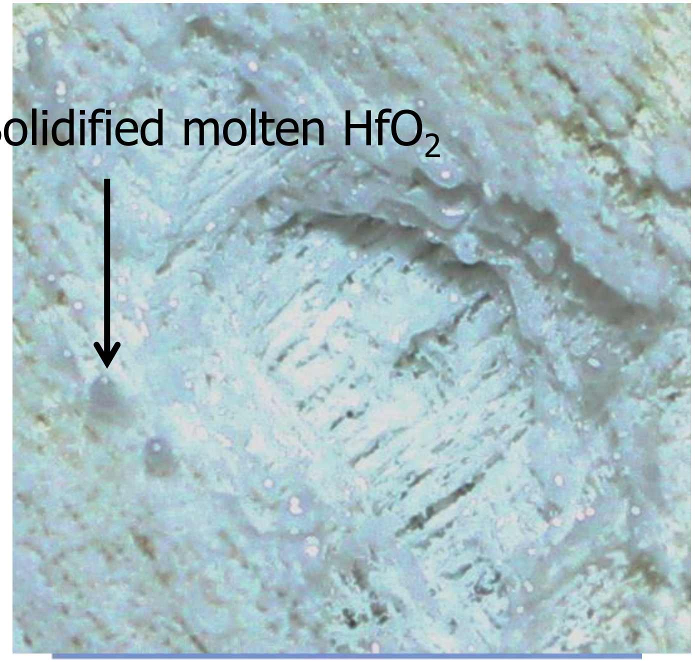


At the end of OAT

0 **0.08** **2.40** **2.48** **4.54** **5.10**

Mins

Thermal imaging videos of C_f-HfB_2 samples (edited time frame)



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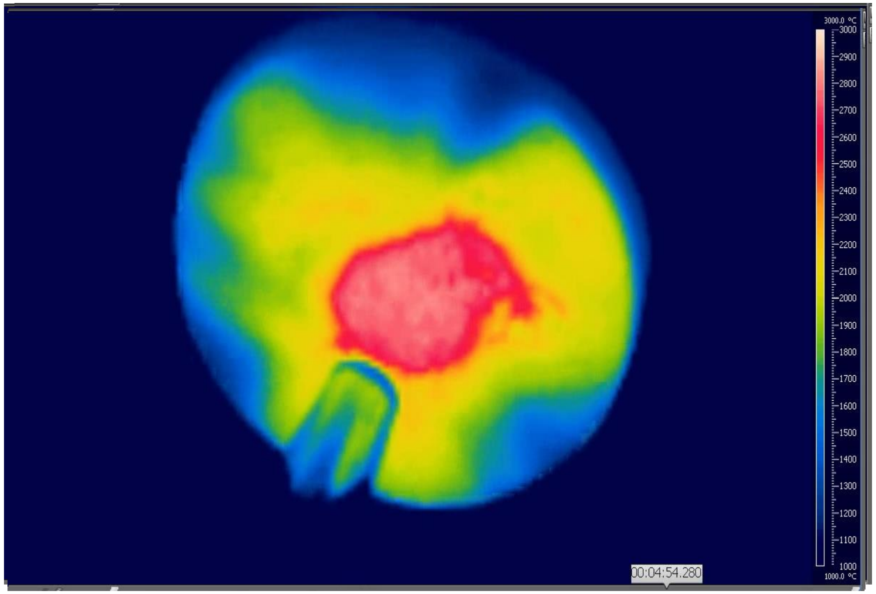

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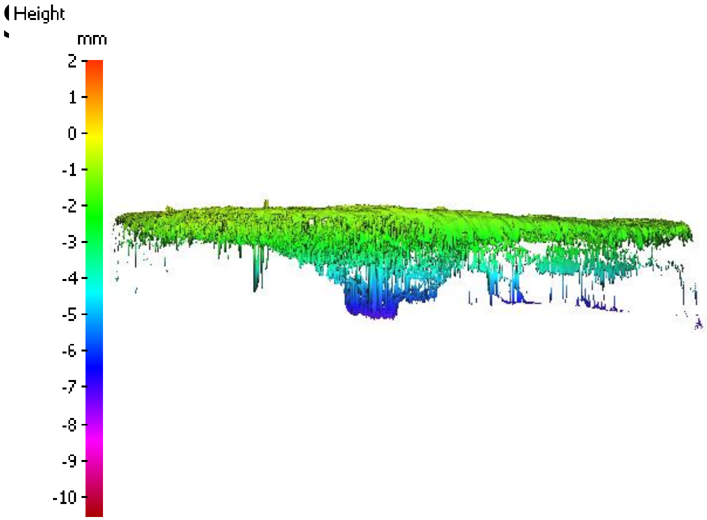

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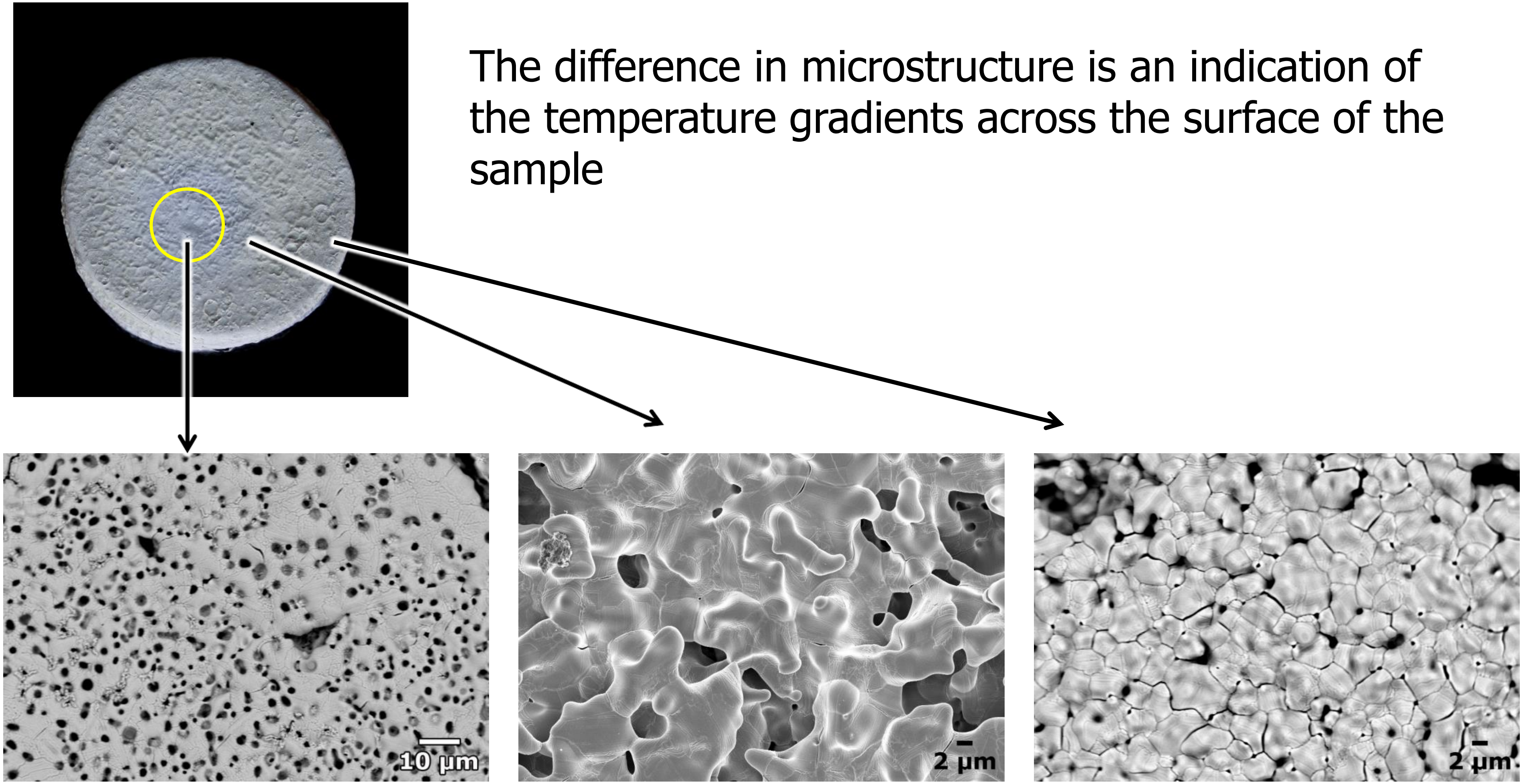
Oxyacetylene Torch Testing (OAT) – 17 MW m^{-2} 60 s

The difference in microstructure is an indication of the temperature gradients across the surface of the sample



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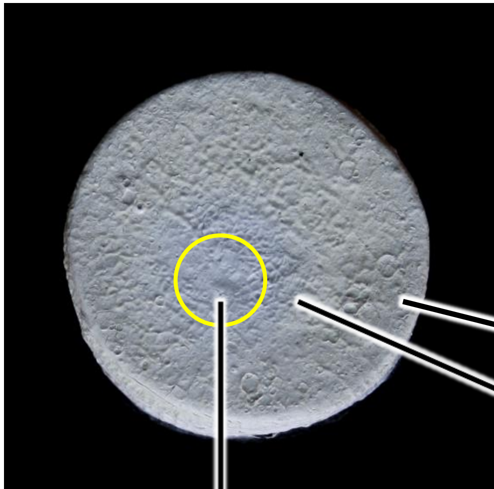
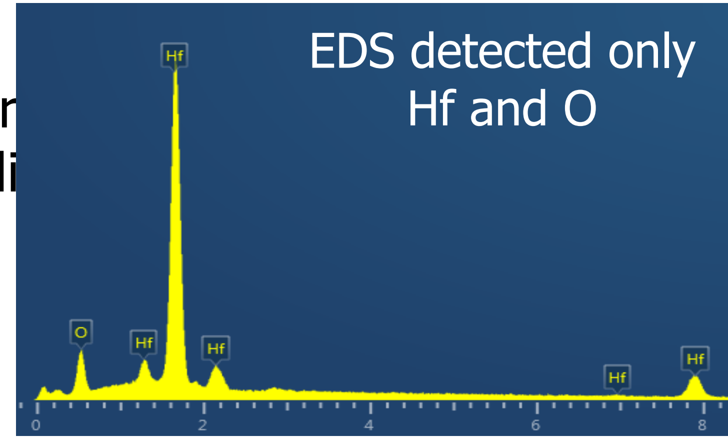
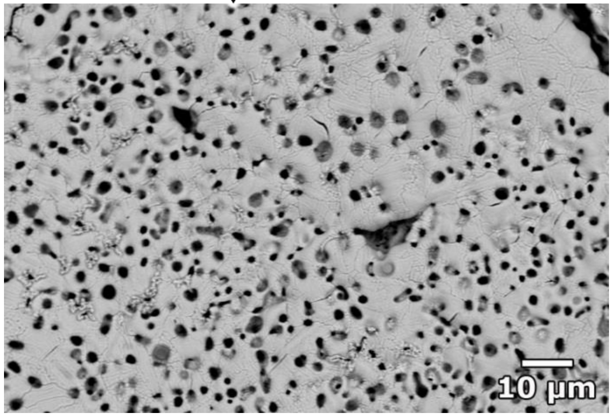
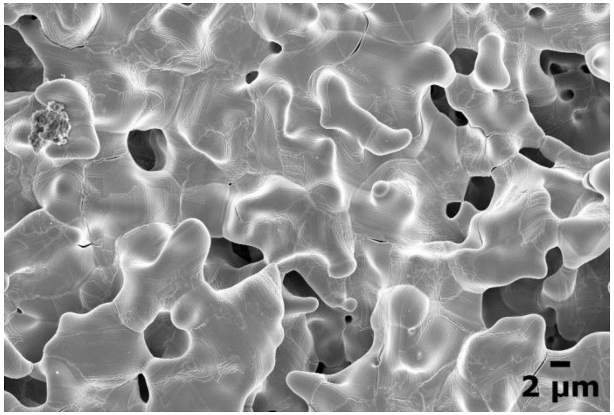
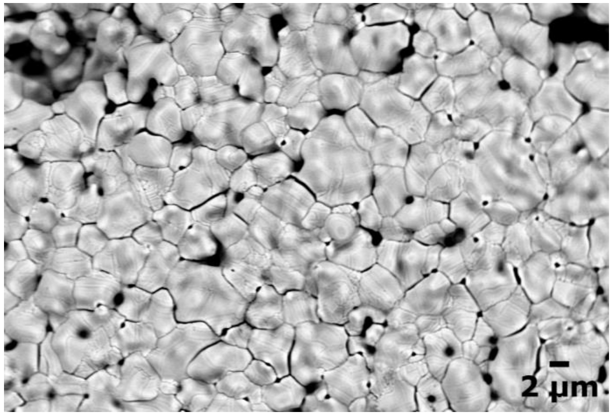


The difference in micr
the temperature gradi
sample

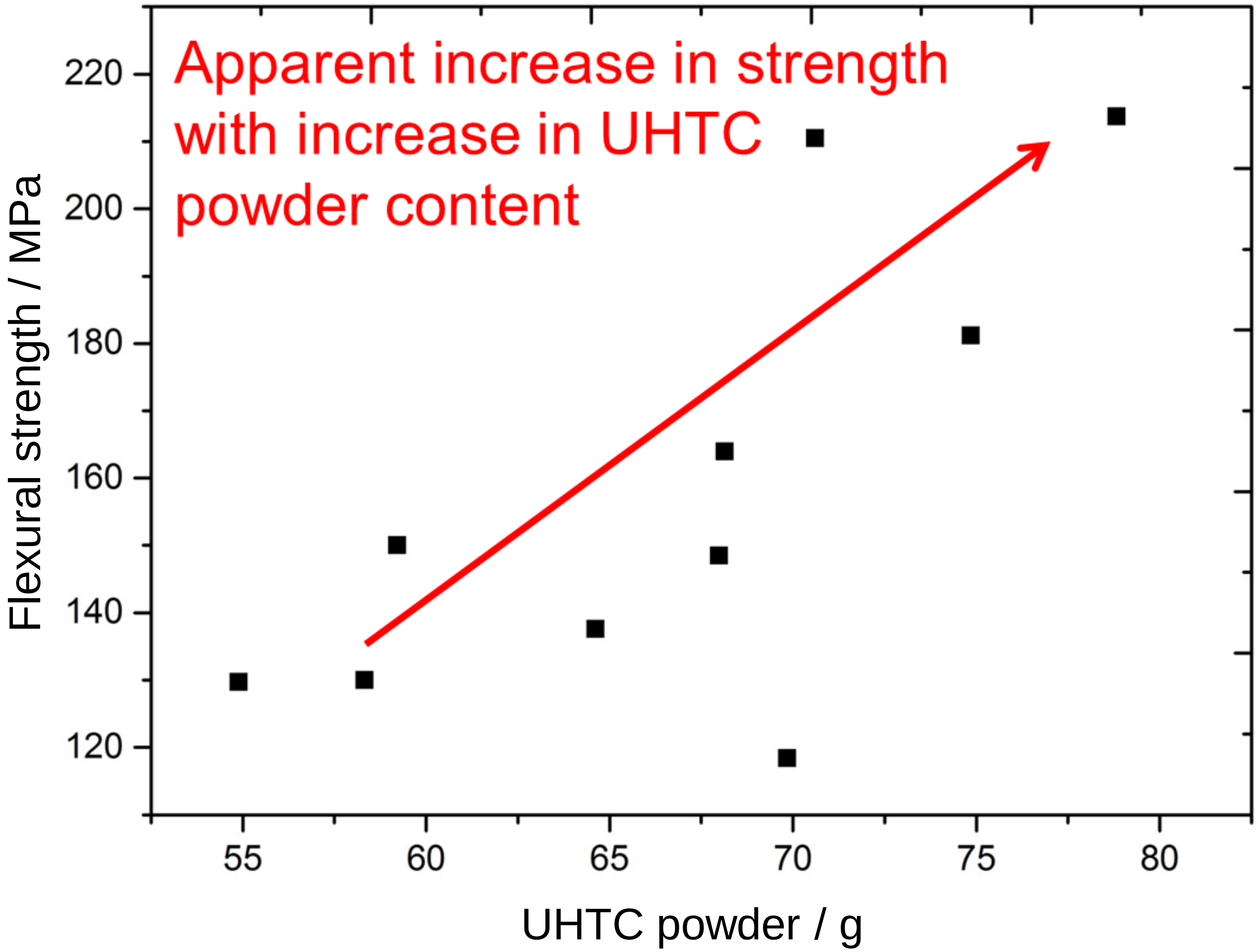




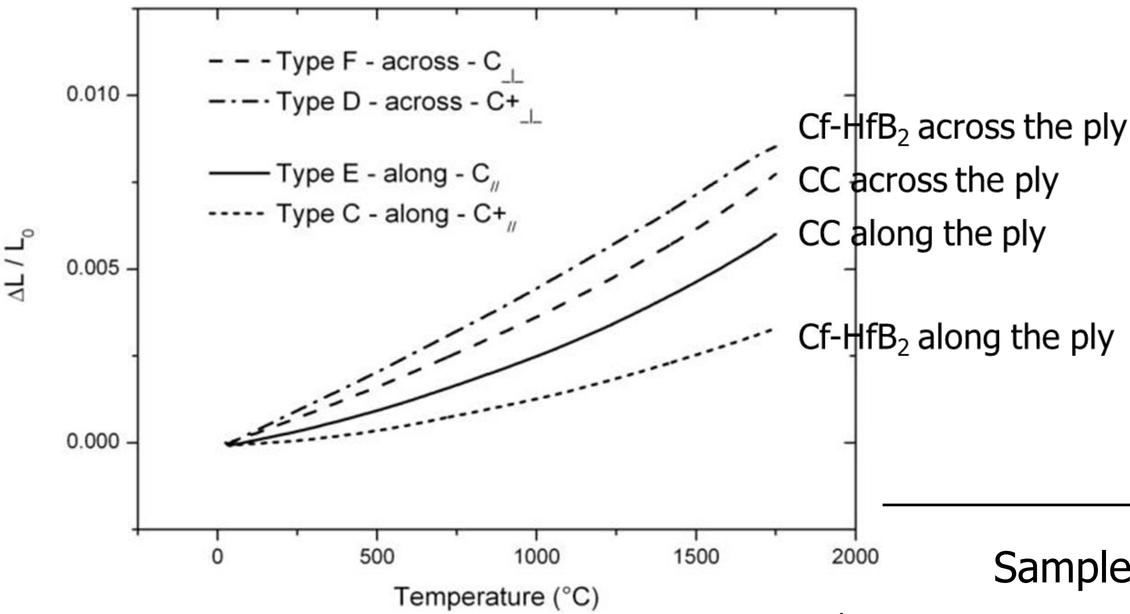




Flexural Strength vs Final Density



Thermal Expansion



Measured at Imperial College

Sample	Temperature range	Average CTE ($x 10^{-6} K^{-1}$)
CC along the ply	25 – 1700°C	2.23 ± 0.01
CC across the ply	25 – 1700°C	3.92 ± 0.01
Cf-HfB_2 along the ply	25 – 1700°C	1.77 ± 0.01
Cf-HfB_2 across the ply	25 – 1700°C	4.70 ± 0.01

The variation along and across the ply will need to be taken into account when designing components.

Imperial College London Vandeperre

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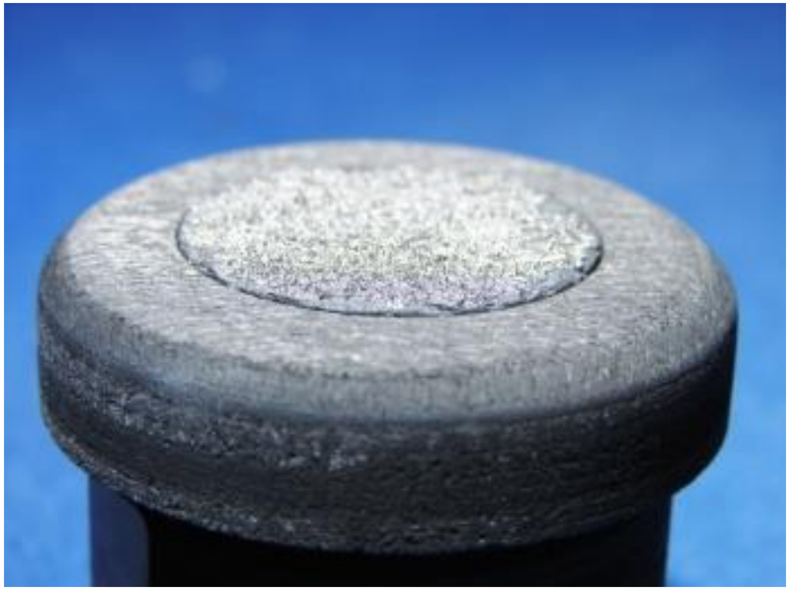
Arc Jet Testing

- 5 MW m^{-2} for 20 s; Peak T ~2200°C
- 10 MW m^{-2} for 10 s; Peak T ~2700°C
- Diameter of the jet ~100 mm
- 30 mm dia x 5 mm thick samples



Before

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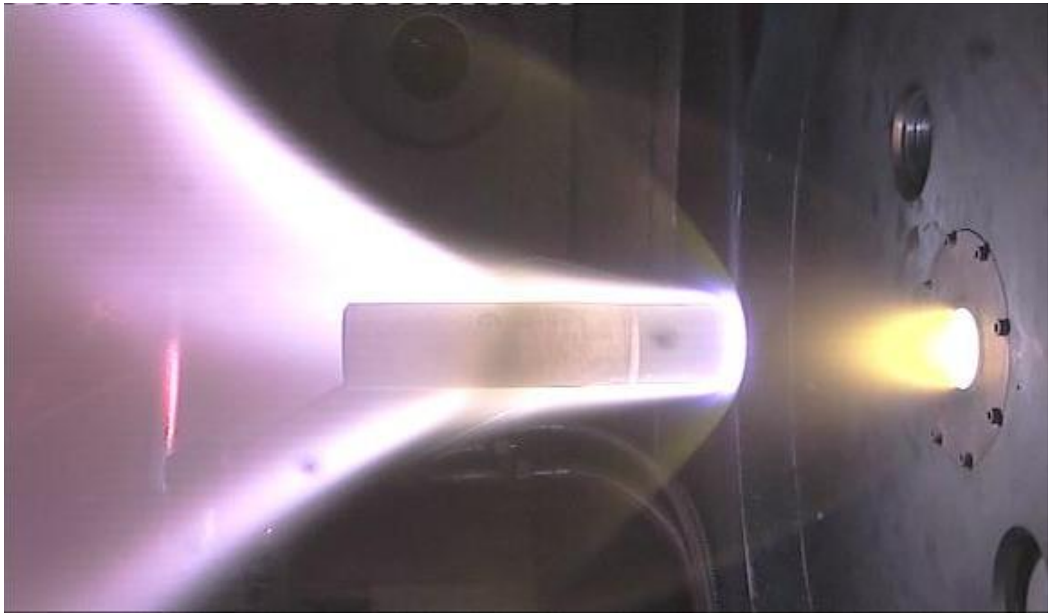

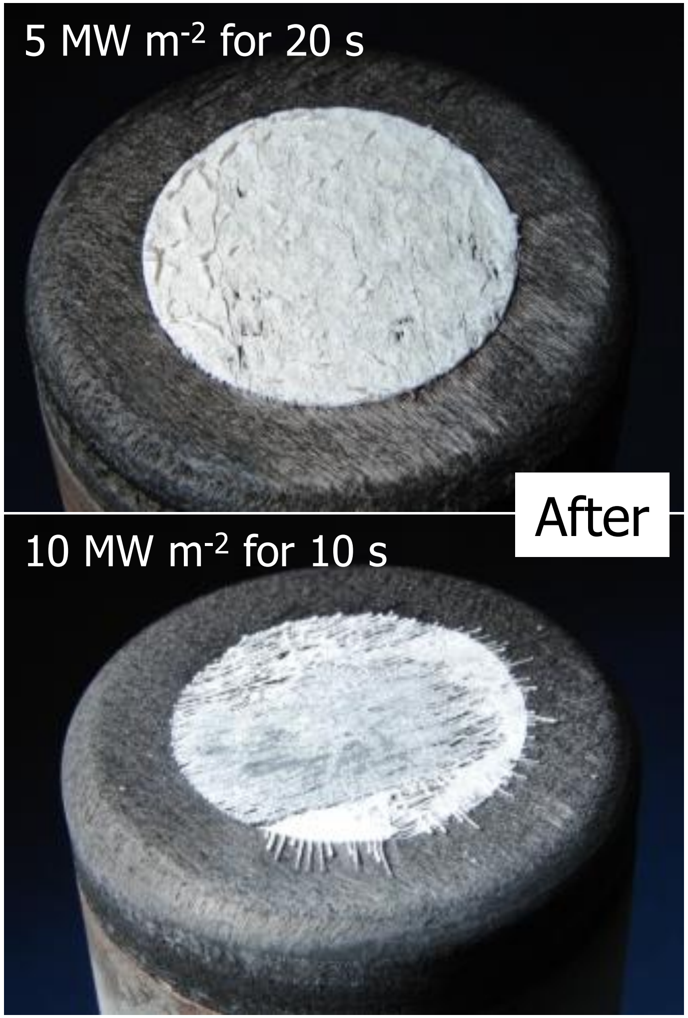

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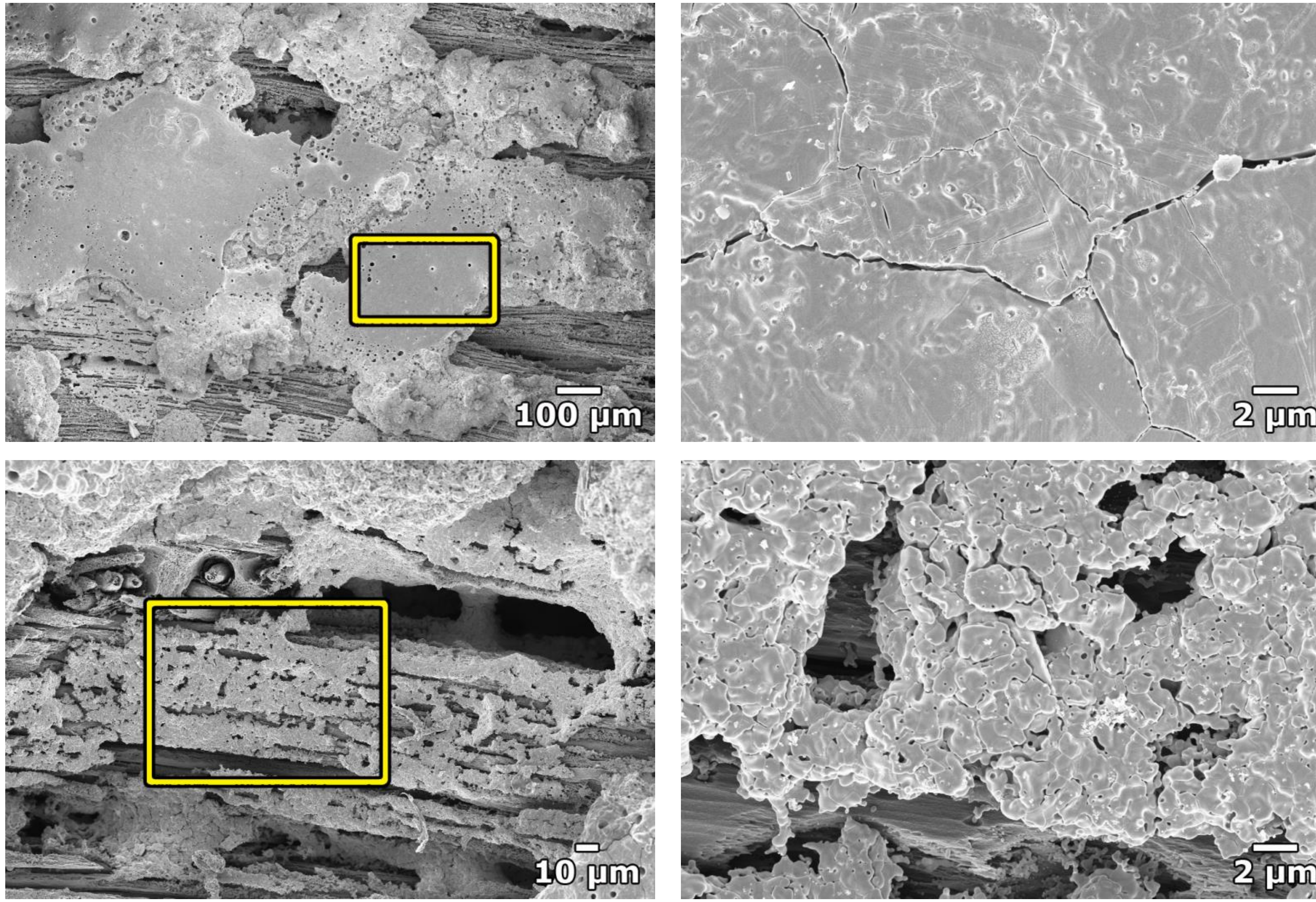
Arc Jet Testing – 10 MW m^{-2} 10 s

Notable melting

The UHTC phase is protecting the fibres.



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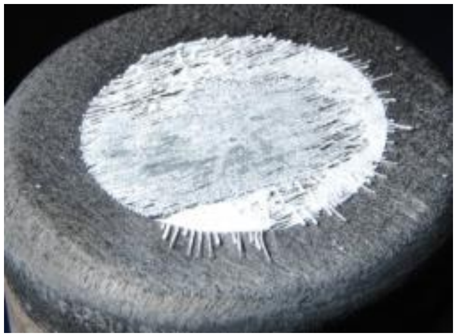

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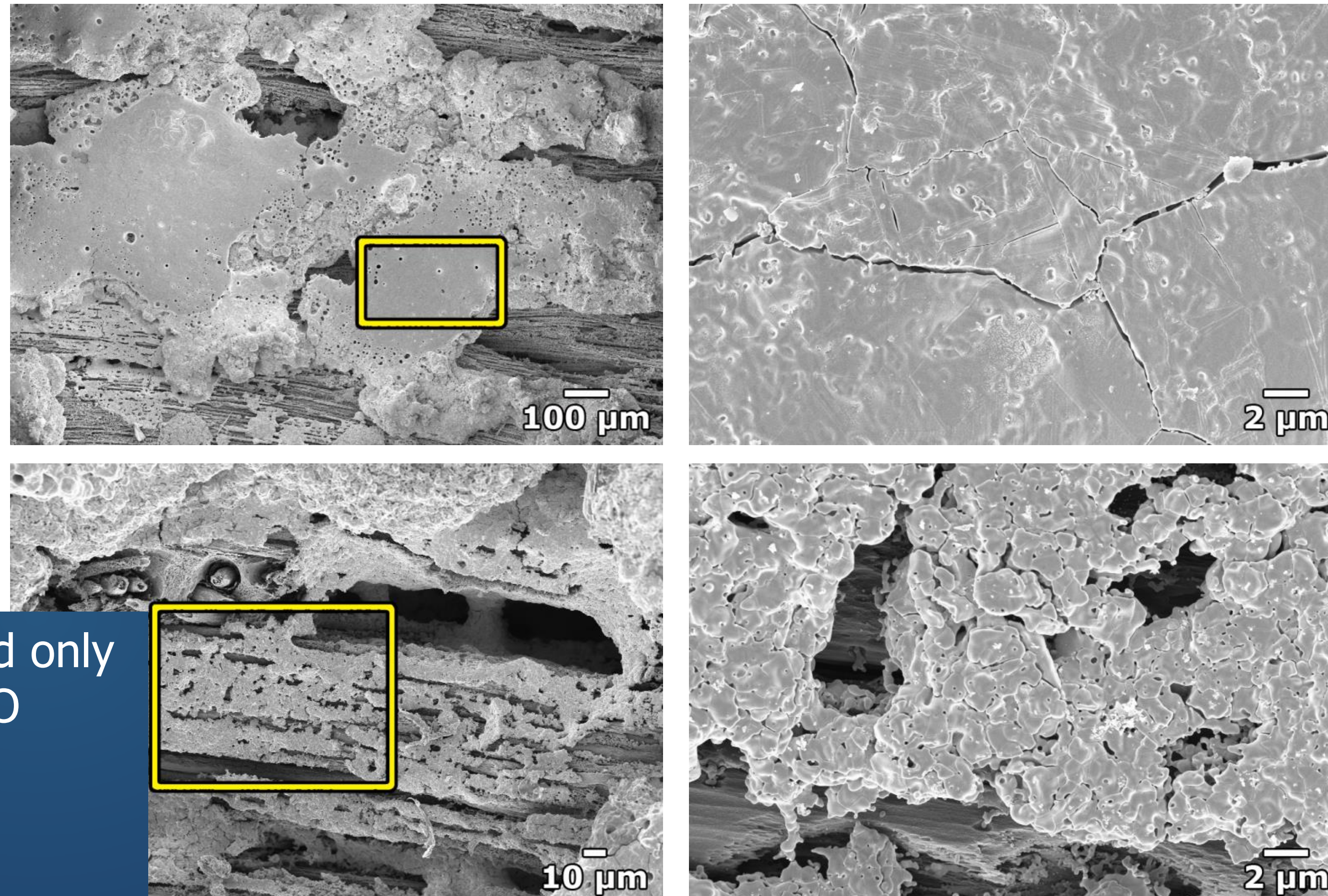
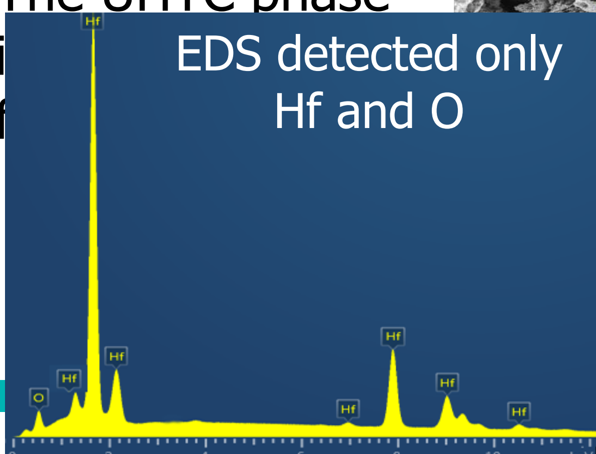
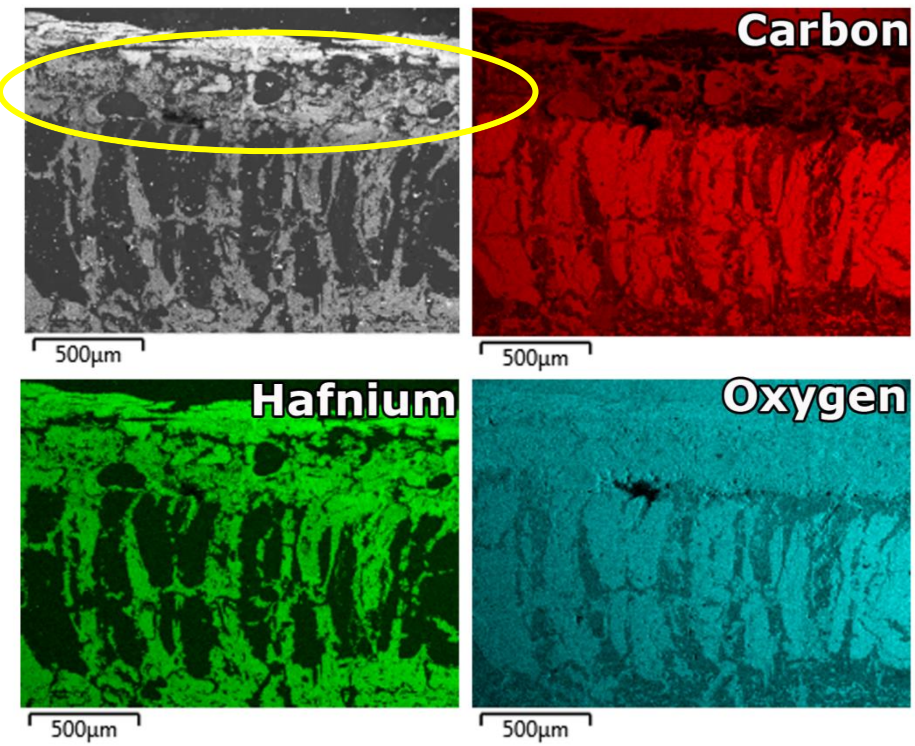


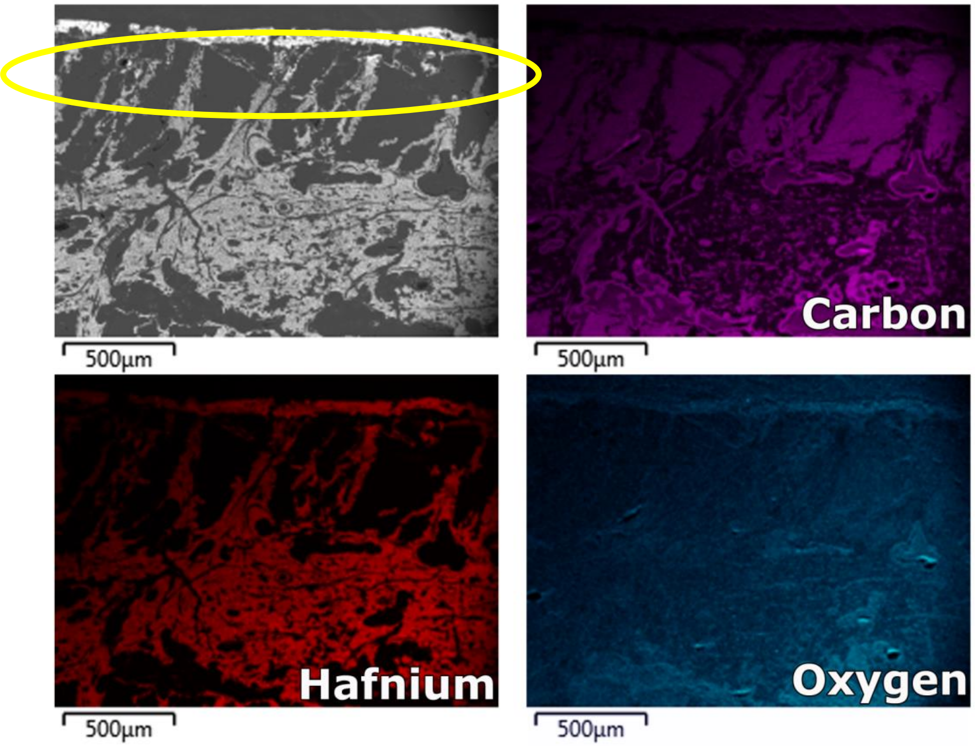
The UHTC phase
i
f



Oxyacetylene and Arc Jet Cross Section – EDS



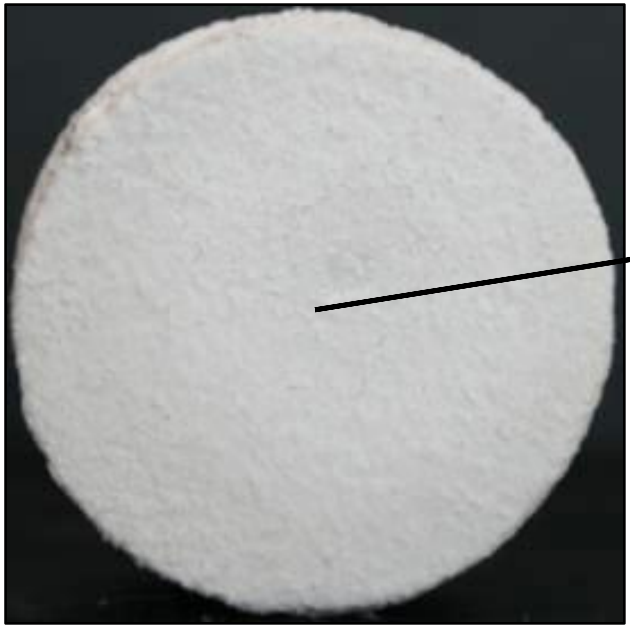
Oxyacetylene 17 MW m^{-2} 60 s

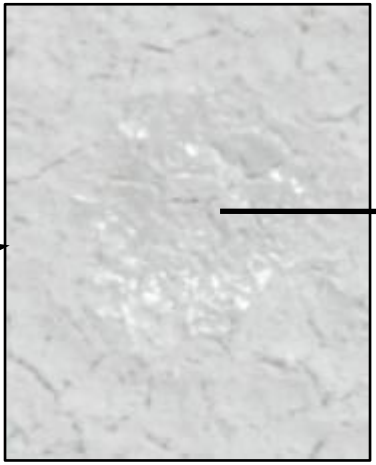


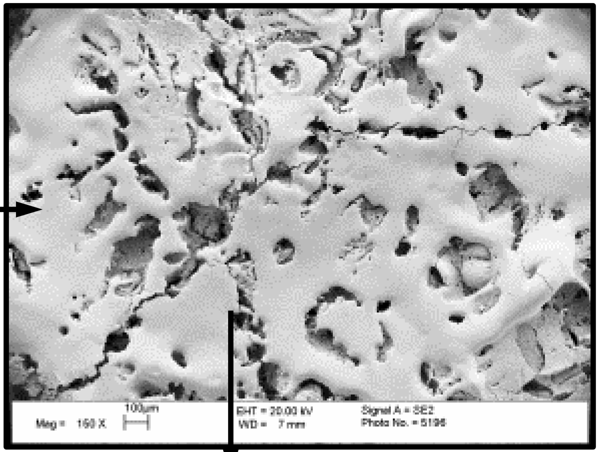
Arc-jet 10 MW m^{-2} 10 s

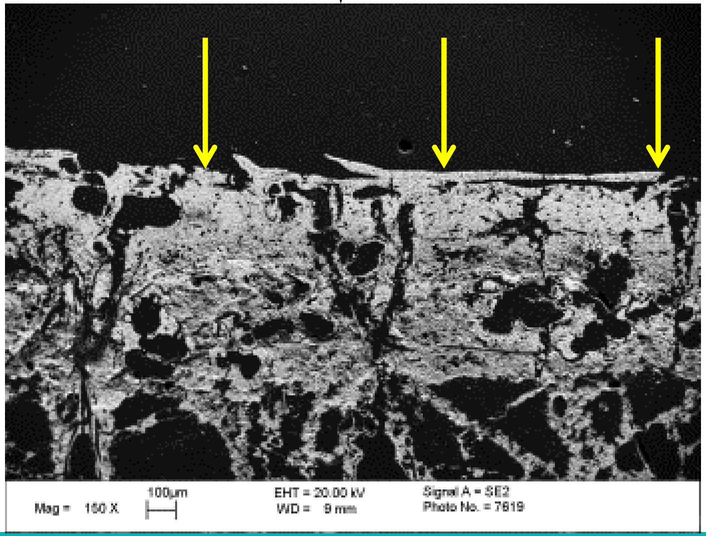
Oxidation only observed near the surface layer; depth is ~150 µm for the OAT sample and ~45 µm for the arc-jet sample.

Development Of Porosity During Thermal Testing









- The carbon matrix burns out so will replace with a UHTC matrix.
- This should reduce the porosity and improve crack sealing.
- Isothermal CVI is SLOW.

Chemical Vapour Infiltration (CVI)

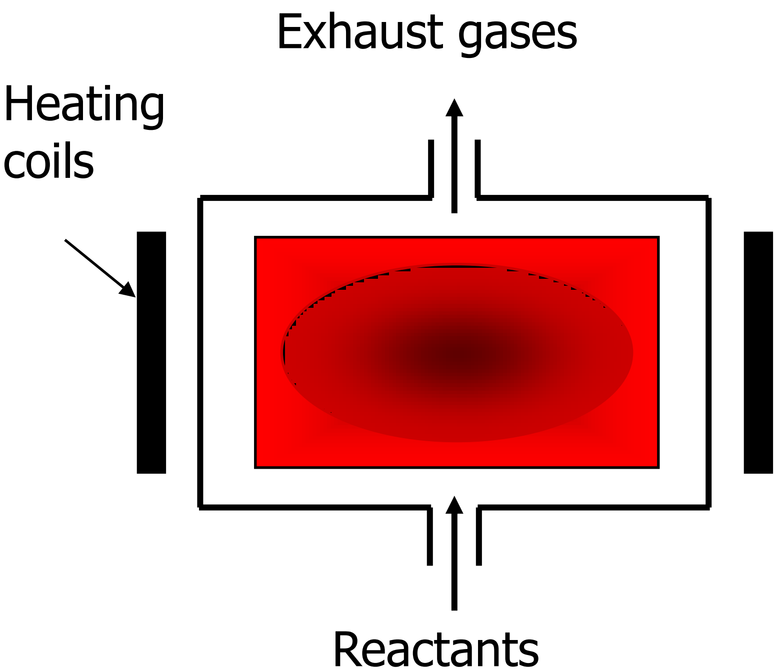
Advantages

- Near net shape
- Wide range of compositions
- Processing T typically <1000^{o}C
- Matrix is pure and fine grained
- Near-zero porosity possible
- Can deposit interfacial layers *in-situ* to enhance fibre pullout

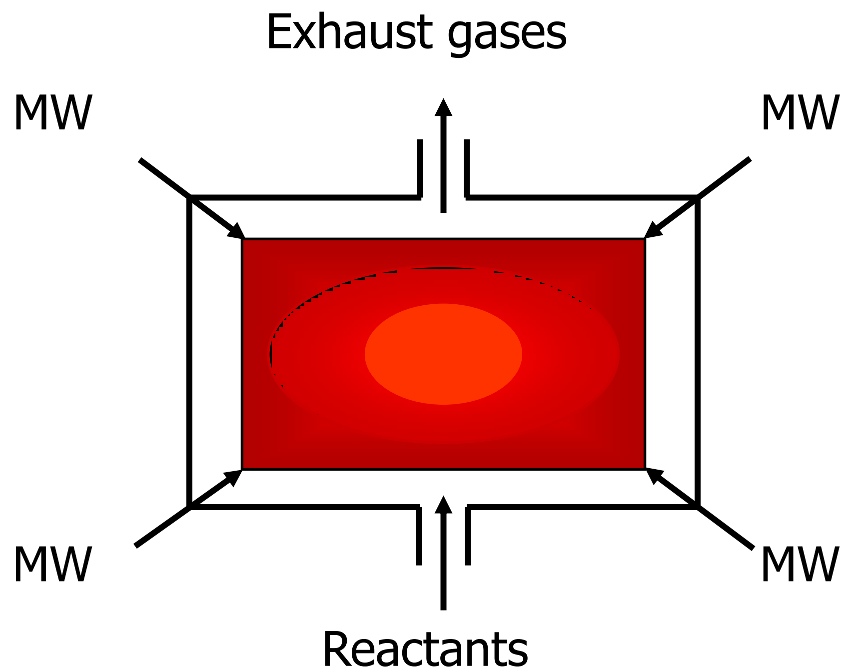
Disadvantage

- Conventional isothermal, isobaric (I-CVI) process, very slow
- Many variations:
  - pressure & conc^{n} gradient
  - temperature gradient
  - forced flow (F-CVI)
  - pulsed-flow (P-CVI)
  - *microwave heated (M-CVI)*

Conventional vs Microwave CVI

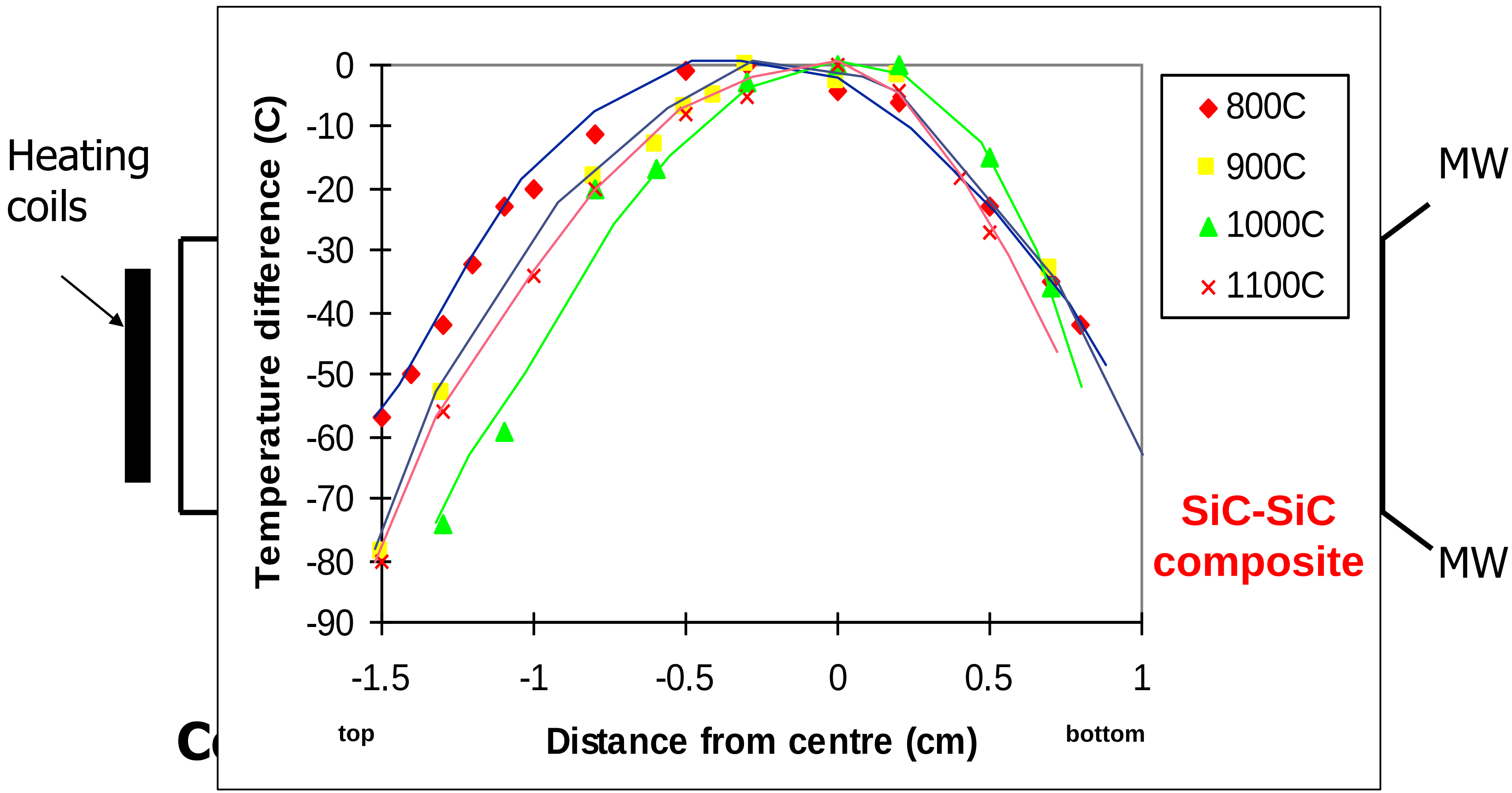


Conventional CVI

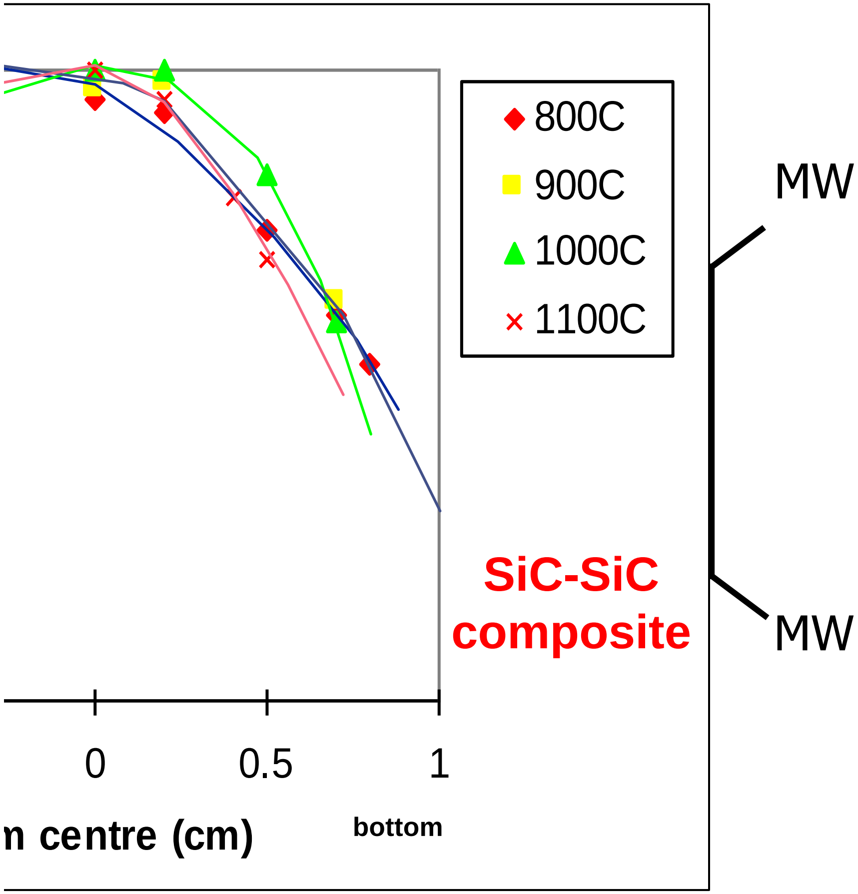


Microwave CVI

Conventional vs Microwave CVI



Conventional vs Microwave CVI



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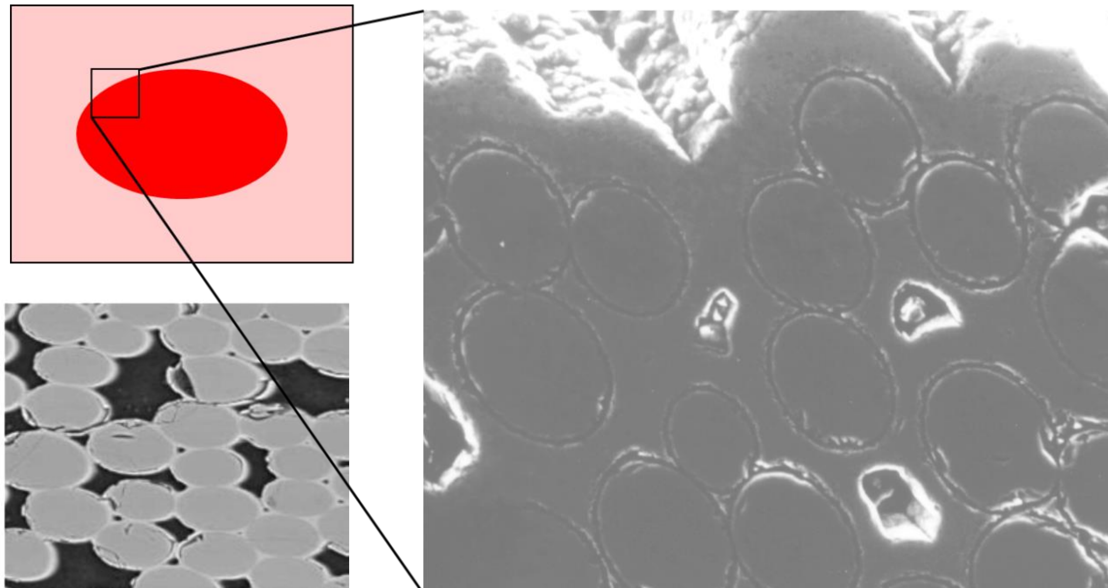
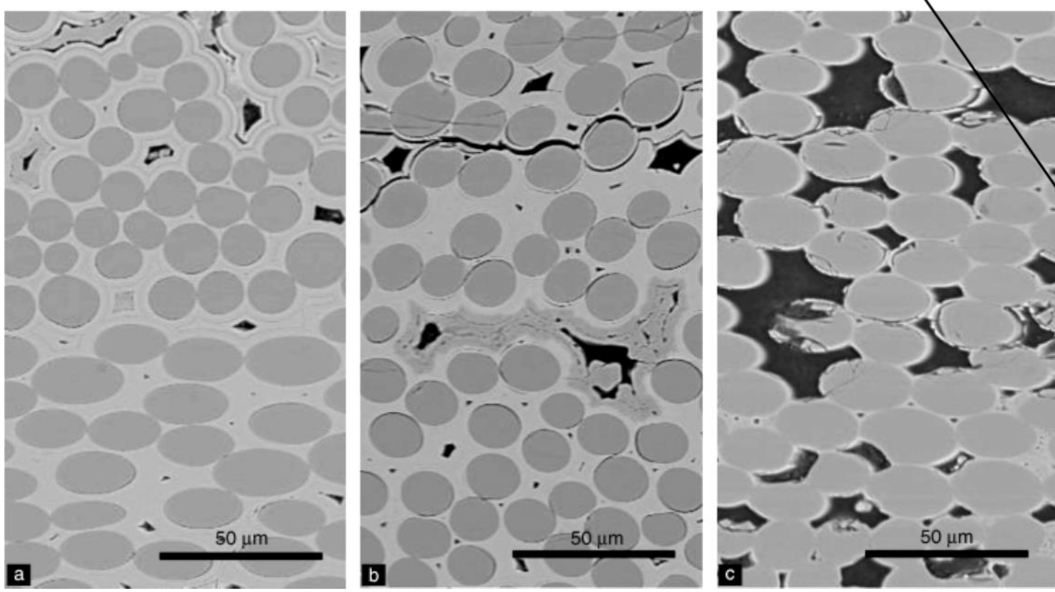
Microwave CVI – SiC-SiC Composites



Microstructure after 24 h

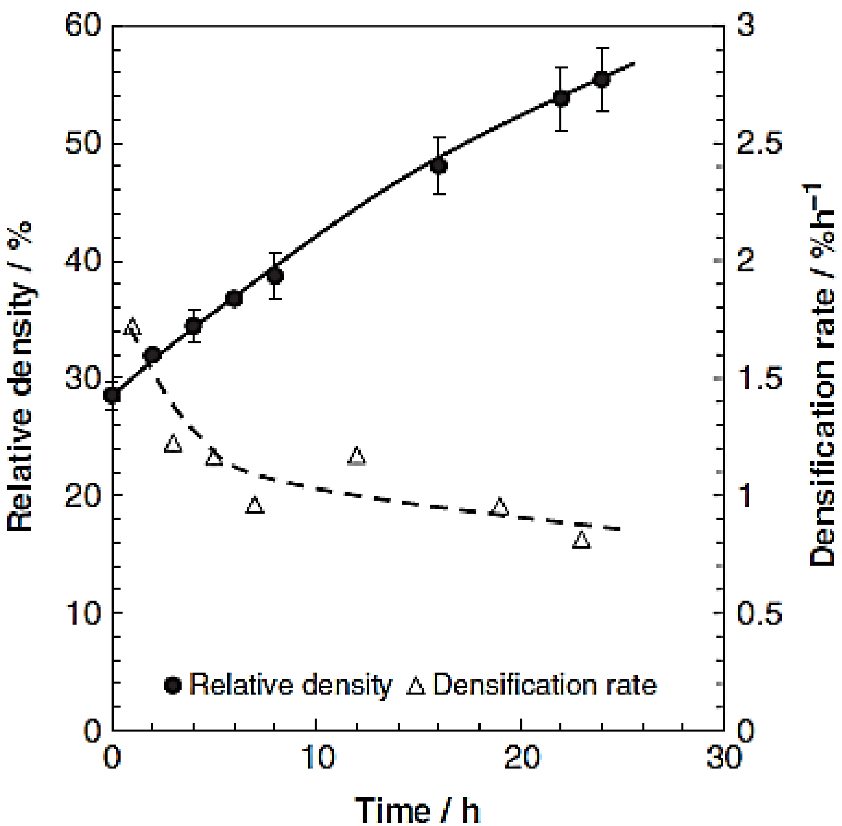


Centre

10 mm from centre

20 mm from centre

Microwave CVI – Densification Rate



Density vs Time

- Densification occurs from the inside out, hence no crusting.
- Almost fully dense matrix with no density gradients.
- Cold zone restricted to surface, which can be machined off or infiltrated conventionally.
- Opportunity to produce fibre reinforced CMCs in 48 – 72 h instead of 3 months.
- Plan is to repeat for C_f-HfB_2 composites with UHTC matrices.

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Summary and Where Next

- C_f-HfB_2 composites show excellent thermal shock, ultra-high temperature and ablation resistance when either oxyacetylene torch or arc jet tested.
- Variability in strength has been addressed by the development of a new impregnation technique.
- Future work is focused on reducing the porosity at high temperature, making both larger (325 x 325 x 5 mm) and more complex-shaped components.
- Final components are probably going to consist of joined combinations of composites and monolithics; work has recently started on this topic too.

Thank You

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