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Rapid Fabrication Of Fibre Reinforced CMCs By Microwave CVI

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EPSRC
Engineering and Physical Sciences Research Council

XMat
Materials Systems for Extreme Environments

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Background

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 their Programme Grant scheme. It formally started on the 1st February 2013 and is valued at £4.2M (~€6M) over 5 years. Additional programmes valued at nearly £0.5M (~€0.7M) have been received to date.

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[dstl]

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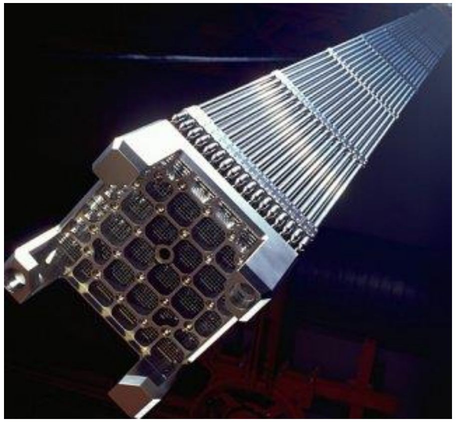
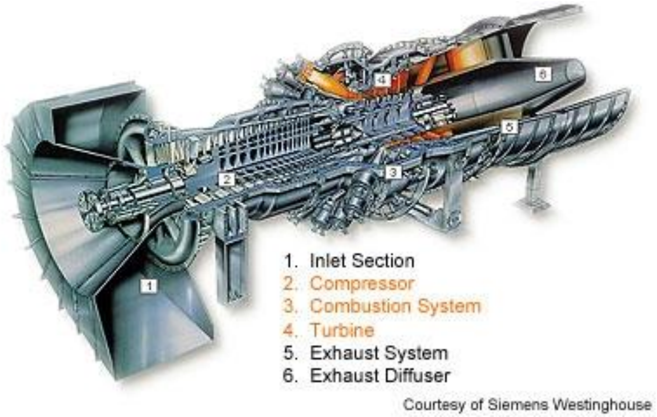
High Temperature Materials

There are many applications that require:

- Light weight
- Excellent mechanical properties to over 1000°C
- Resistance to mechanical and thermal constraints (shocks or cycles)
- Chemical resistance
- Toughness



Nuclear fuel cladding

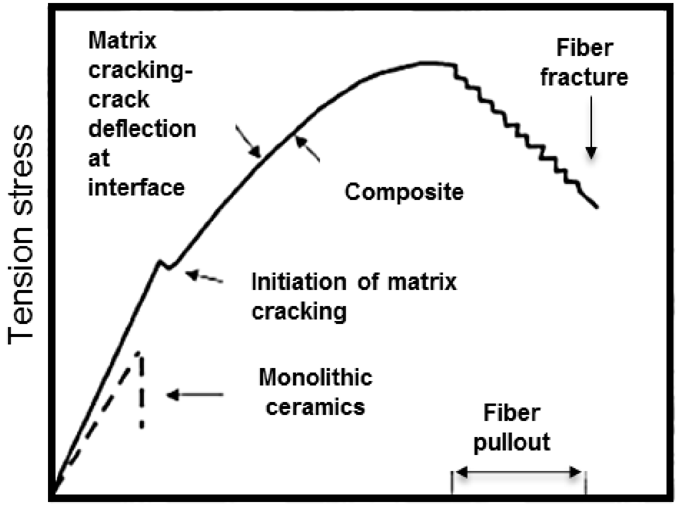


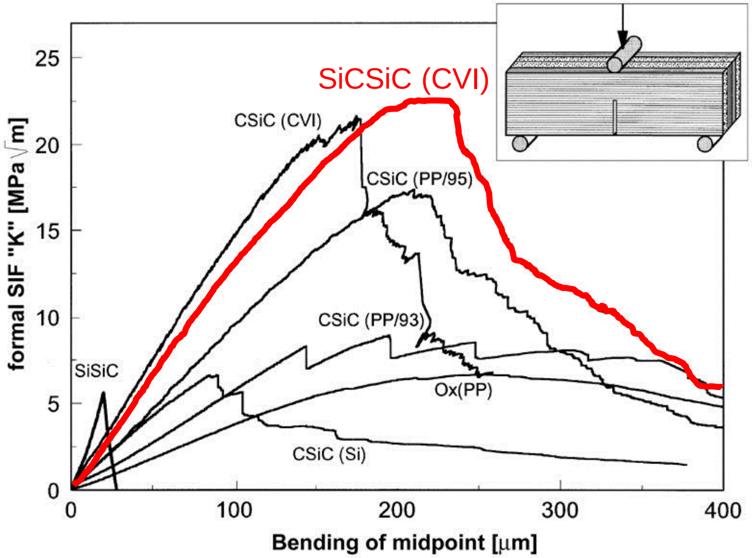
Turbines

Nozzle flaps

Why SiC_f/SiC Composites?

- Light weight
- Chemically resistant
- Excellent thermo-mechanical properties
- Shock resistant
- Elongation to rupture
- Good oxidation resistance
- No sintering
- **Tougher than monolithic ceramic SiC**

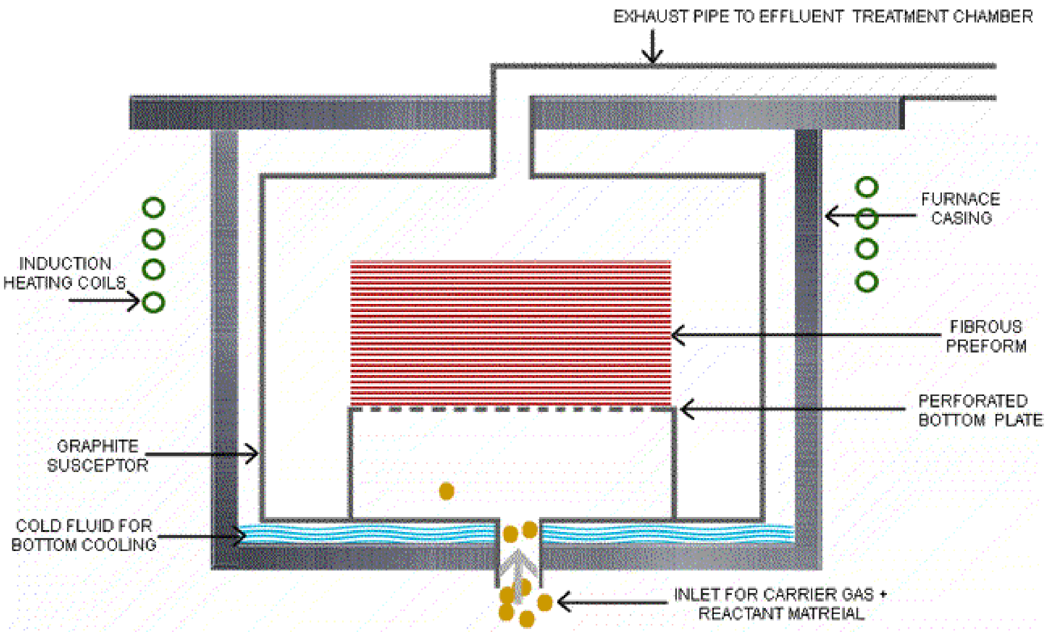




M. Kuntz, *cfi/Bericht der DKG*, **49** [1] 18 (1992)

Chemical Vapour Infiltration

CVI is a process in which a solid matrix is deposited in a porous preform by the thermal decomposition of a reactive gas mixture.



- *It is a variant of chemical vapour deposition (CVD).*
- *A coating is produced with CVD, whilst a solid body is obtained from a porous preform with CVI.*
- *Major applications for C_f – C composites (aircraft brakes) and SiC_f – SiC composites.*

Deposition of SiC by decomposition of methyltrichlorosilane in hydrogen

$$\mathbf{CH_3SiCl_{3(l)} + H_{2(g} \rightarrow SiC_{(s)} + 3HCl_{(g)} + H_{2(g)}}$$

Chemical Vapour Infiltration

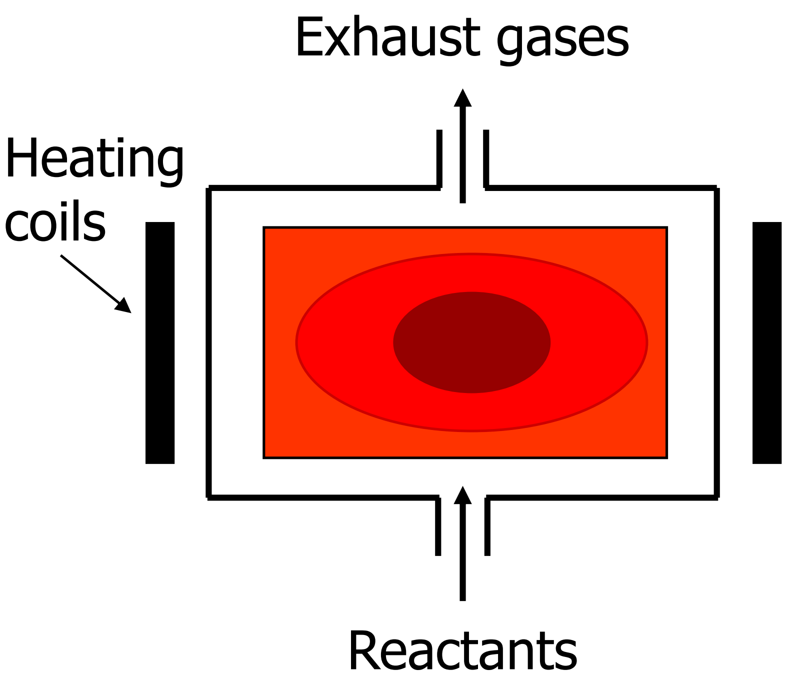
Advantages

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

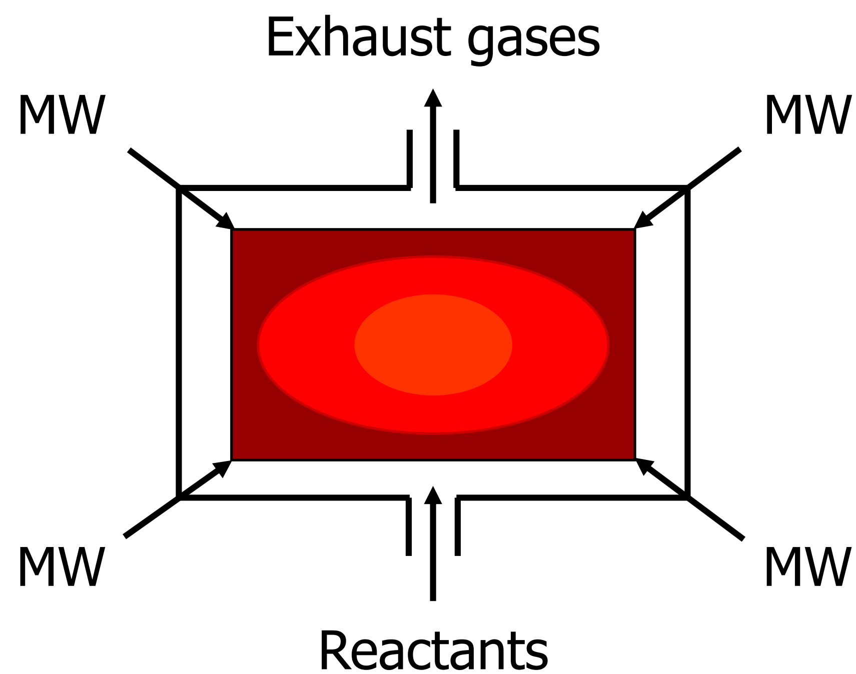
Disadvantage

- Conventional isothermal, isobaric (I-CVI) process is very slow
- Requires repeated machining of the surface to re-open porosity
- Many variations:
  - pressure & conc^{n} gradient
  - temperature gradient
  - forced flow (F-CVI)
  - pulsed-flow (P-CVI)
  - *microwave heated (M-CVI)*

Conventional CVI



Microwave CVI



Microwave heating yields an inverse temperature profile and hence inside-out infiltration ⇒ Reduction of premature pore closure ⇒ Short processing times.

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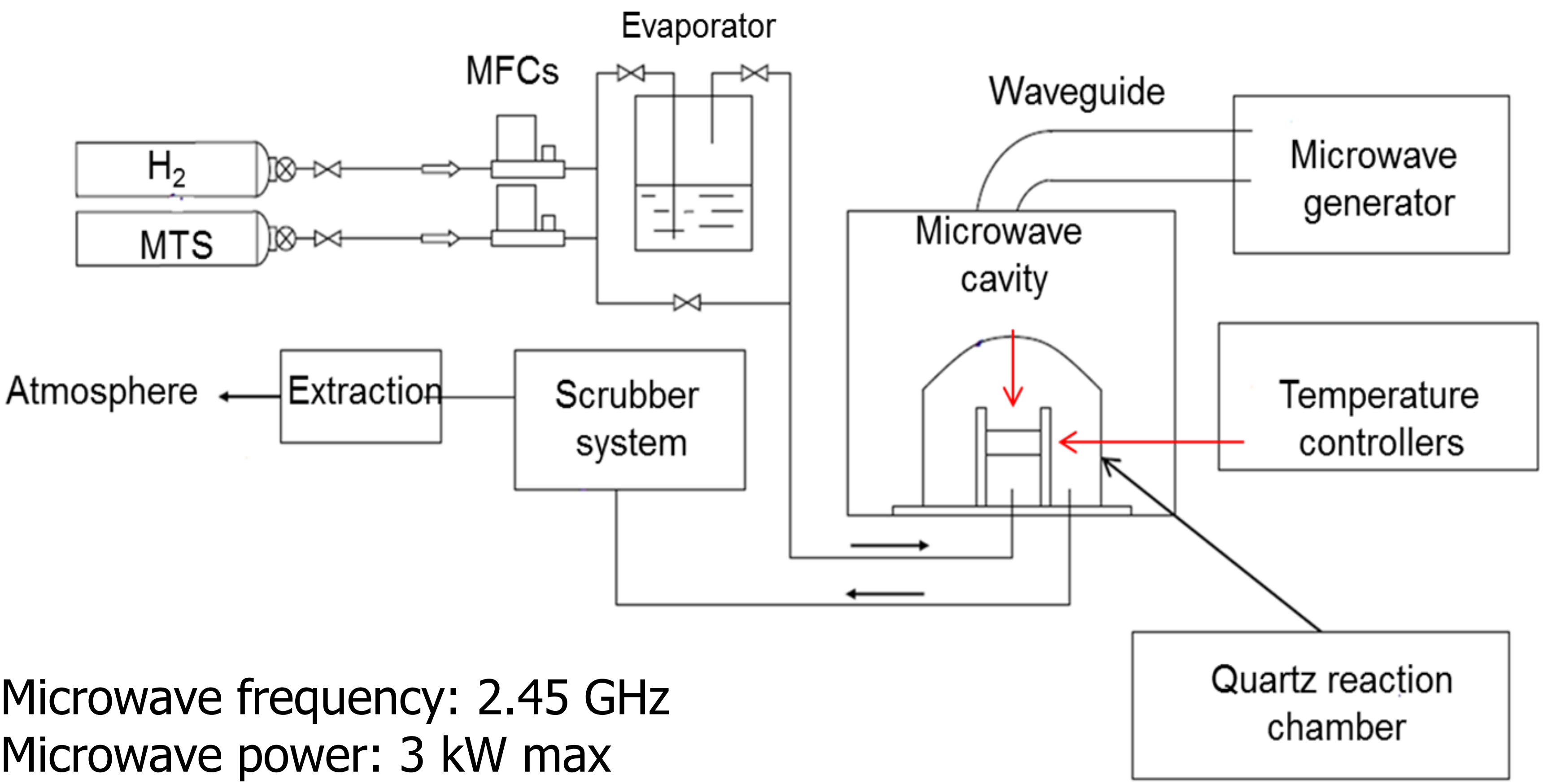
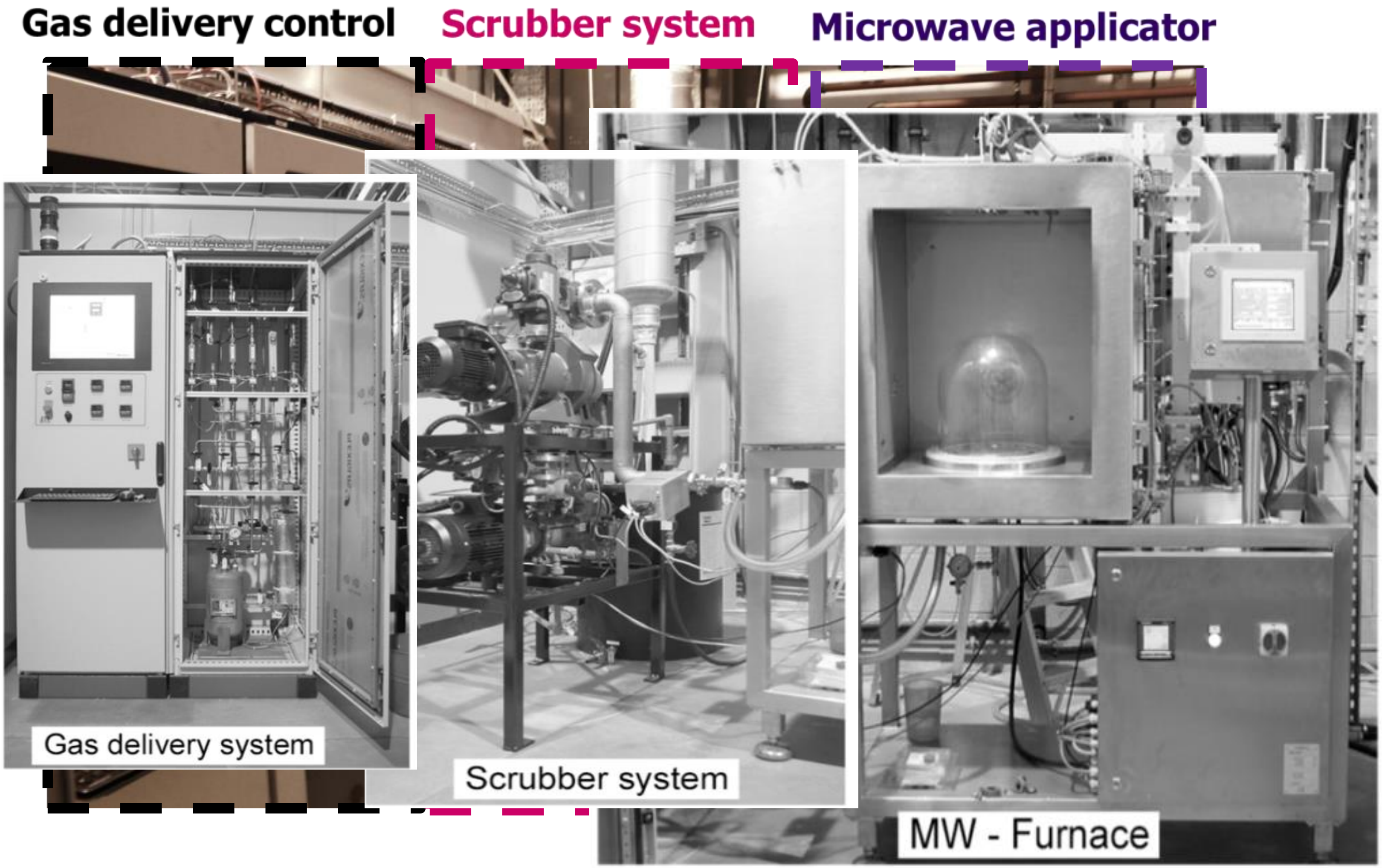
Schematic of the MCVI

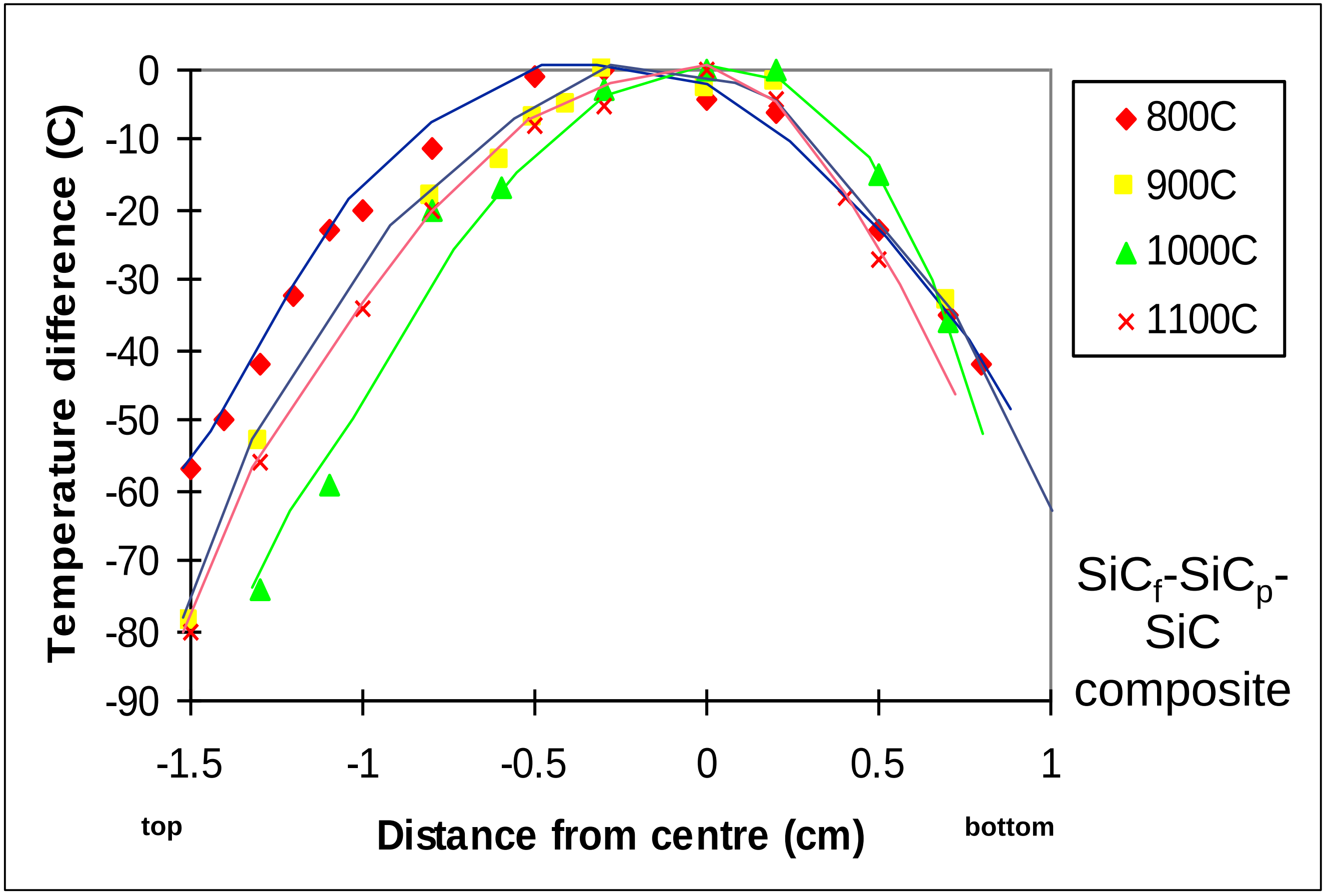


Microwave frequency: 2.45 GHz
Microwave power: 3 kW max

MCVI Equipment



Temperature Profile



Jaglin at al. *J. Am. Cer. Soc.* 89 [9] 2710-2717 (2006)

MCVI of SiC_f Preforms

Preparation of the preform

- Si-Ti-C-O (Tyranno grade S, Ube Industries Ltd) fibres*
- Composition: non-stoichiometric Si:C= 1.65, 19 at% O
- Stacking and stitching of 32 mm discs up to 10 mm in thickness
- Deseizing at 550°C in an argon atmosphere

Microwave heated chemical vapour infiltration

- Temperature at the top: from 850 to 950°C
- Partial pressure: from 100 to 700 mbar
- Input gas ratio (Q_{H2}/Q_{MTS}): from 5 to 50
- Power: 0.5-0.7 kW
- Monitoring of the mass gain (and hence matrix growth rate) after 1, 2, 4 h

*Si-Zr-C-O (Tyranno ZMI) and crystalline SiC fibres (Tyranno SA-3) are also available

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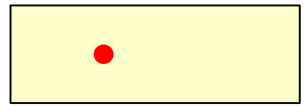
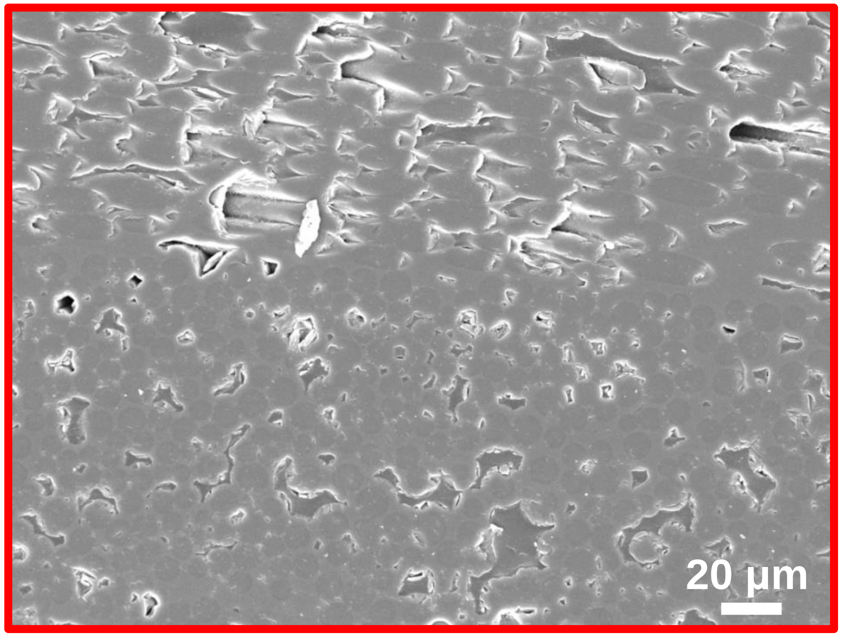
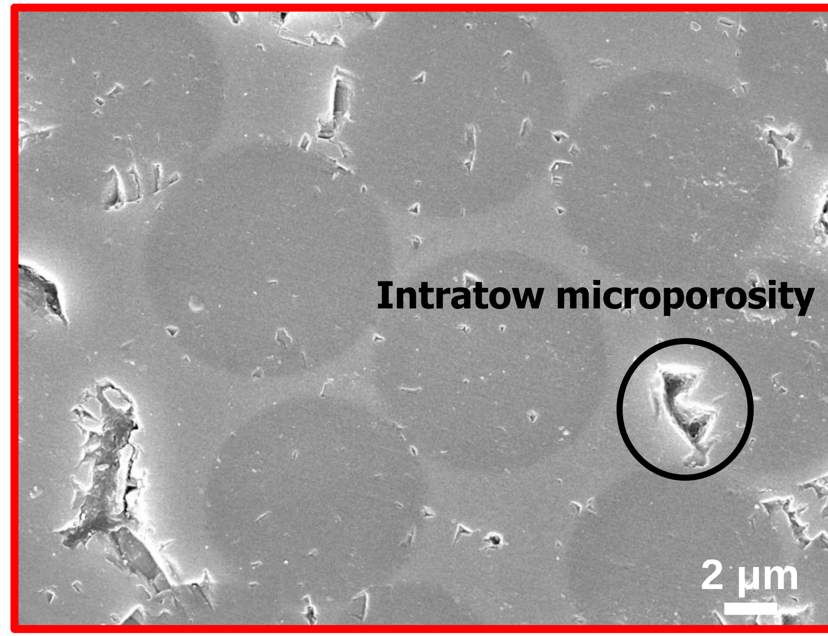
Deposit Thickness

10 mm from the centre along the diameter







Good intratow infiltration after 4 h at a location 10 mm from the sample centre

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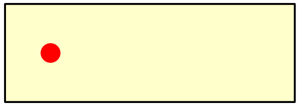
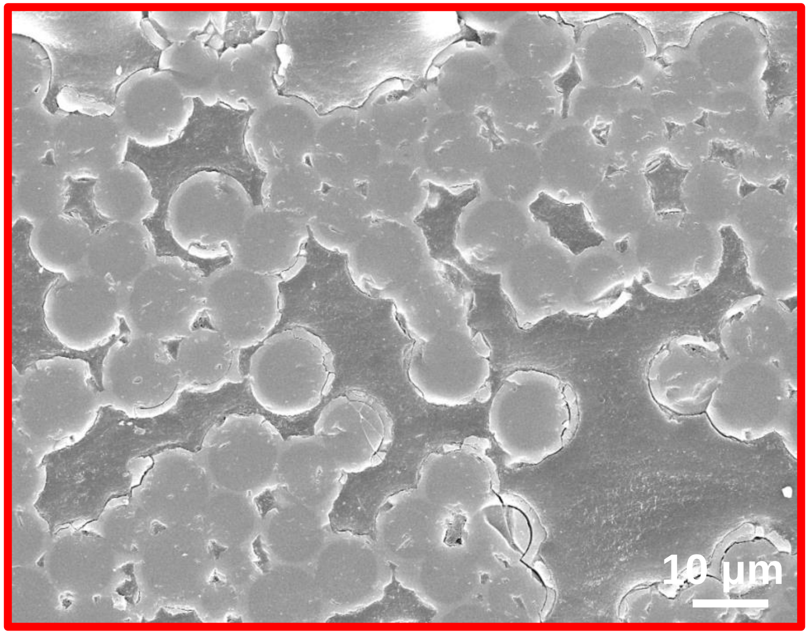
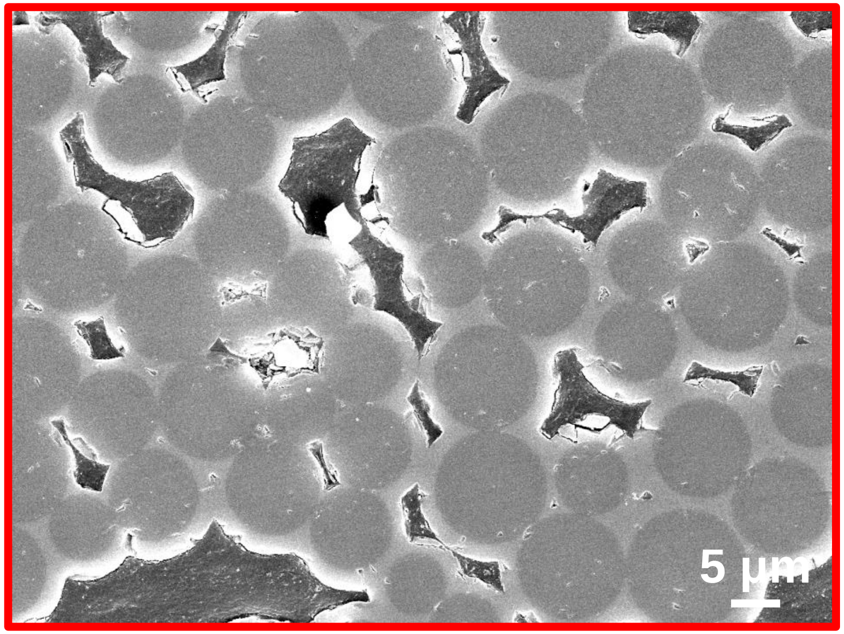
Deposit Thickness

5 mm from the centre along the diameter







Deposit is between 1 and 2 µm thick with evidence of individual deposits merging

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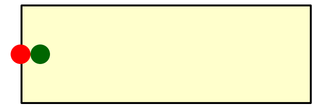
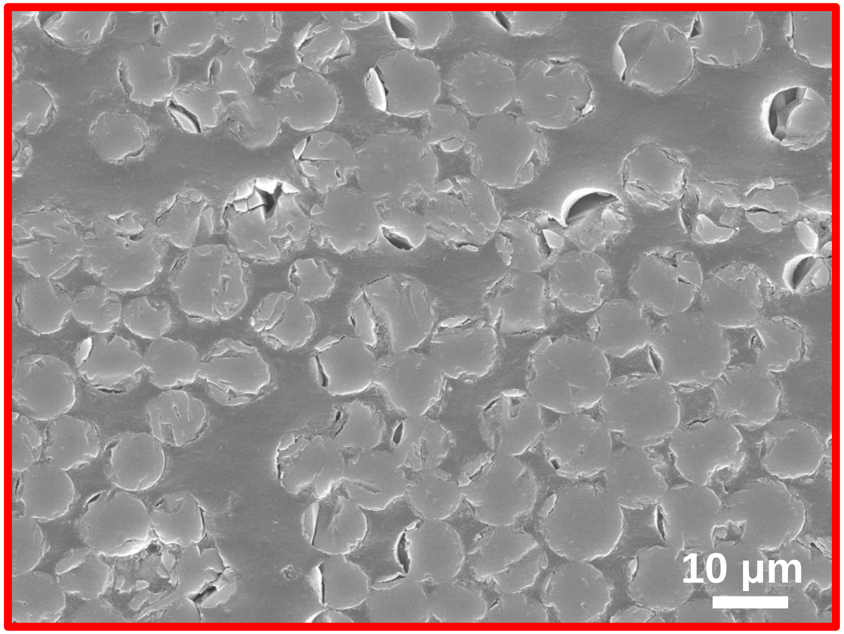
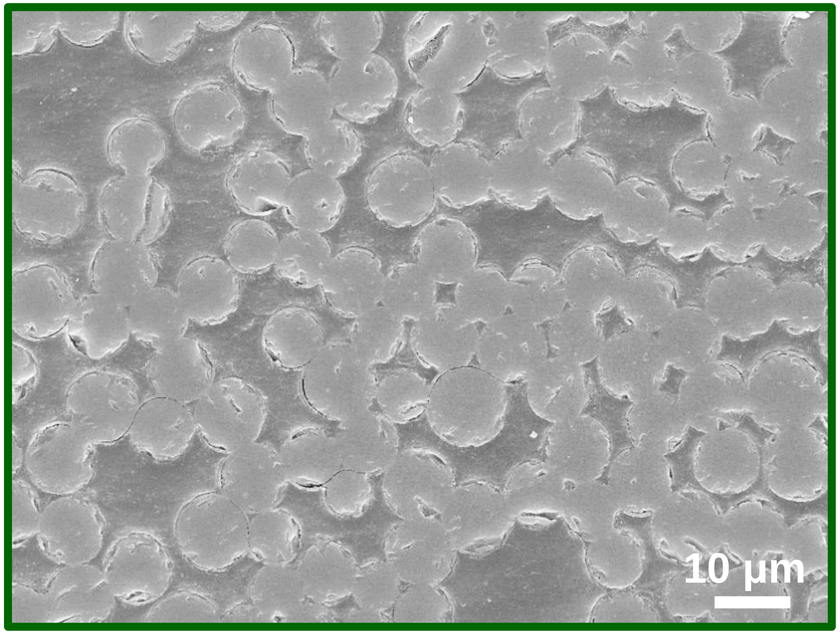
Deposit Thickness







Edge of sample
No deposit

Just in from the edge
Deposit avg thickness: 800 nm

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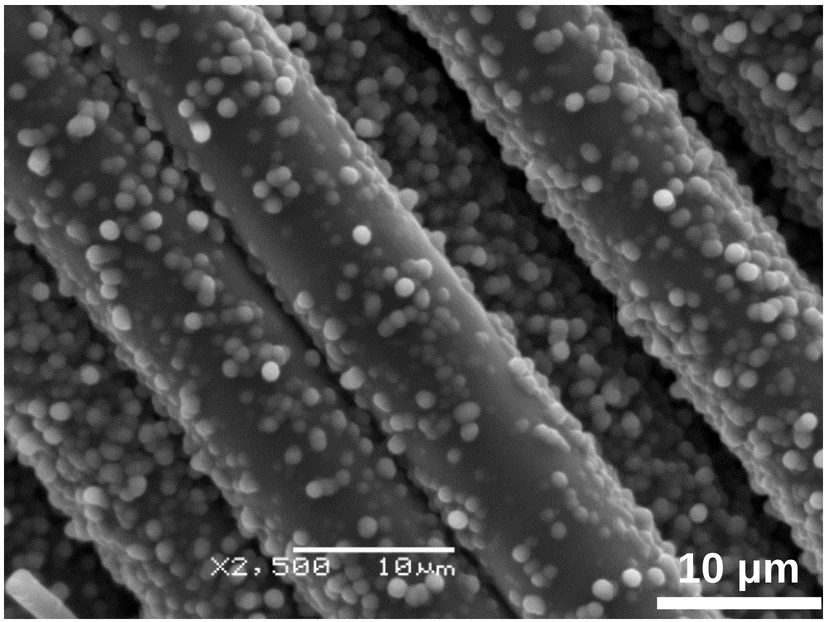
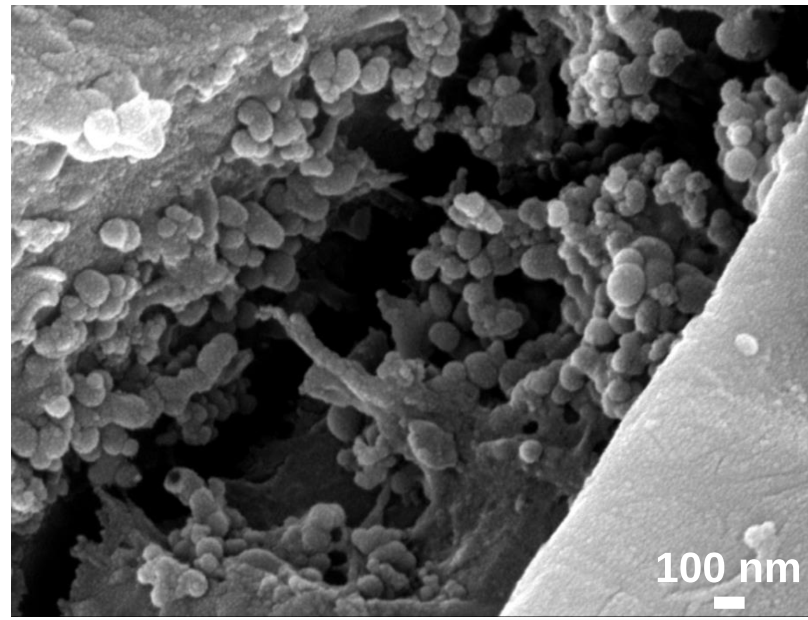
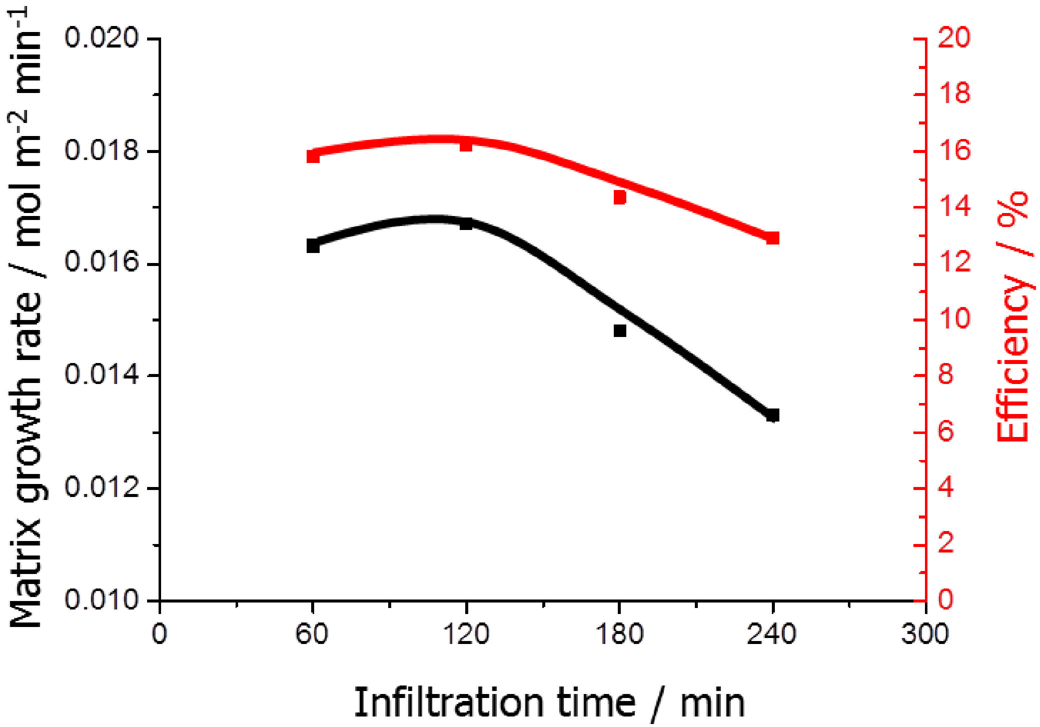
Deposit Morphology





Deposit particle size is around 100 nm

Matrix Growth Rate & Efficiency



- Efficiency is higher than the 5-8% of the conventional industrial process
- The decrease over time is due to a reduction in the size of the pore channels

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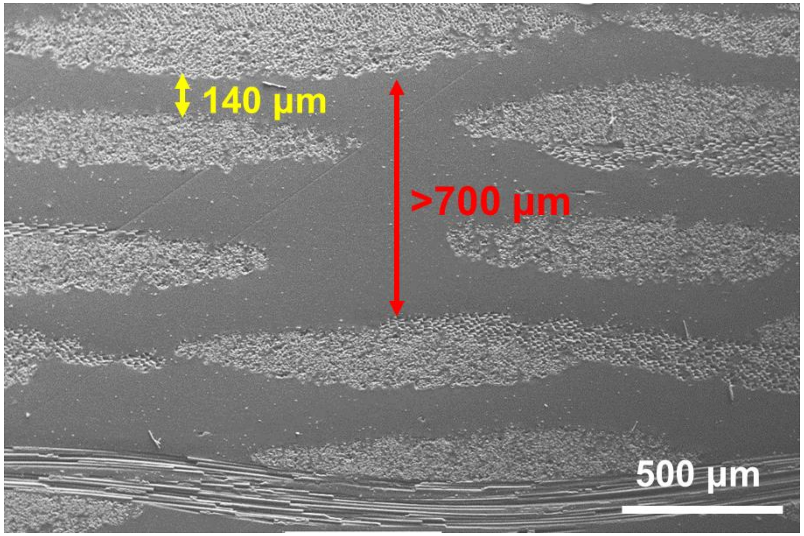
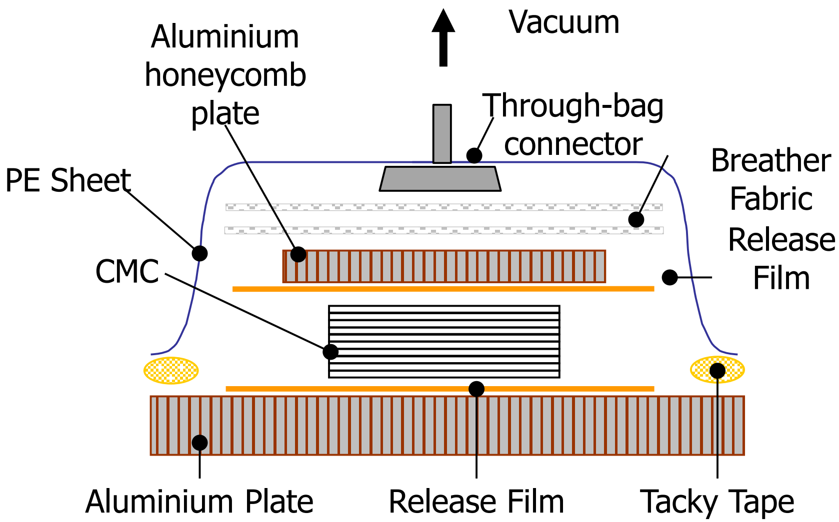
SiC_f / SiC_p Preform

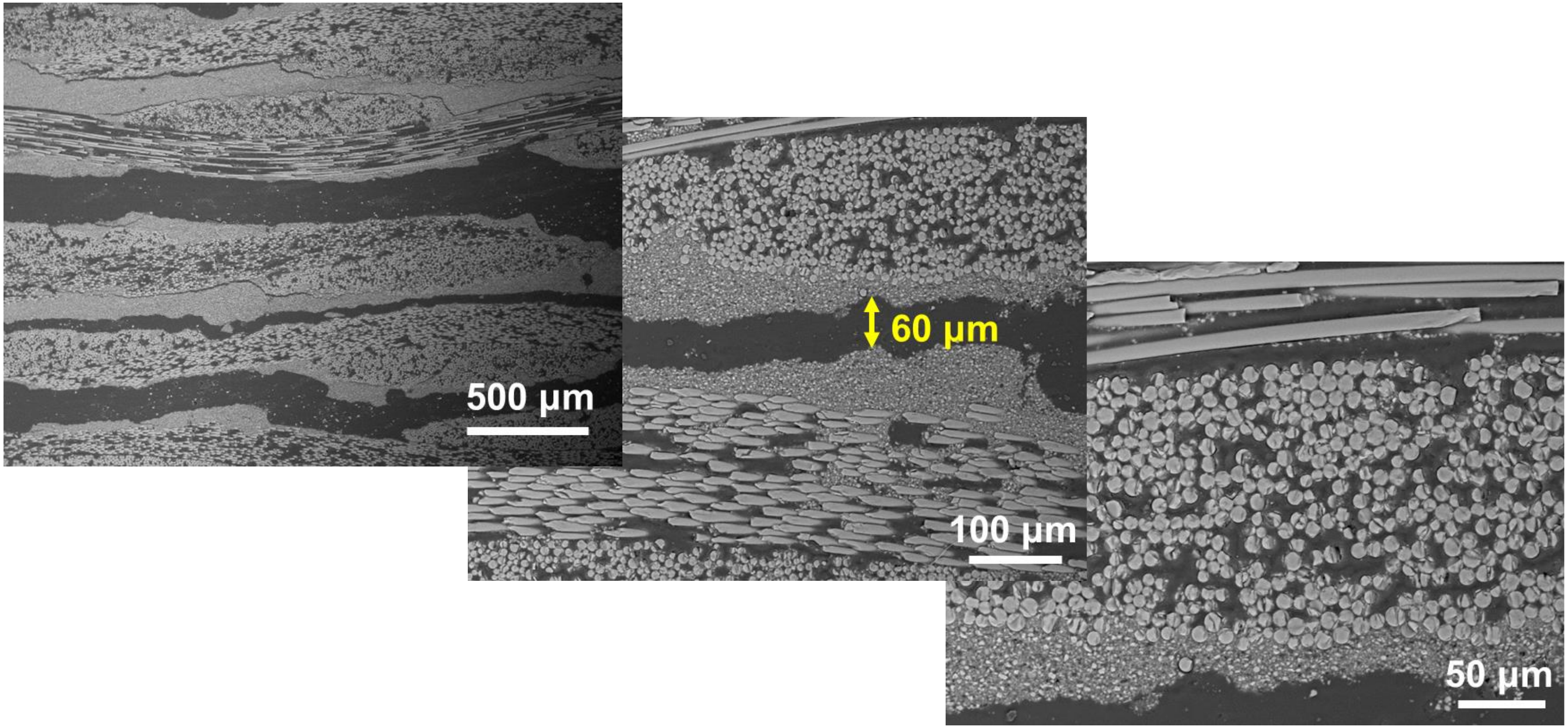
- CVI takes a long time to fill macroporosity between the cloth layers and failure to fill it is deleterious to the final mechanical properties.





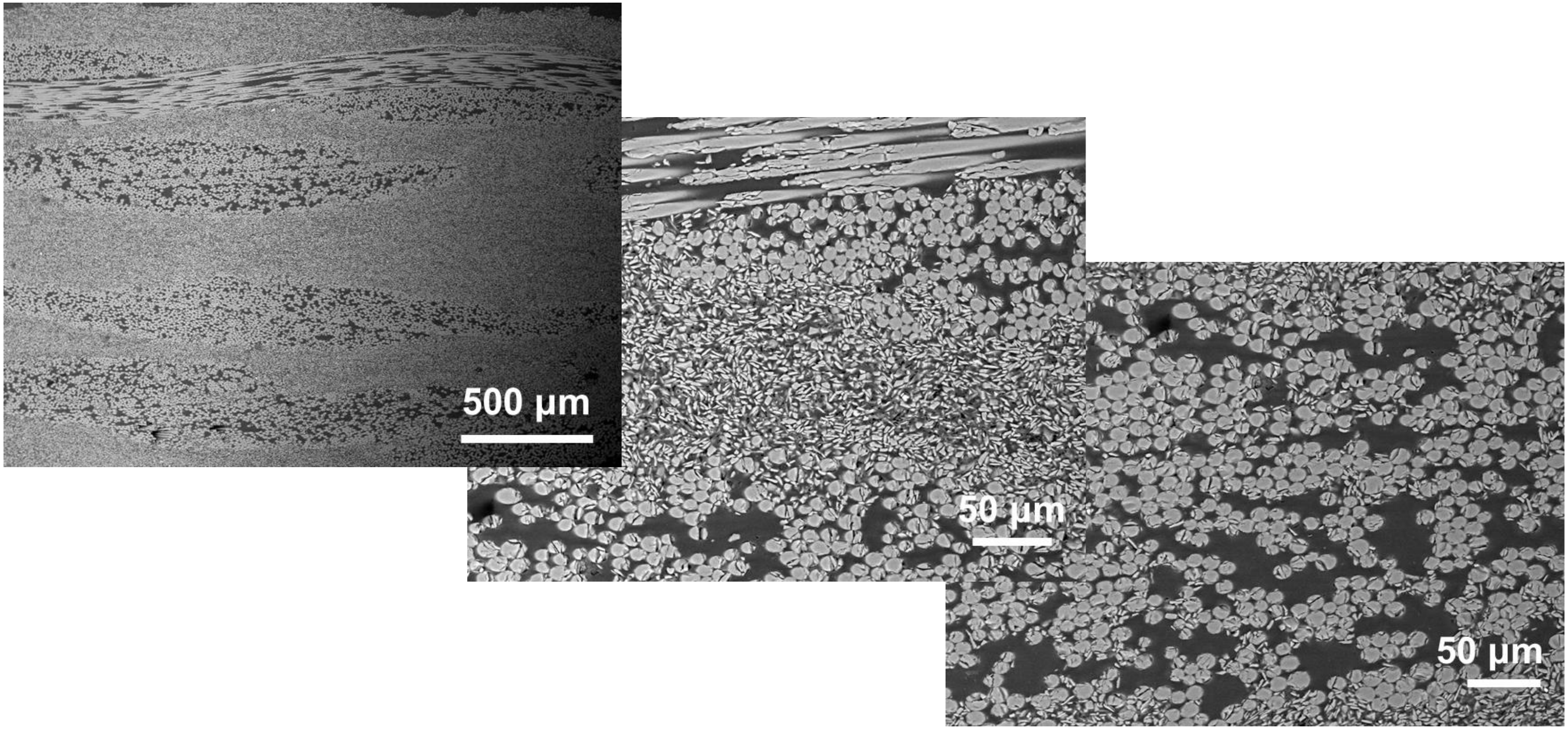
- Impregnation of the preforms with an aqueous SiC slurry (30-35% solids) followed by vacuum bagging (VB) reduces the macroporosity and hence speeds up the process
- Different particle sizes being investigated: 1-2, 6, 8 µm
- V_f= 22-27 vol% V_p= 20-27 vol%

Macroporosity Reduction by VB



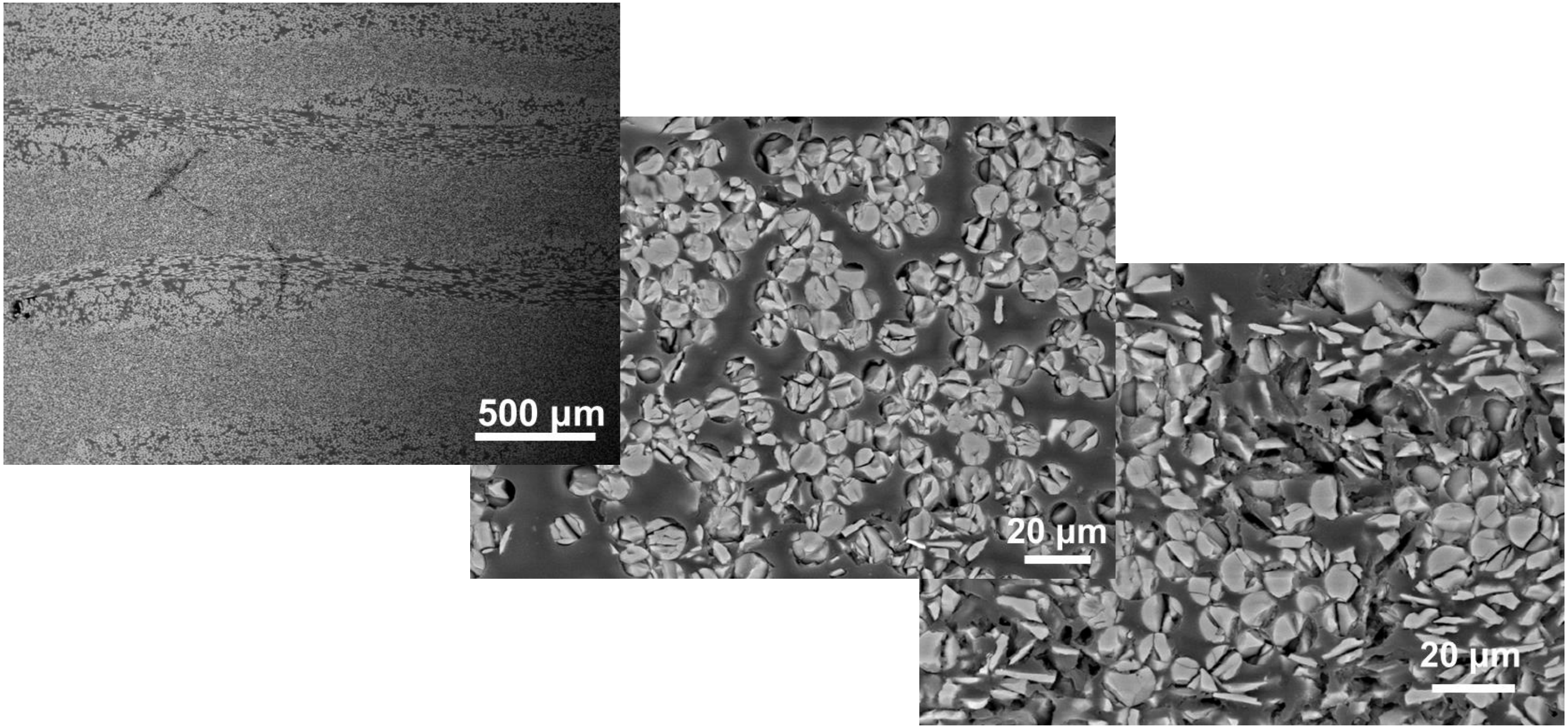
Impregnation with a (high viscosity) 1 – 2.5 µm SiC slurry reduces the intertow porosity but does not penetrate within the tows

Macroporosity Reduction by VB



Impregnation with a (lower viscosity) 6 µm SiC slurry completely fills the intertow porosity, with very little penetration within the tows

Macroporosity Reduction by VB



Impregnation with an (even lower) 8 µm SiC slurry completely fills the intertow porosity, but with partial impregnation within the tows

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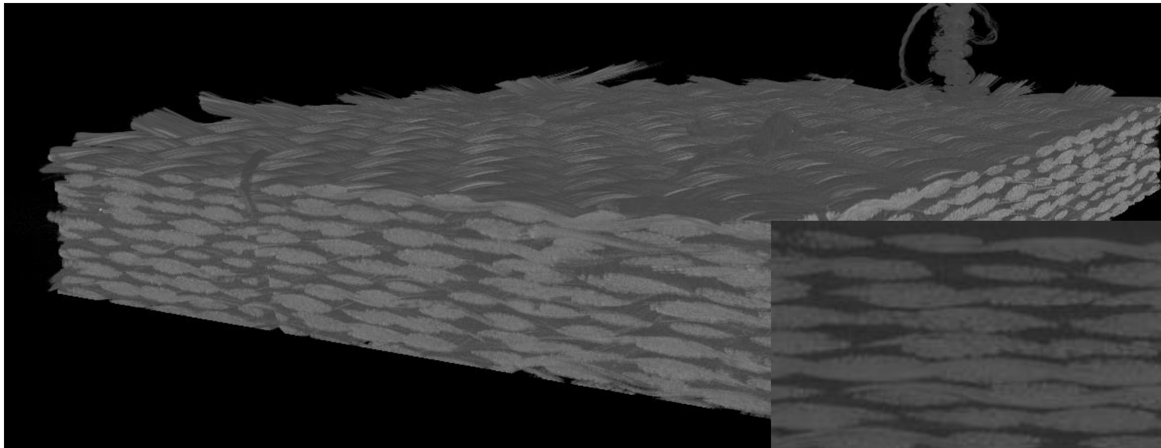
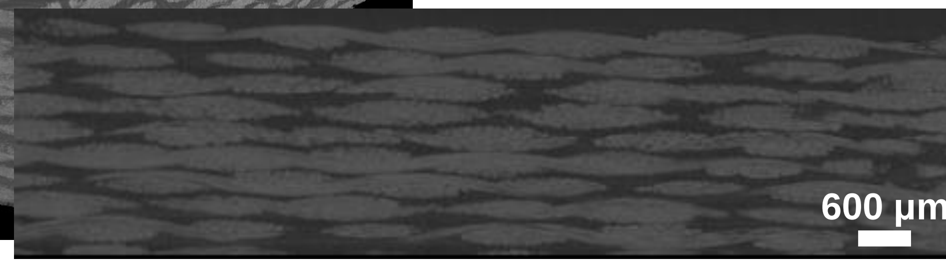
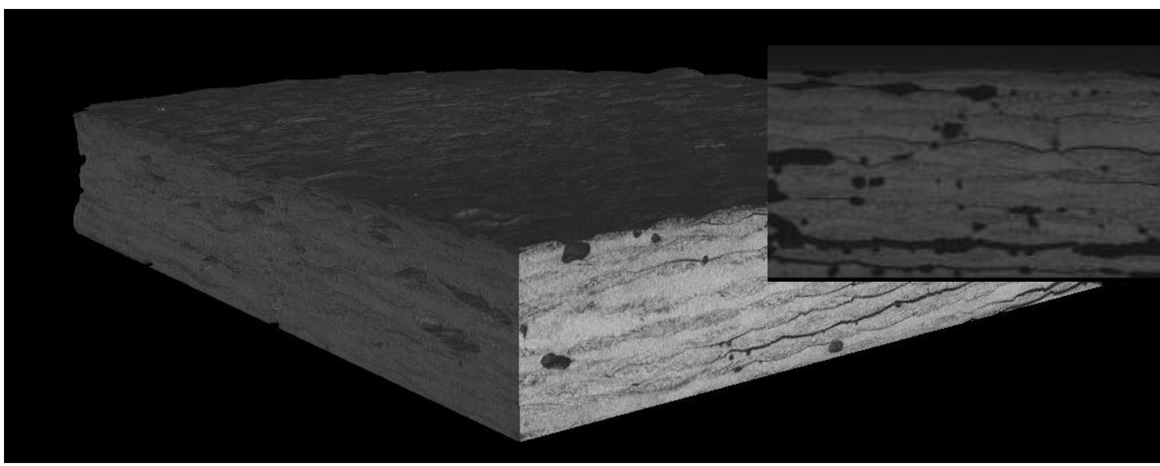
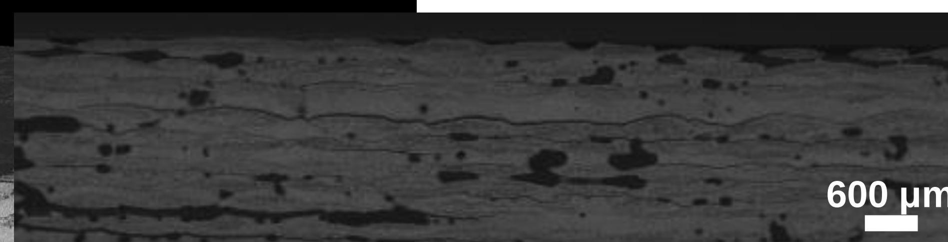
X=Ray Micro-CT





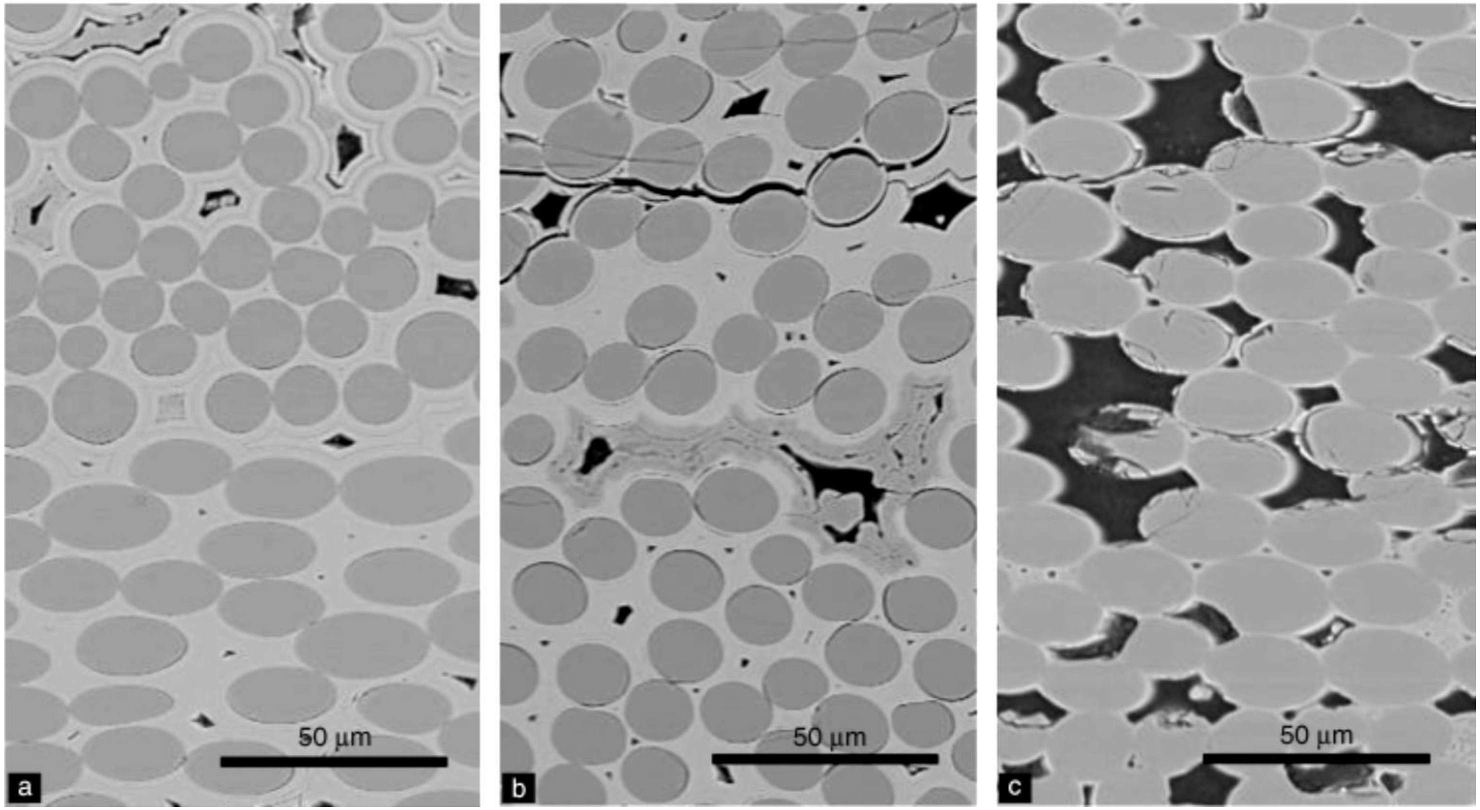
Unimpregnated





Impregnated with 6 μm SiC

Effect of Inverse Temperature Profile



Centre

10 mm from centre

20 mm from centre

Microstructure after 24 h MCVI

Next Steps for MCVI of SiC_f – SiC_p - SiC

Phase 1

- Optimization of M-CVI
- Characterization of SiC deposited
  - Study of the kinetics
  - Chemical and microstructural (SEM-WDS, EBSD, XRD, Micro-CT and TEM)

Phase 2

- Mechanical characterization (flexural strength, toughness, TSR). Activity will be carried out at MS&T (Rolla, US) funded by JECS Trust.

Phase 3

- Deposition of an interfacial layer of Pyr-C or BN (to enhance pullout) prior to infiltration
- Chemical and mechanical characterization

Phase 4

- Evaluation of proton irradiation

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C_f-HfB_2 Composites

HfB_2
H.C.Starck 7.6 µm
Treibacher 3.7 µm

Surface Transforms

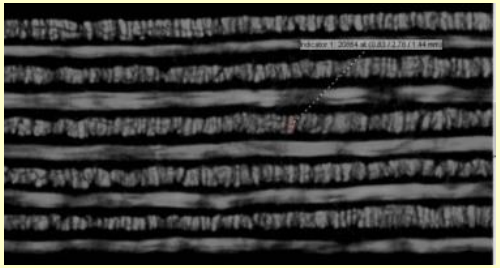
2.5 D Cf preform
35 mm x 20 mm

HfB_2 + phenolic slurry
↓
Vacuum impregnation
↓
Drying
↓
Curing
↓
Pyrolysis
↓
C-CVI

Preform 2.5D

Impregnation & curing

Pyrolysis



Structure: RO/90º/RO/0º/RO
23% fibre; 77% porosity
Bulk density = 0.36 g cm^{-3}
Random orientation (RO) arises from the needling process

Front

Back

Carbon CVI

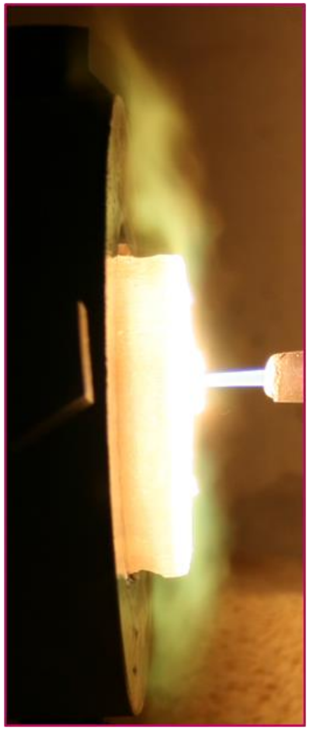
Oxyacetylene Torch Testing

Oxyacetylene Torch (OAT) Test

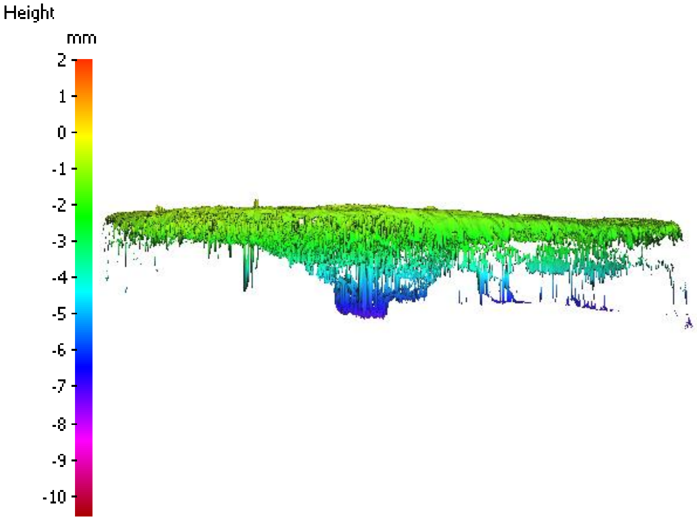
Duration: 300 s

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

Heat flux >17 MW m^{-2}



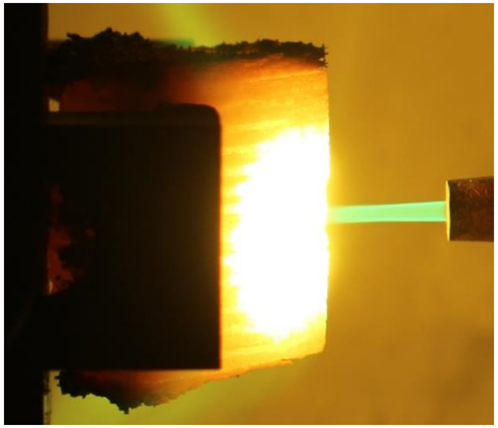
Sample after
300 s OAT @ ~2900^{o}C



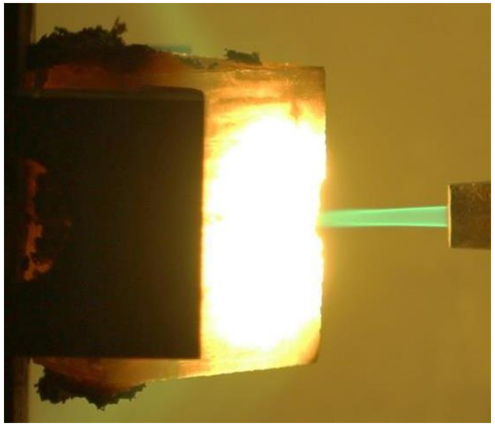
Mass loss: 2.1 g

Erosion depth: ~5 mm

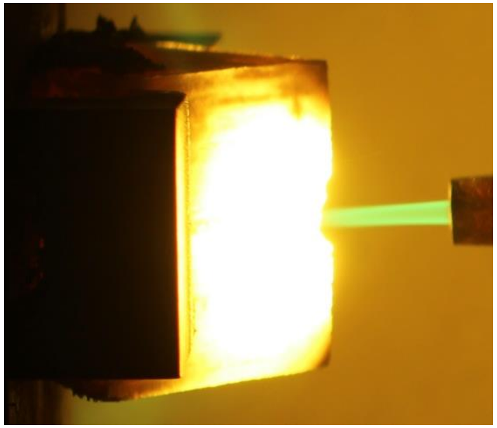
OAT Testing Of Wedge-shaped Composites



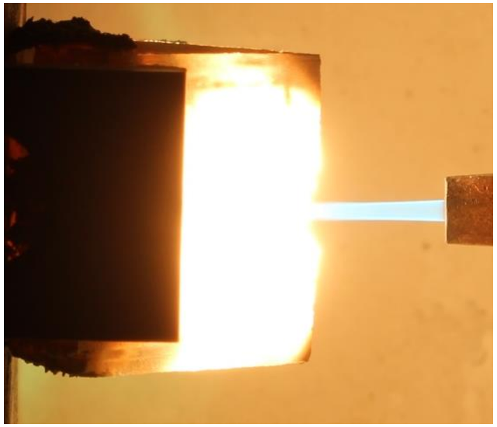
60 s



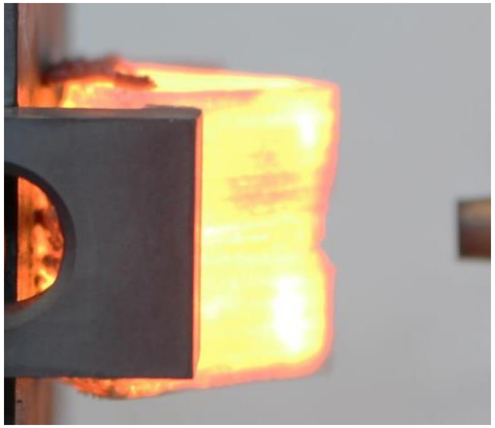
120 s



180 s



240 s



After 300 s

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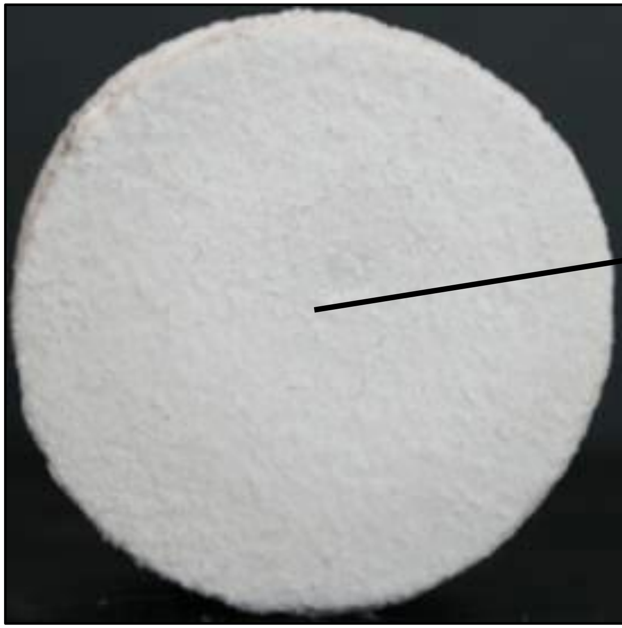
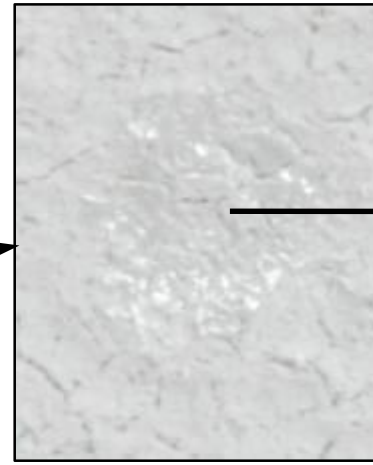
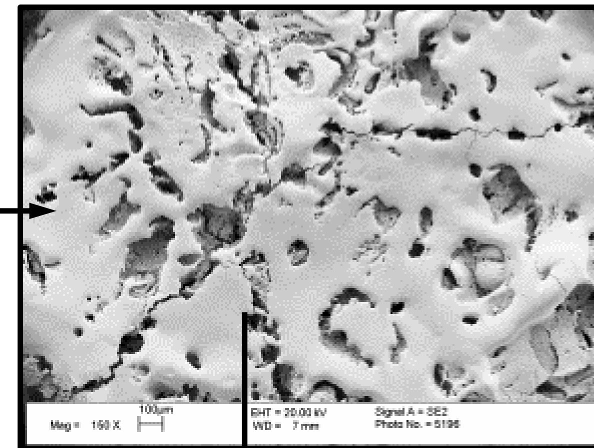
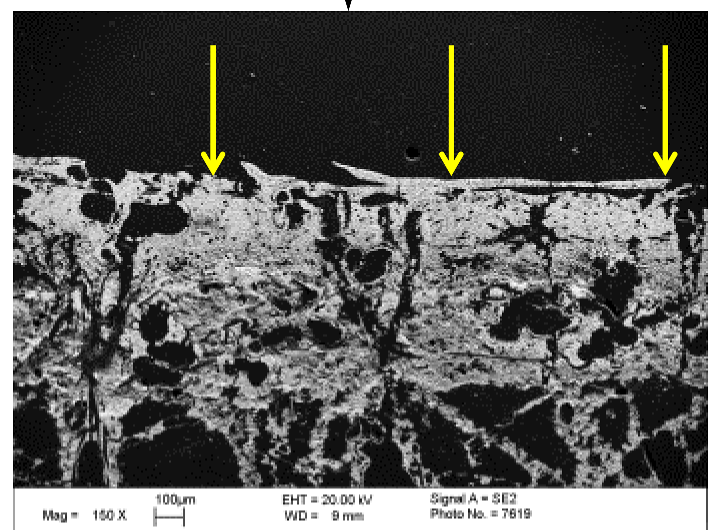
Development Of Porosity During Thermal Testing









- The carbon matrix burns out → replace with a UHTC matrix.
- This should reduce the porosity and improve crack sealing.

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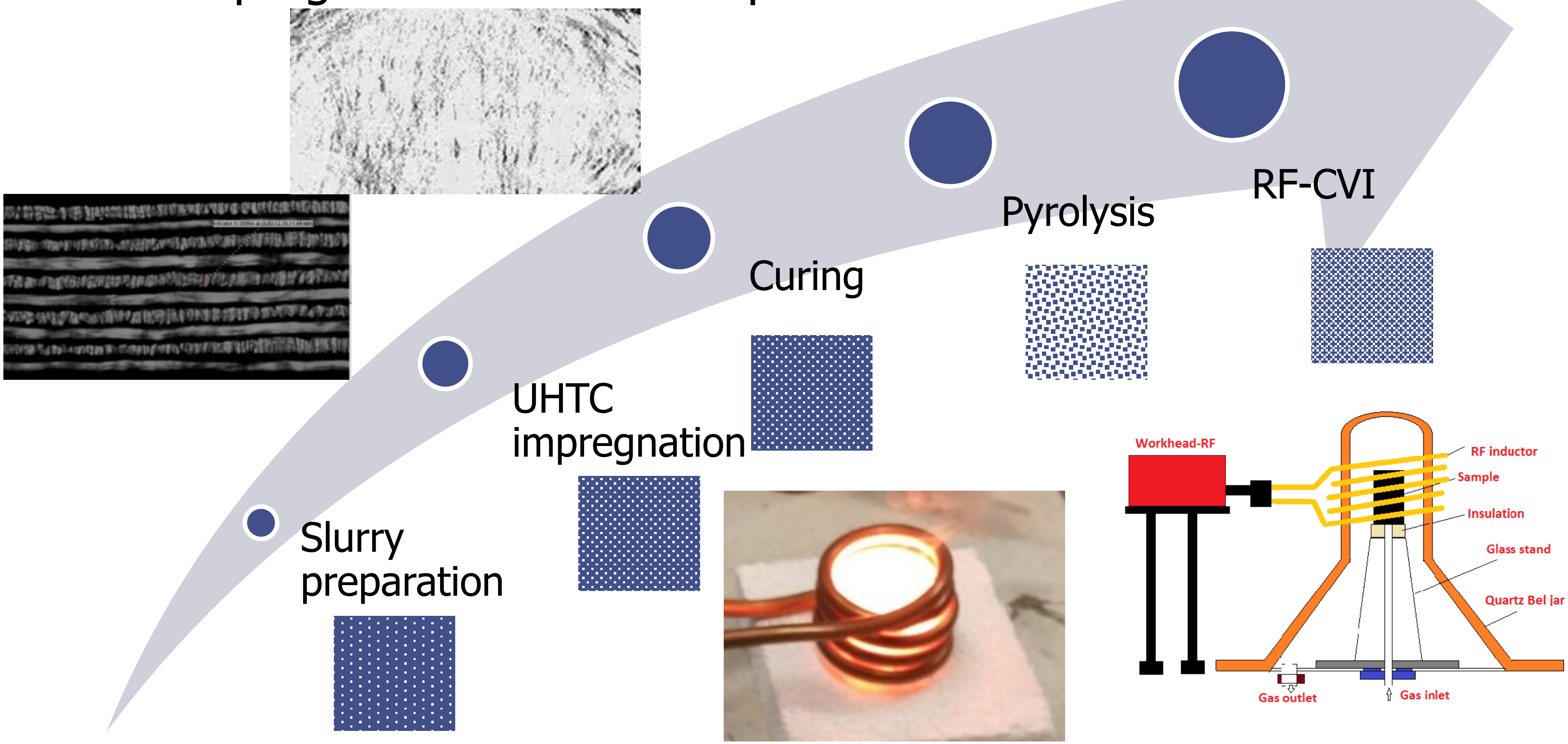
C_f-HfB_2-UHTC Composites

UHTC impregnated carbon fibre preform



Conclusions

- With microwave heated CVI, densification occurs from the inside out, hence no crusting occurs allowing fibre reinforced SiC_f/SiC CMCs to be produced in 3 – 4 days instead of 3 months.

- The final matrix is almost fully dense with no density gradients and the cold zone restricted to the surface, which can be machined off or infiltrated conventionally.

- The work is now being broadened to C_f-HfB_2 composites with the aim of developing materials that can withstand temperatures up to approx. 3000°C. RF heating is needed, but the principles are the same.

Thank You

Acknowledgements

- We would like to thank all of our co-workers, Bala Vaidhyanathan, Anish Paul, Prabhu Ramanujam, Dhava Ramachandran, Virtudes Rubio, Saranya Venugopal, Ji Zou, Penxiang Zheng and all of the other students and interns who have been involved.
- The research on microwave CVI of SiC_f-SiC composites is funded as a PhD studentship by the University of Birmingham in support of the XMat grant from EPSRC.
- Some of the research reported here was performed under a Project Arrangement between DSTL in the UK and AFRL in the USA, whilst other research was funded by MBDA under the ITP programme.

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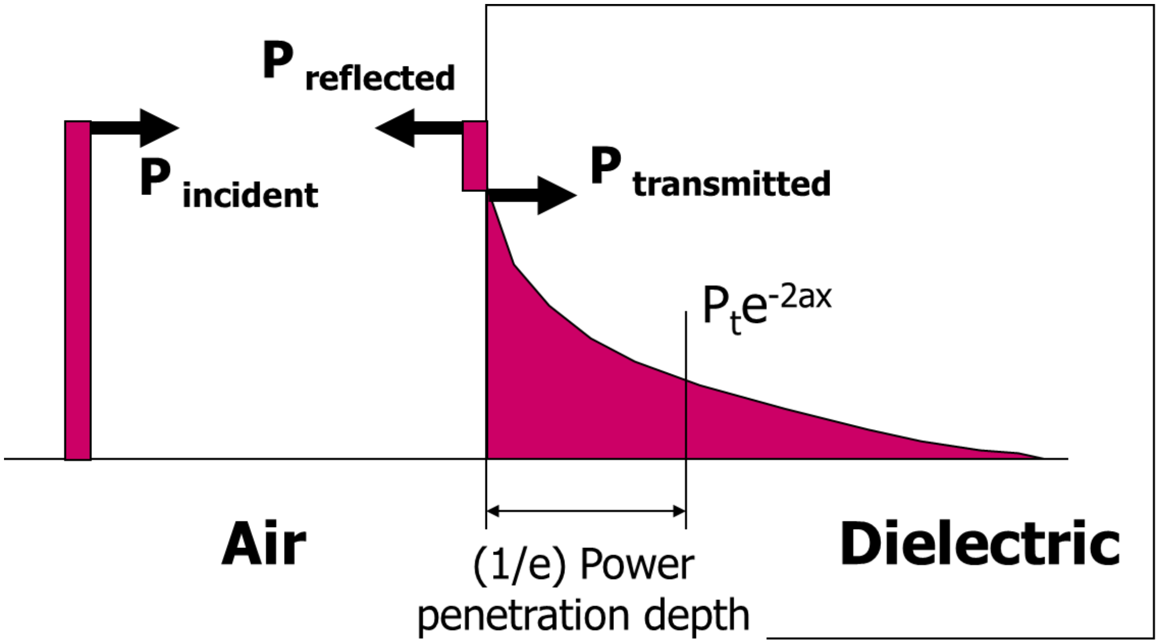
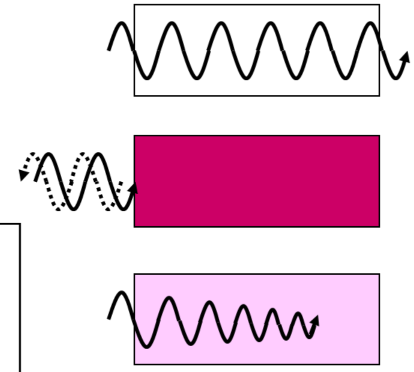
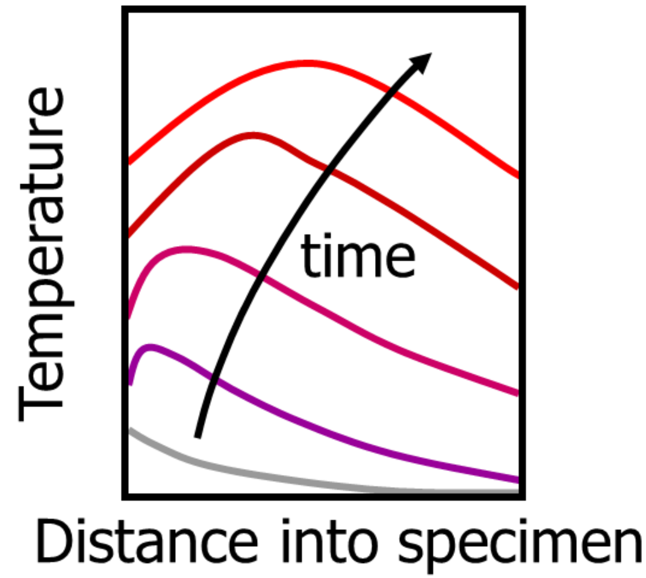
Inverse Temperature Profile







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