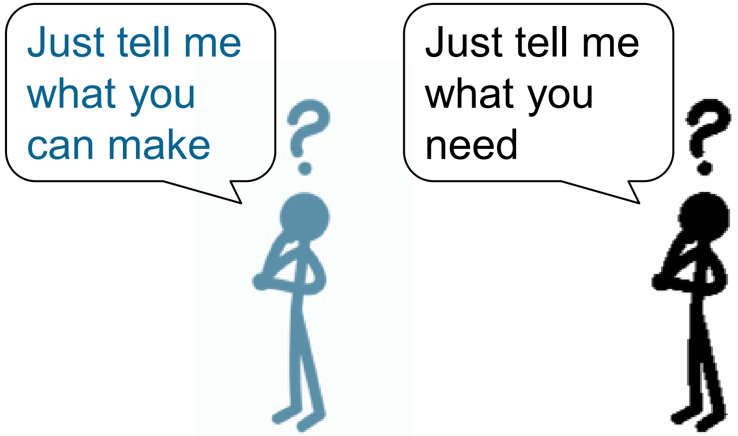
A Buffet Table of CMCs
An Update

Prof Jon Binner
School of Metallurgy & Materials
University of Birmingham, UK

High & Ultra-high Temp. CMCs



Designer

Materials scientist & engineer

The goal is to design and develop new ceramic-based composites that offer a wide range of (tuneable) properties; effectively a ‘buffet table’ of ceramic composite materials.

‘New Routes’

- UoB is examining a number of non-standard processing routes to achieve new CMCs for the ‘buffet table’, including the use of:
    - **Prepreg-based approaches to Ox-Ox CMCs**
    - **Weak interface Ox-Ox CMCs**
    - **Graded UHTCMCs**
    - **Additive manufacturing of CMCs**
    - **Polymer-derived ceramics**
    - **Joining and repair of ceramics**
- The advantages and challenges of each route will be highlighted.

Ox-Ox CMCs

Thomas Nelson

Question: *Can towpreg-based CMCs be made by adapting the process used for making polymer matrix composites?*

Approach: Towpreg used as feedstock for automated fibre placement (AFP) to avoid hand lay-up.

Sintered similarly to traditional ox-ox CMCs.

Image from Coriolis Composites

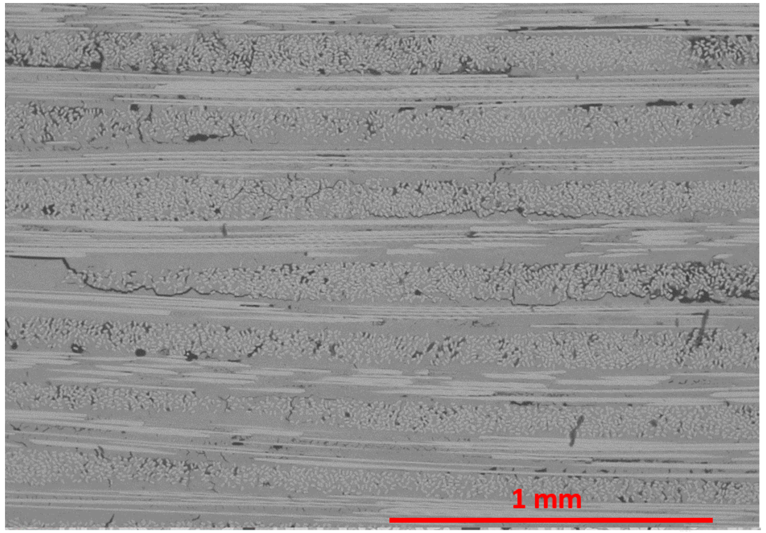
Ox-Ox CMCs

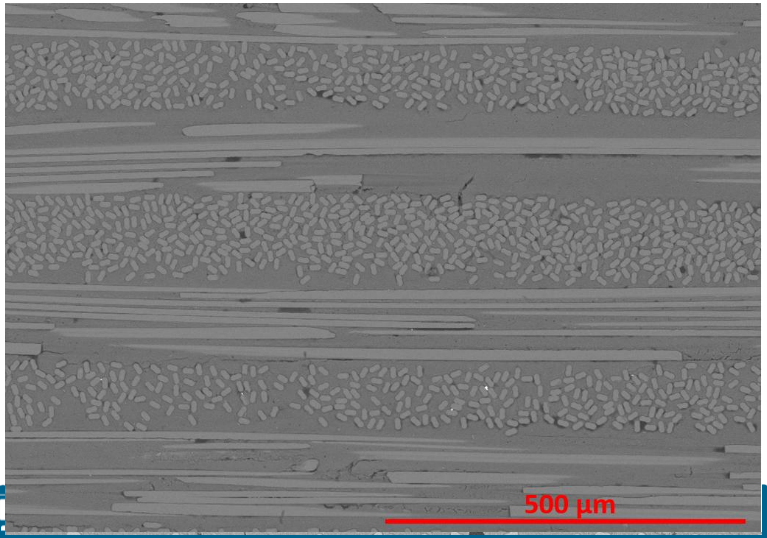
Benefits:

- Complex geometries possible
- Fibre orientation can be tailored to match stresses exerted on component
- Comparable microstructure to optimised woven fabric pre-preg systems

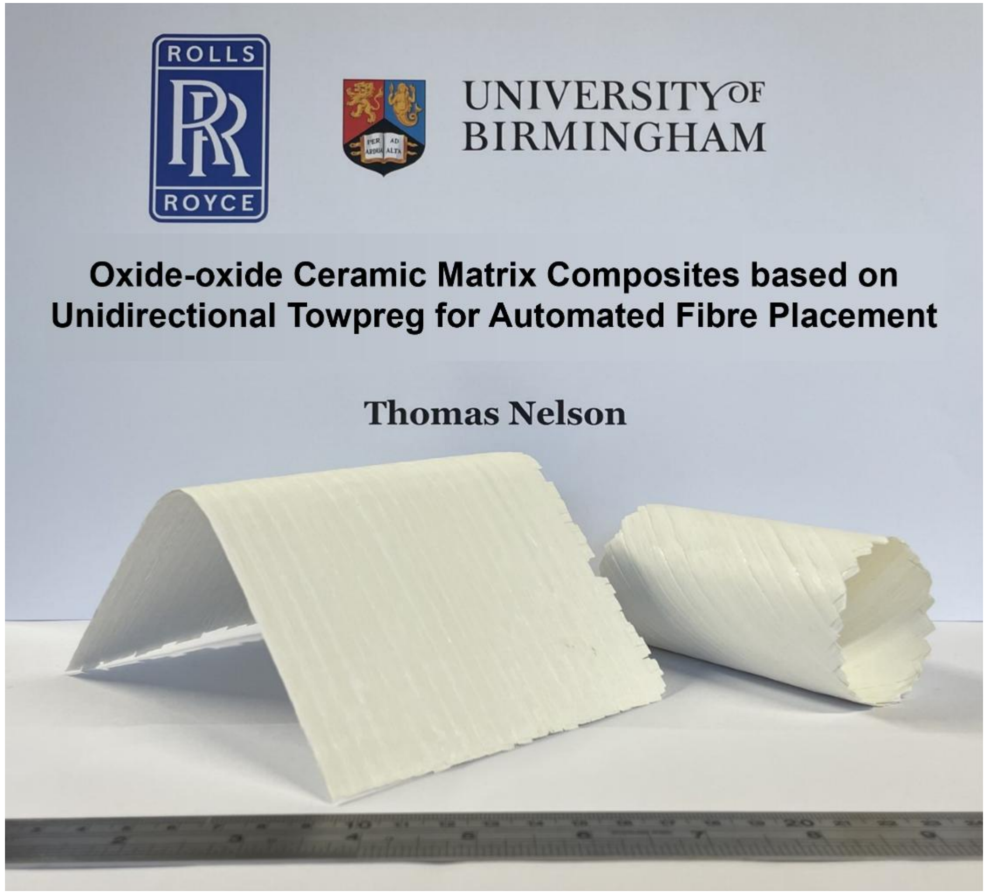
Challenges:

- Tow impregnation
- Dried slurry causes issues with consolidation
- High, autoclave pressures required for consolidation
- Gaps remain between tows if processing sub-optimal

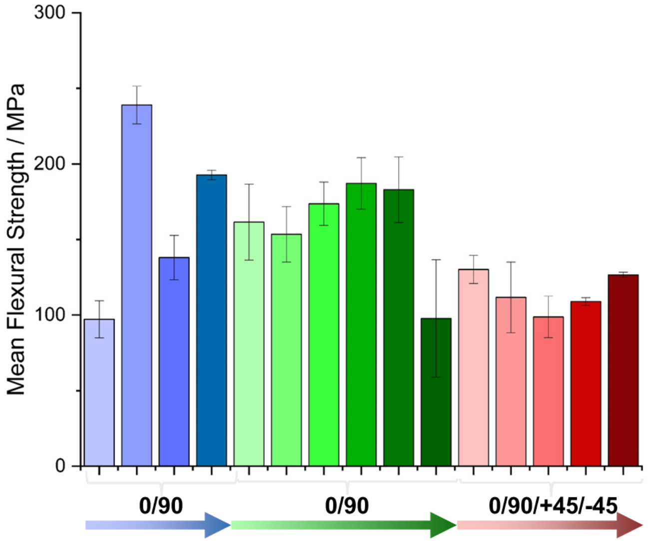


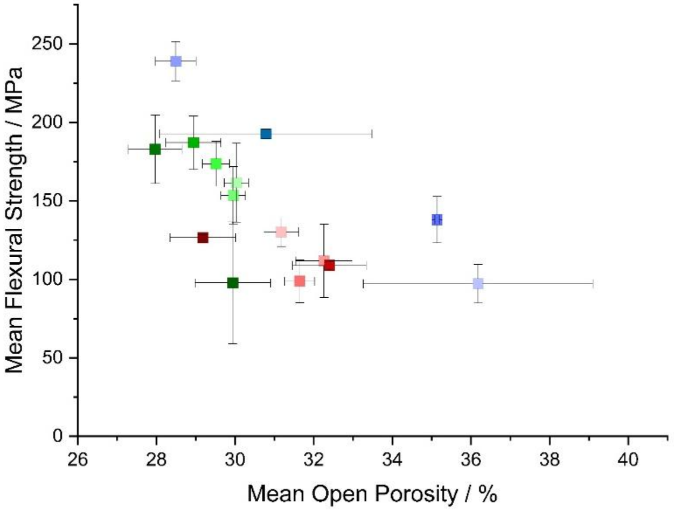


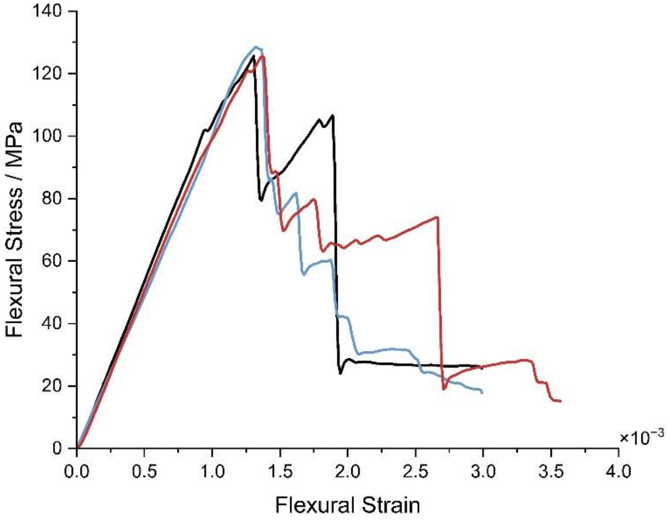
Ox-Ox CMCs


Oxide-oxide Ceramic Matrix Composites based on Unidirectional Towpreg for Automated Fibre Placement

Thomas Nelson



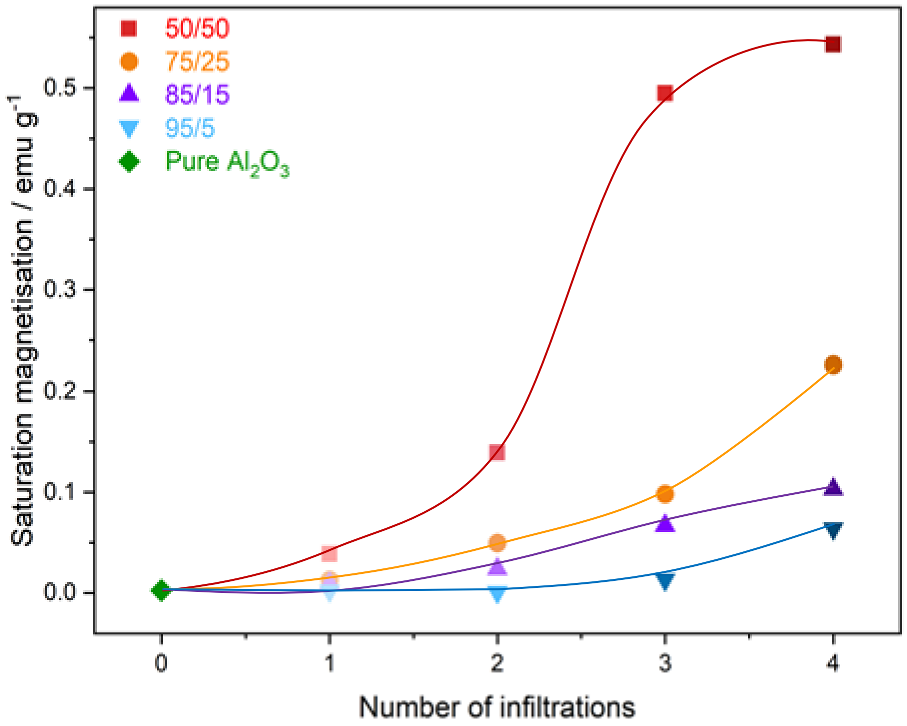


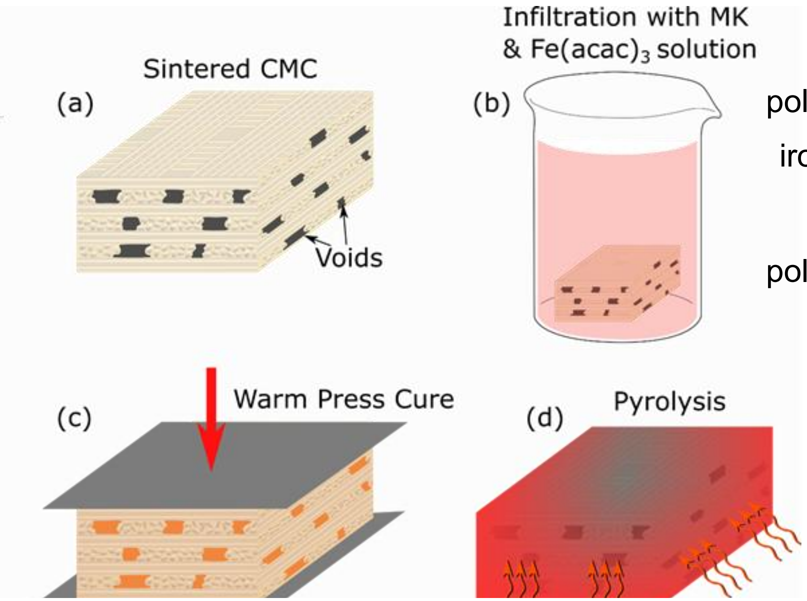


Ox-ox diffuser

Polymer-derived Ox-Ox CMC with soft magnetic properties

The main objective was to assess the feasibility of creating a soft magnetic ceramic matrix composite





Silres MK powder: polymethylsilsesquixoane

iron(III) acetylacetonate
↓
iron-modified polymethylsilsesquioxane
↓
FeSiOC

Magnetic properties were successfully incorporated and soft ferromagnetic behaviour achieved.

Potential applications include electric motors, transformers, electronics and magnetic shielding.

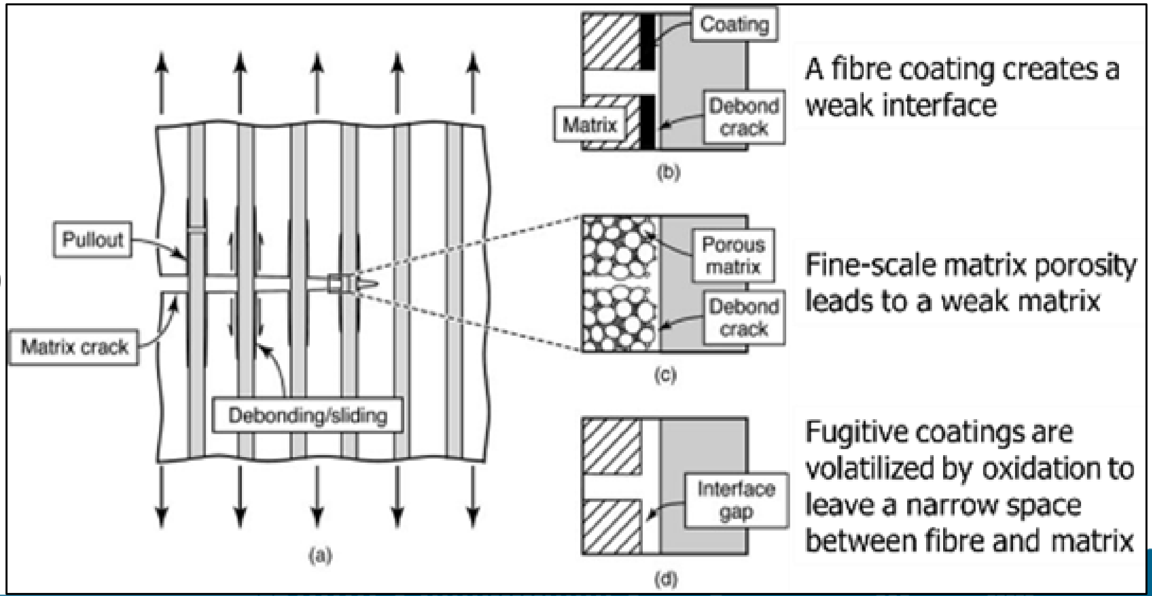
Ox-Ox CMCs

Dr Zhongmin Li

Question: *Can dense Ox-Ox CMCs be made with an appropriate fibre coating that will provide the weak interface toughening mechanism?*

Approach: The idea was tried in the 1990s but failed; this is why we have weak matrix Ox-Ox CMCs. So, the idea was to use microwave-enhanced chemical vapour infiltration to deposit an alumina matrix around coated alumina fibres. Since alumina is (more or less) microwave transparent at room temperature, the coating had to fulfil two roles; a good microwave absorber and a suitable weak interface.

Coatings investigated included: carbon, zirconia & monazite (lanthanum phosphate)



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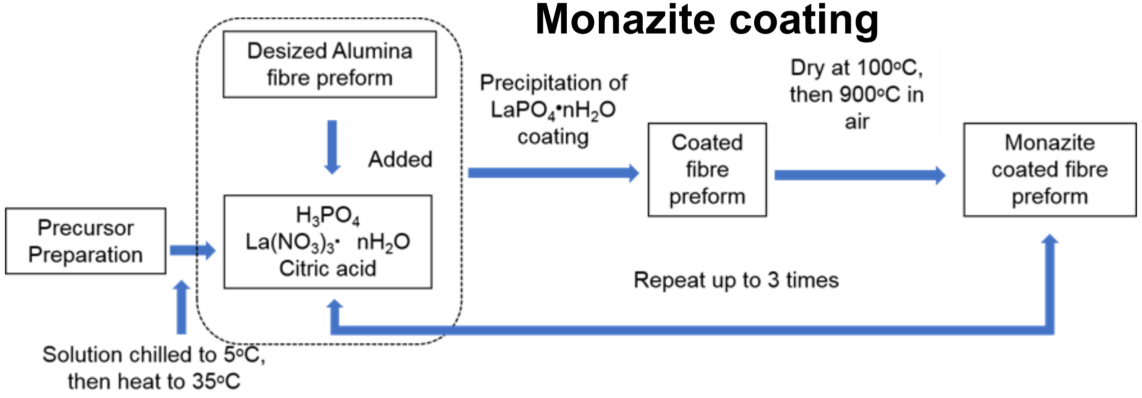
Ox-Ox CMCs

Monazite coating


Desized Alumina fibre preform

Added

Precursor Preparation

H_3PO_4
$La(NO_3)_3\cdot nH_2O$
Citric acid

Solution chilled to 5°C, then heat to 35°C

Precipitation of $LaPO_4{\bullet}nH_2O$ coating

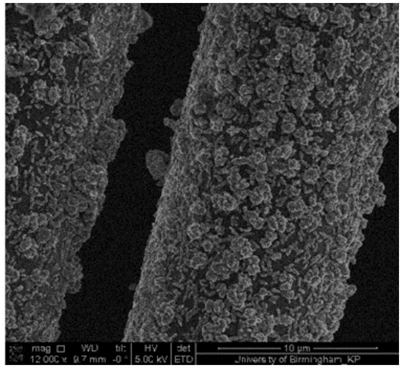
Coated fibre preform

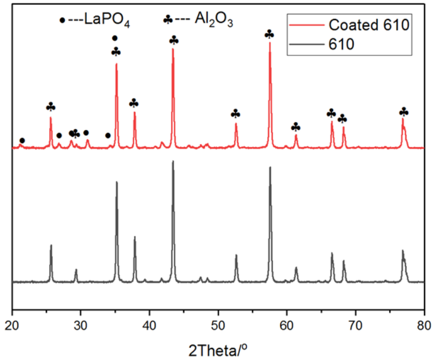
Dry at 100°C, then 900°C in air

Monazite coated fibre preform

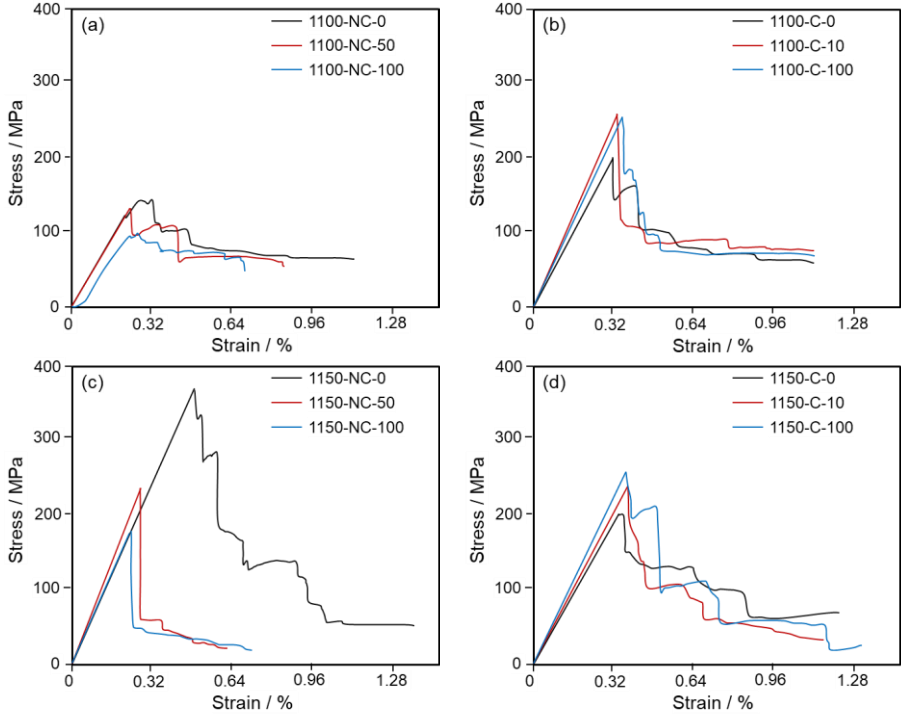
Repeat up to 3 times

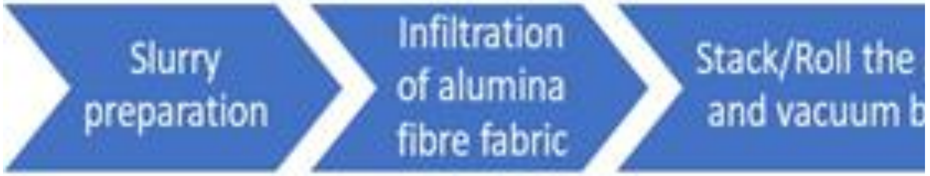
$$La(NO_3)_3\text{-}nH_2O + H_3PO_4 \rightarrow LaPO_4\text{-}nH_2O + 3HNO_3$$





Low cost, WIC ox-ox CMCs by prepreg route





- Coating promoted non-brittle failure, even after 100 h at 1200°C.
- Coated CMCs increased in strength after thermal ageing (unexpected).
- Uncoated CMCs displayed brittle failure after just 10 h at 1200°C and strength significantly reduced.

Monazite-coated CMCs very promising as low cost materials for long periods at high temperatures.

Advantages and Challenges

Towpreg-based processing offers:

+

- Ability to make complex geometries.
- Storage easy due to ‘dry’ nature.
- Controllable fibre orientation.
- Comparable microstructures to conventional CMCs (high pressure autoclave best process).
- Seems it may be possible to produce weak interface Ox-Ox CMCs.

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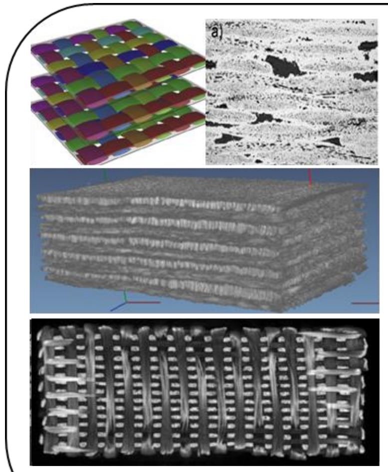
- Tow impregnation challenging.
- Dried slurry causes issues with consolidation.
- Current limitations with high T performance of oxide fibres.

UHTCMCs

The UoB approach

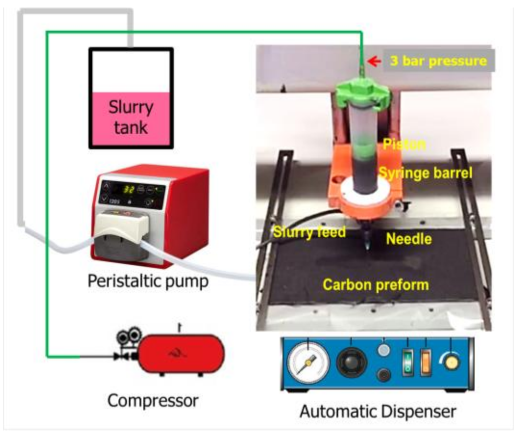


Stacked 2D

Needled 2.5D

Woven 3D

Fibre preforms



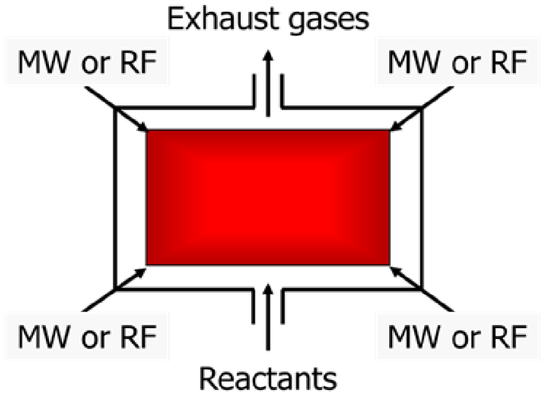
Impregnate with powder using injection vacuum impregnation

Impregnation technique that yields excellent, and local, control

Dr Vinu Venkatachalam
Dr Becky Steadman

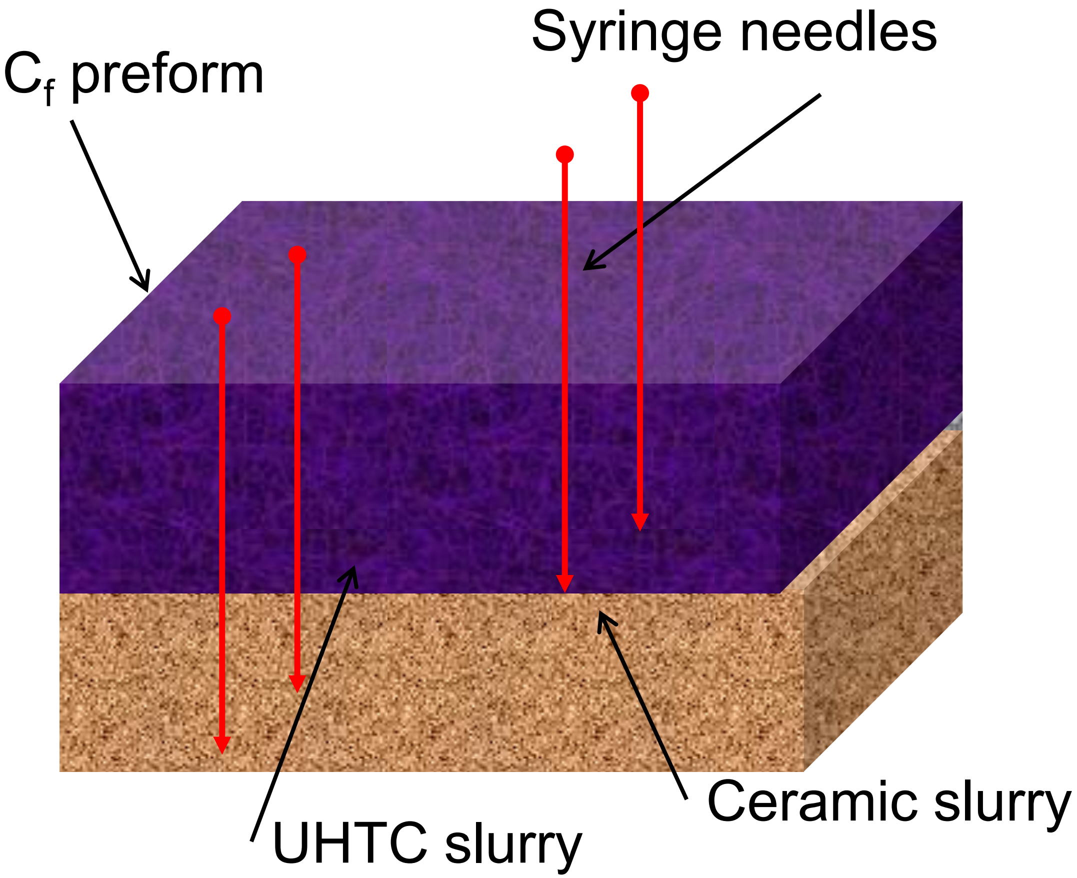
Infiltration technique that yields excellent micro-structures AND much faster than conv. CVI

MW or RF CVI



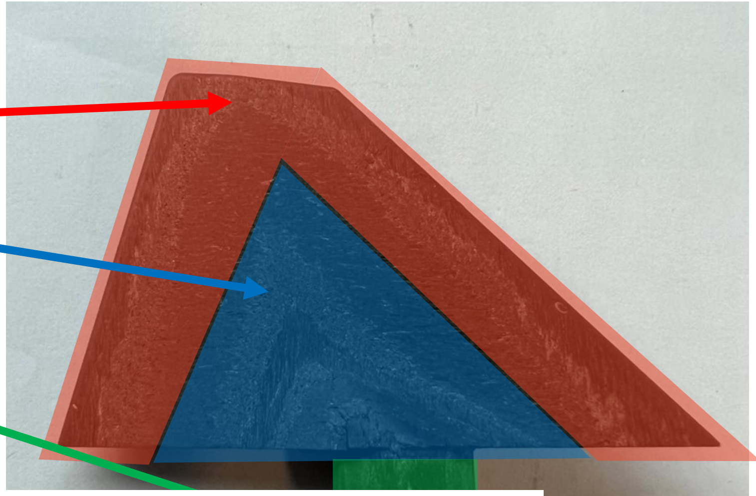
Matrix infiltrated using CVI

Injection vacuum impregnation, IVI

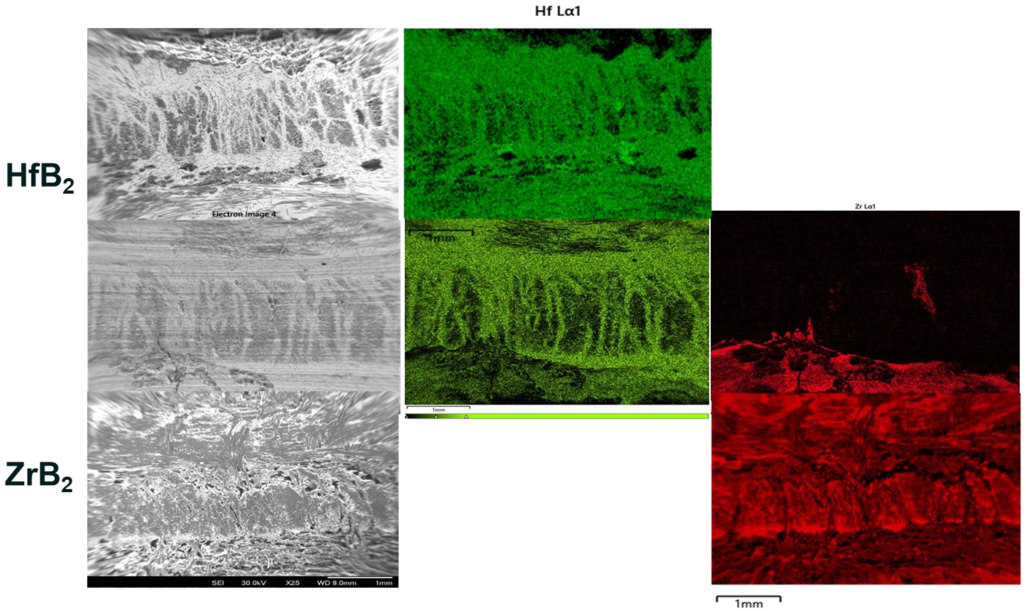


Graded UHTCMC jet vane produced:

- HfB_2
- ZrB_2 or SiC core
- SiC stem

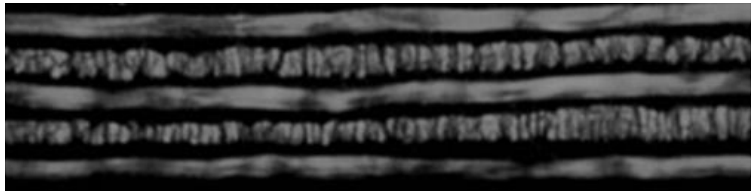


Mate l	np.
Hf	
Zr	
Si	



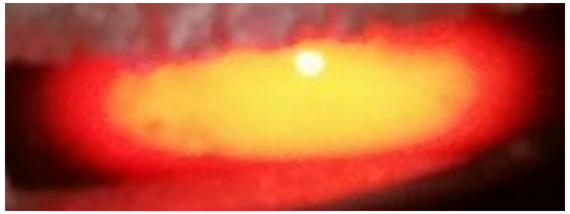
C_f – $Hf/ZrB_{2\ p}$ – C_m Composites

2.5D preform



RF-CVI gas flow

Uniform
RF heating



1000°C
CH_4: 800 ml min^{-1}
H_2: 200 ml min^{-1}

A formal analysis done by QinetiQ indicated that the jet vanes could be made for ~£120 each (based on a 0.4 m³ chamber)

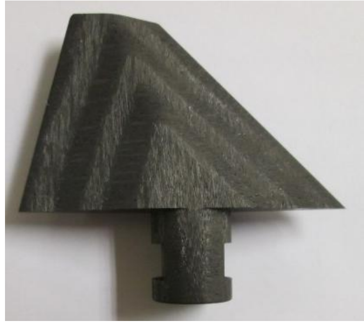
21 h infiltration:	Conventional CVI:
6 h at 5 mbar *16 h at 500 mbar*	~1000 h
10 vol% porosity	11 vol% porosity

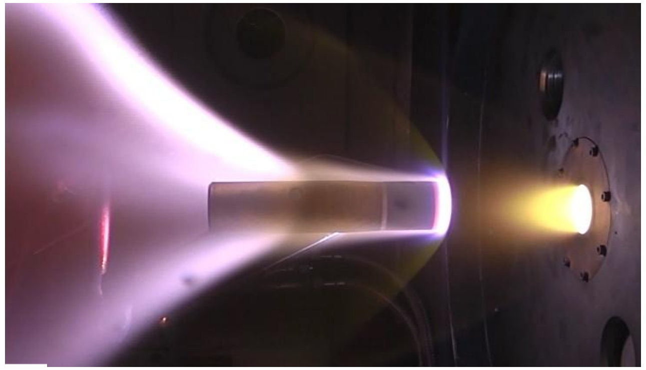
- **Near net shape process**
- **Reduces the processing time by ~40x**
- **Reduces the energy used – and hence costs**
- **Materials can be easily tailored**
- **Scaling up underway**

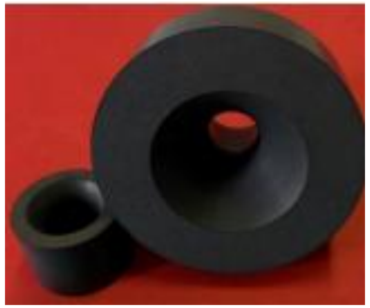
C_f – Hf/ZrB$_{2\,p}$ – C_m Composites

- Cf-HfB$_2$ composites can withstand temps. of ~3000°C, heat fluxes of ~17 MW m^{-2} and gas velocities of about Mach 6 for many minutes.
- Cf-ZrB$_2$ composites are approx. an order of magnitude cheaper, approx. 50% less dense and will withstand ~2500°C for many mins.
- Both can take heating rates of >1000°C s^{-1}.
- Materials can withstand multiple cycles under these conditions.
- Graded materials can also be made, where the composition changes across the component.

Edited video of 1 min OAT test

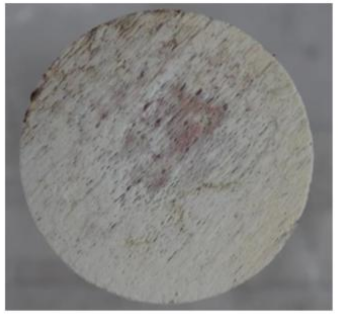




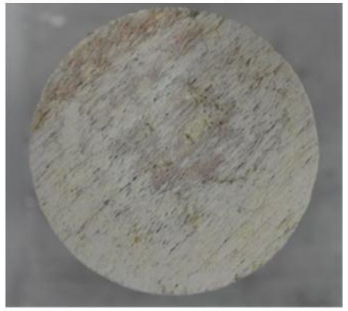


After 1st cycle

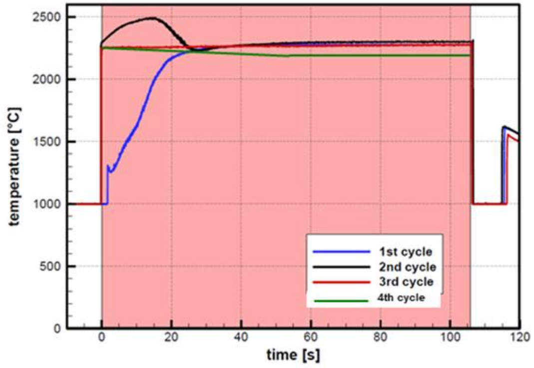
After 2nd cycle



After 3rd cycle



After 4th cycle



Advantages and Challenges

UHTCMCs made by RF-CVI offers:

⊕

- Materials that can survive multiple cycles up to ~3000^{o}C with Mach 5 gas flows & 1000^{o}C s^{-1} heating rates.
- Excellent compositional & microstructural control; grading possible.
- Low processing temp. (~1000^{o}C); no risk of fibre damage.
- 24 h is MUCH faster than the ~1000 h of conventional CVI.

⊖

- CVI results in ~10% residual porosity (RF-CVI is slightly better).
- Even 24 h is still a long process.

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Additive Manufacturing, AM

Dolly Ye

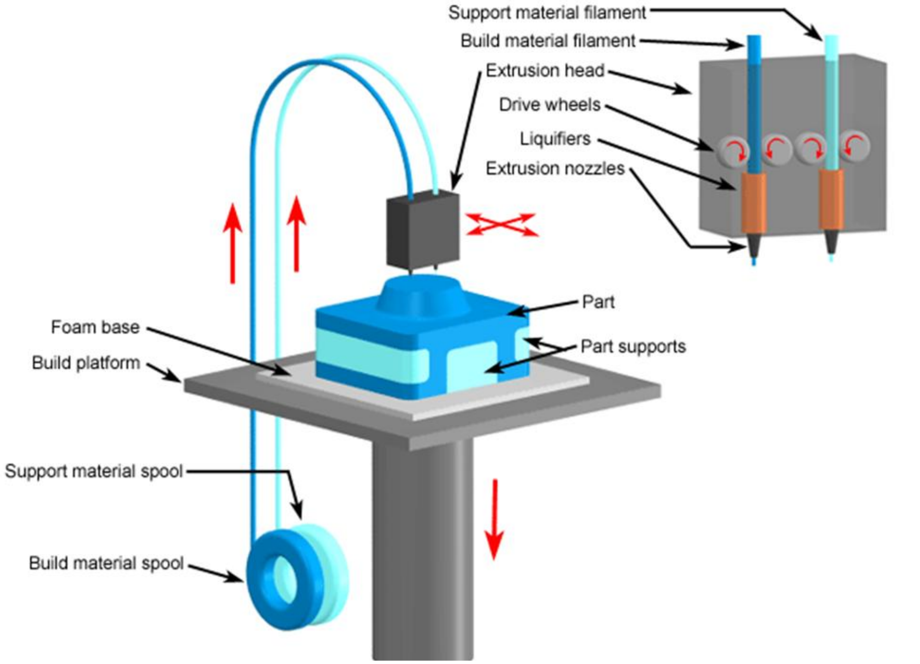
Question: *Can we use additive manufacturing to create fibre-reinforced CMCs?*

Approach: AM offers new opportunities to manufacture ceramic components without the need for expensive tooling, thereby potentially reducing production costs, lead times and increasing design freedom.

In conv. FFF a polymer is extruded through a heated nozzle, where it hardens and bonds to the layer below. The process is repeated and the part built layer-by-layer.

Having multiple nozzles allows different material types to be deposited simultaneously.

Goal: To adapt FFF to allow the production of *continuous* C_f-reinforced SiC CMCs.

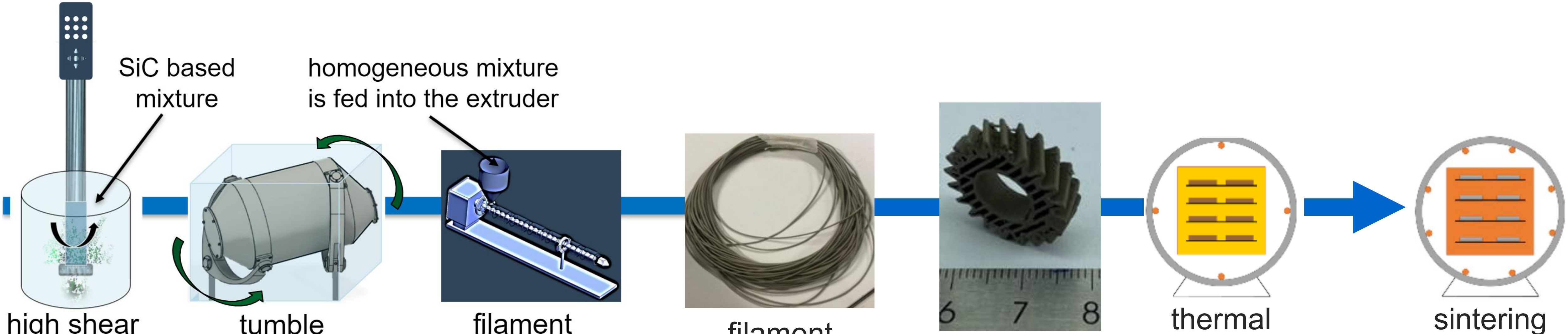


https://www.custompartnet.com/wu/fused-deposition-modeling

Fused Filament Fabrication, FFF

FFF of CMCs

Ceramic filament preparation



SiC based mixture

homogeneous mixture is fed into the extruder

high shear mixing

tumble mixing

filament extrusion

filament

printed part

thermal debinding

sintering

DSC, FTIR & SEM used to design filament composition and evaluate filament homogeneity & potential degradation during processing

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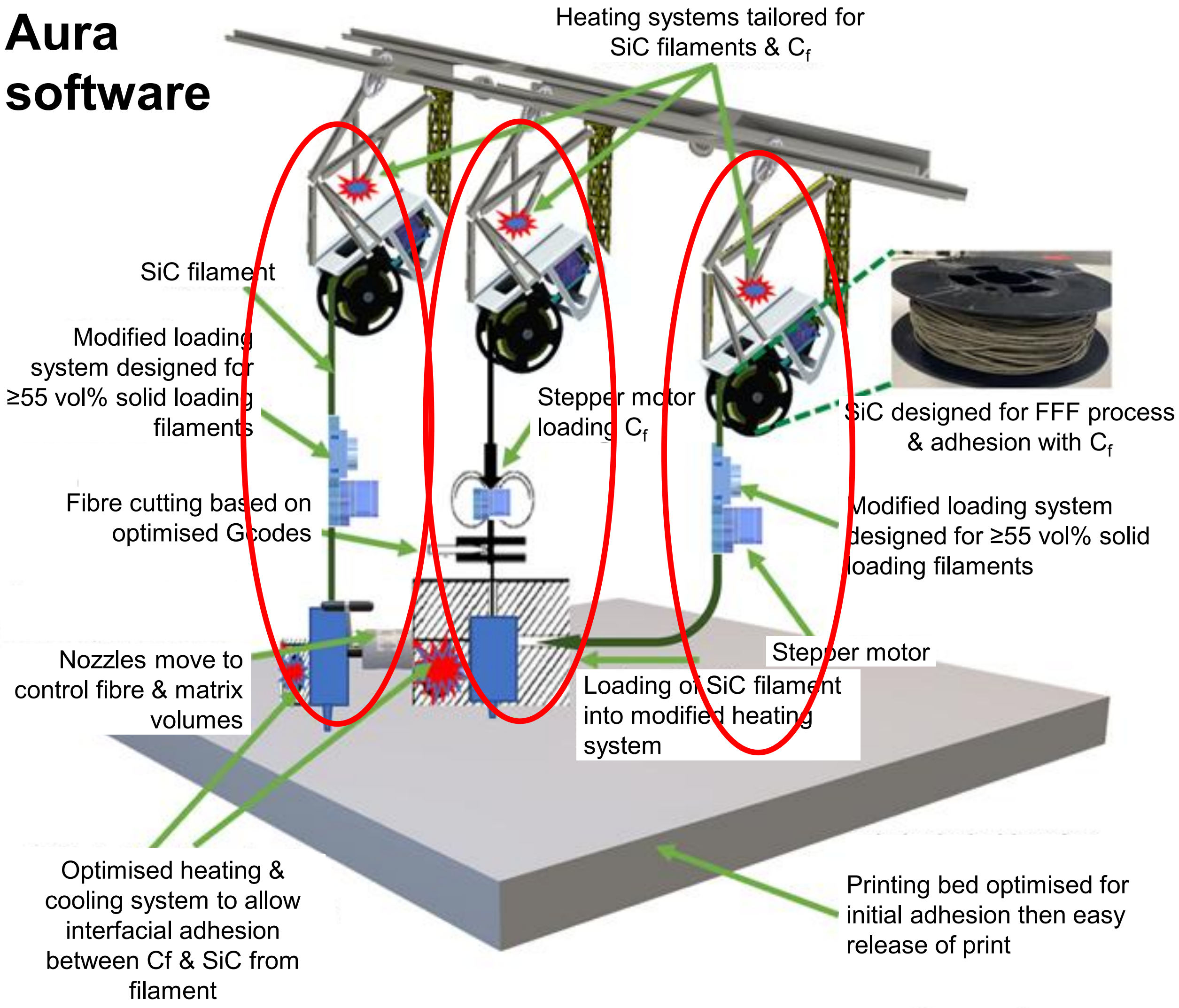
Printing

Anisoprint FFF Composter A4 Aura software



Heating systems tailored for SiC filaments & C_f

SiC filament

Modified loading system designed for ≥55 vol% solid loading filaments

Fibre cutting based on optimised Gcodes

Nozzles move to control fibre & matrix volumes

Optimised heating & cooling system to allow interfacial adhesion between Cf & SiC from filament

Stepper motor loading C_f

SiC designed for FFF process & adhesion with C_f

Modified loading system designed for ≥55 vol% solid loading filaments

Stepper motor

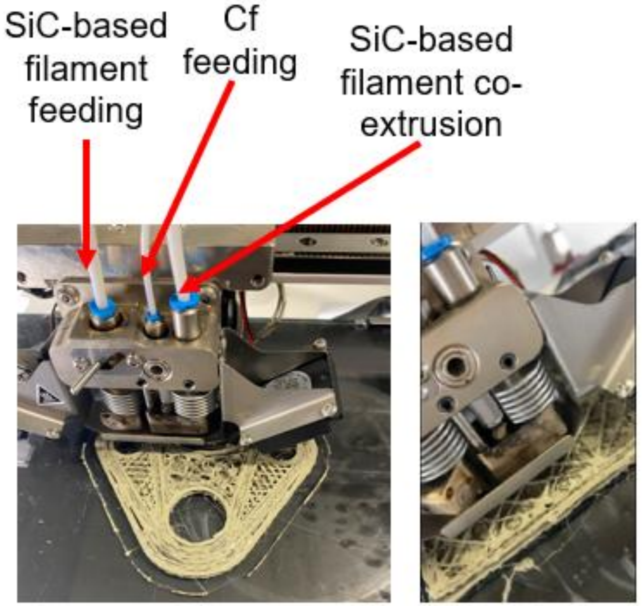
Loading of SiC filament into modified heating system

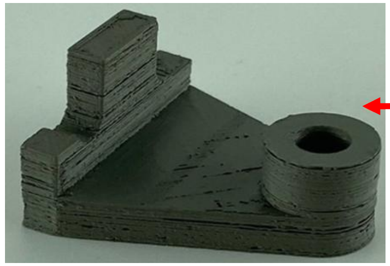
Printing bed optimised for initial adhesion then easy release of print

The 3rd nozzle is starting to be used to print SiC-based matrix to achieve complex geometries and local variation in composition.

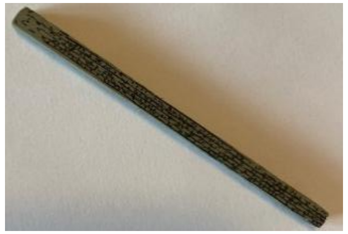
Hence essential to control solidification rate

Outputs



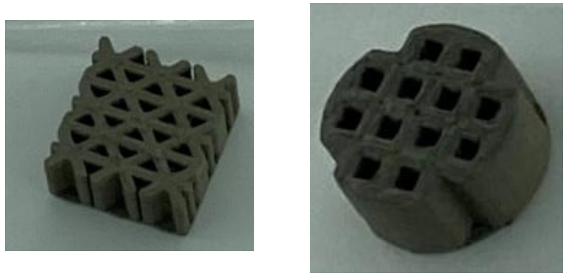


Manufacturing video x100

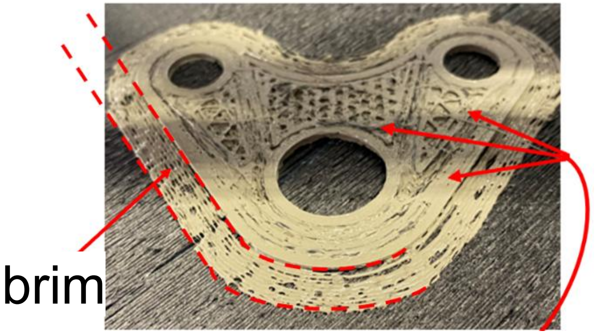


2D (0° / 90°) C_f reinforced 4-point bend bars

Continuous carbon fibre reinforced silicon carbide being made as an exemplar



Chopped C_f / SiC



Continuous C_f / SiC

Advantages and Challenges

AM of continuous fibre reinforced CMCs offers:

➕

- Manufacture possible
- Complex shape capability is good
- Short processing time (for AM)
- Thermo-mechanical and chemical properties appear to be tuneable
- Material doping and surface engineering possibilities may exist

➖

- Resolution needs improvement
- Properties still unknown, but measurements started (strength)
- Will almost certainly be limited to small production runs – not a mass manufacturing process

Preceramic Polymers

Dr Mohammed Younas & Dr Elia Zancan

Question: *Can using polymer-derived ceramics be of benefit?*

Approach: Involves the thermal conversion of preceramic polymers to ceramics; studied for decades it has rarely been employed to produce fibre reinforced ceramic matrix composites (FRCMCs).

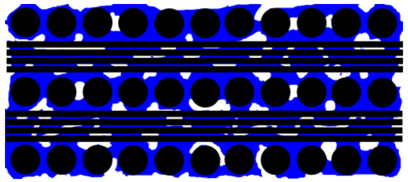
Advantages of preceramic polymers:

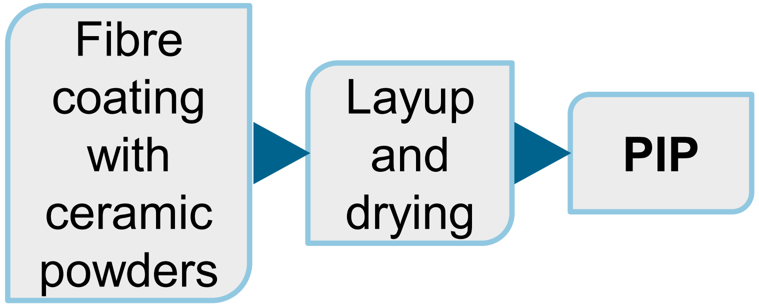
- Relatively low processing temperatures → consequent lower risk of fibre damage.
- Near net shape forming processes possible.
- Ability to tailor the ceramic microstructure for improved high temperature performance.

Processing via PIP

Dr Elia Zancan

C_f /ZrB_2-Si(Hf)CN





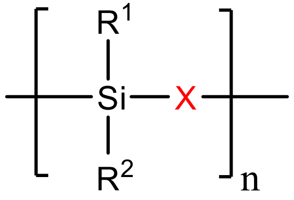
Fibre coating with ceramic powders

Layup and drying

PIP

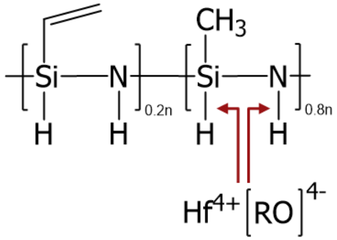
Manufacture

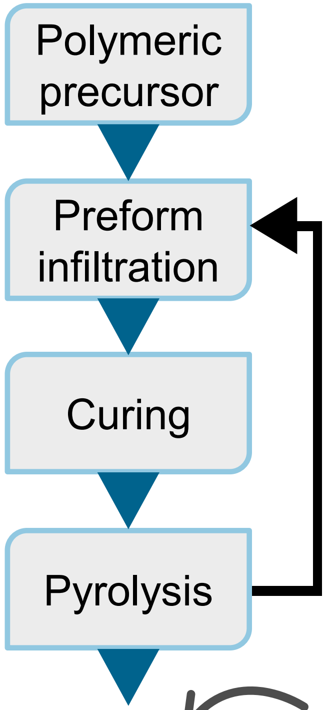
- Mostly Si-based



Polysiloxanes (X = O)
Polycarbosilanes (X = C)
Polysilazanes (X = N)

- Low T (1000-1500°C) conversion to ceramic
- Hf-dopant



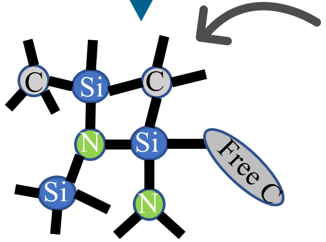


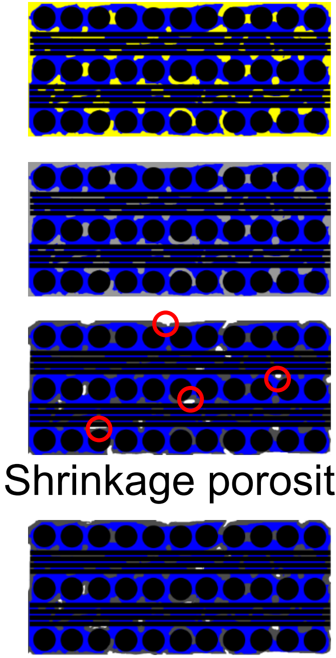
Polymeric precursor

Preform infiltration

Curing

Pyrolysis





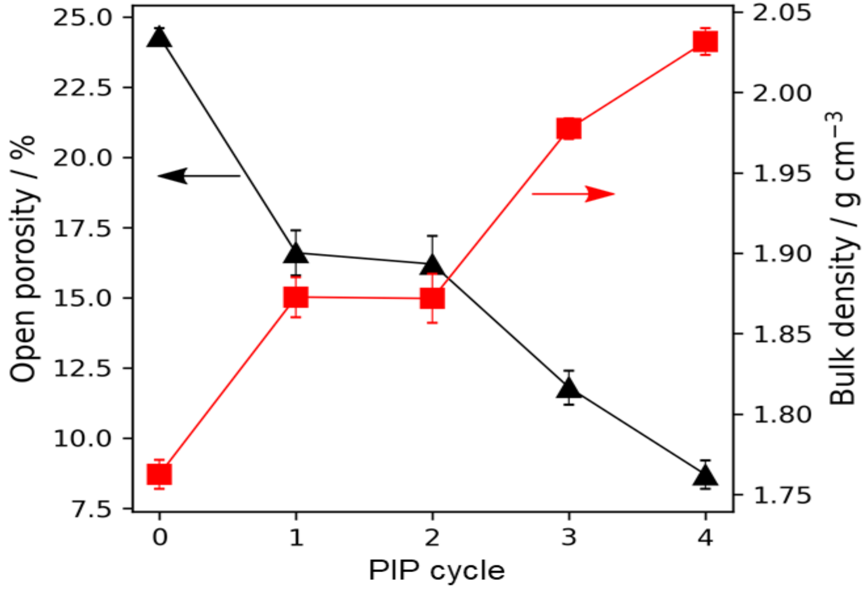
Shrinkage porosity

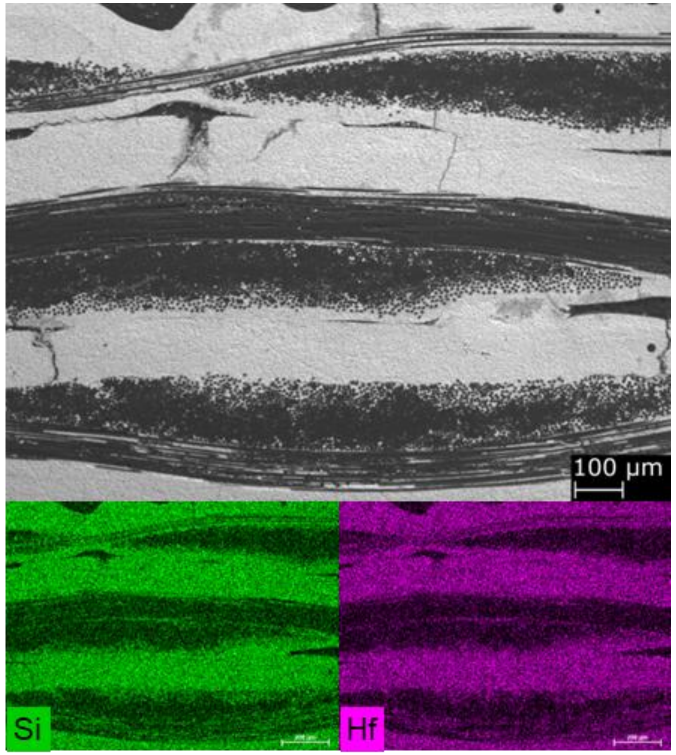
Amorphous matrix (residual porosity)

Results – Processing

C_f /ZrB_2-Si(Hf)CN

35×35×10 mm^3 C_f/ZrB_2-Si(Hf)CN sample with only 8.5% open porosity after only 4 PIP cycles.


C_f/ZrB_2-Si(Hf)CN



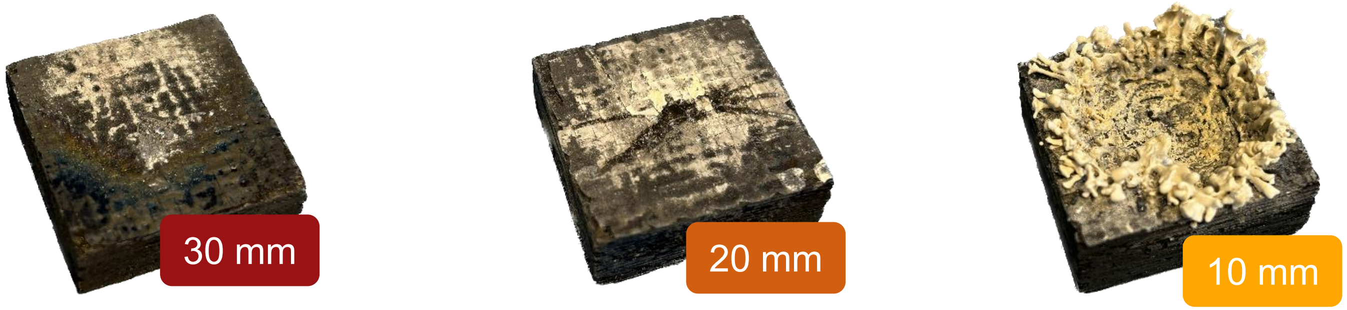
SEM & EDX maps at the centre of a 10 mm sample showing good precursor infiltration & homogeneity.

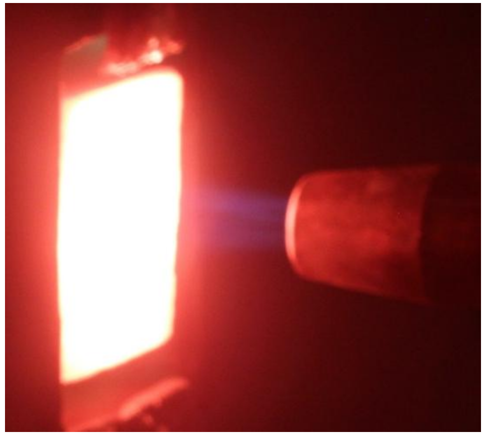
Results – Oxidation

C_f /ZrB_2-Si(Hf)CN

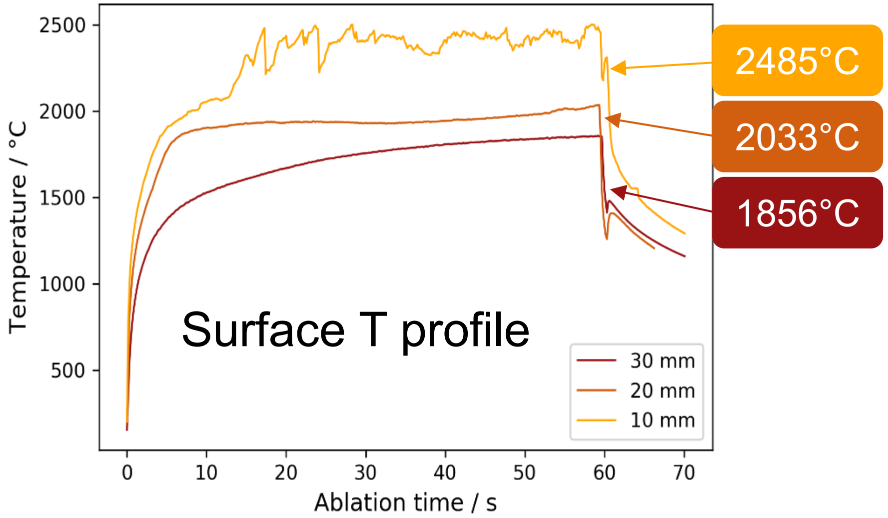
Oxypropane torch: 30, 20 & 10 mm for 60 s

35 × 35 × 10 mm³





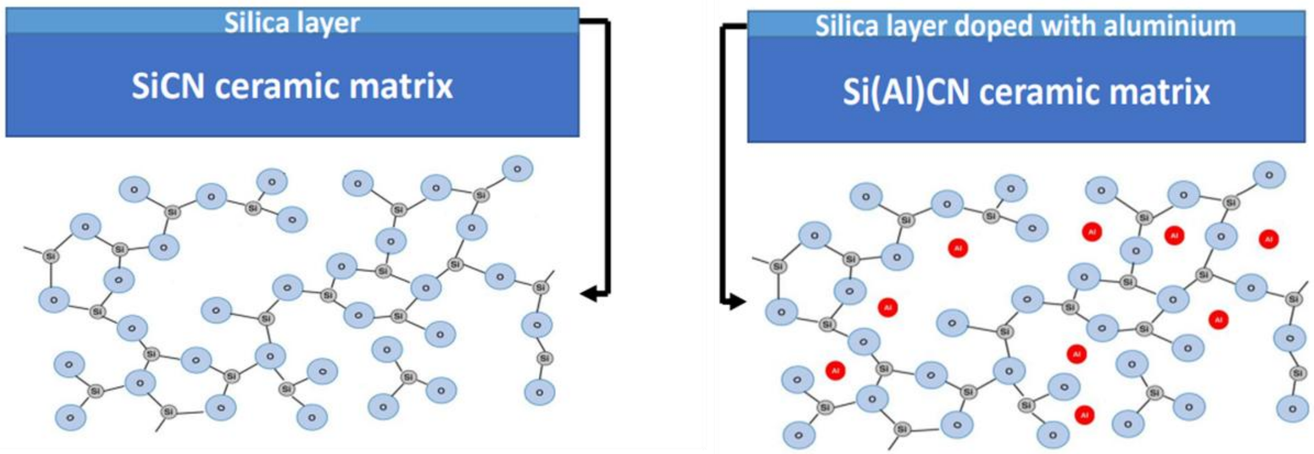
These CMCs offer at least 2000°C oxidation resistance



Internal Environmental Barriers

Si(Al)CN CMCs

- A Si(Al)CN matrix could act as an ‘internal environmental barrier’.
- Si(Al)CN results in the formation of an Al-doped silica layer. This prevents further oxygen ingression and is ‘self healing’ since the aluminium modification is an intrinsic part of the matrix.
- The modification reaction uses inexpensive chemical reagents and requires no post process treatment.

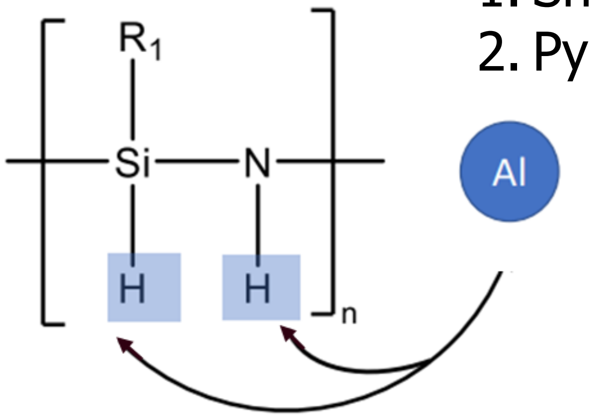


Synthesis of Si(Al)CN CMCs

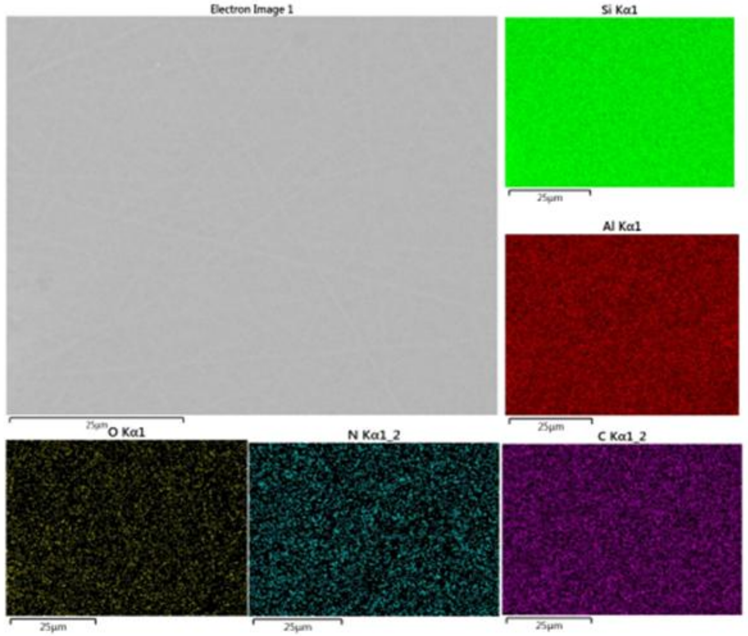
Si(Al)CN CMCs Aluminium is incorporated into the SiCN ceramic on the atomic scale

Doping polysilazane with Al

1. Shape & crosslink
2. Pyrolysis

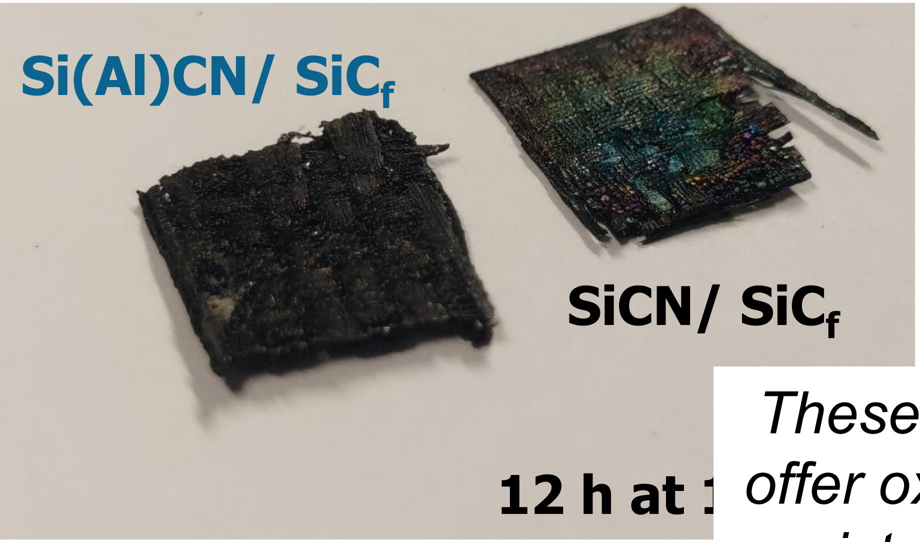


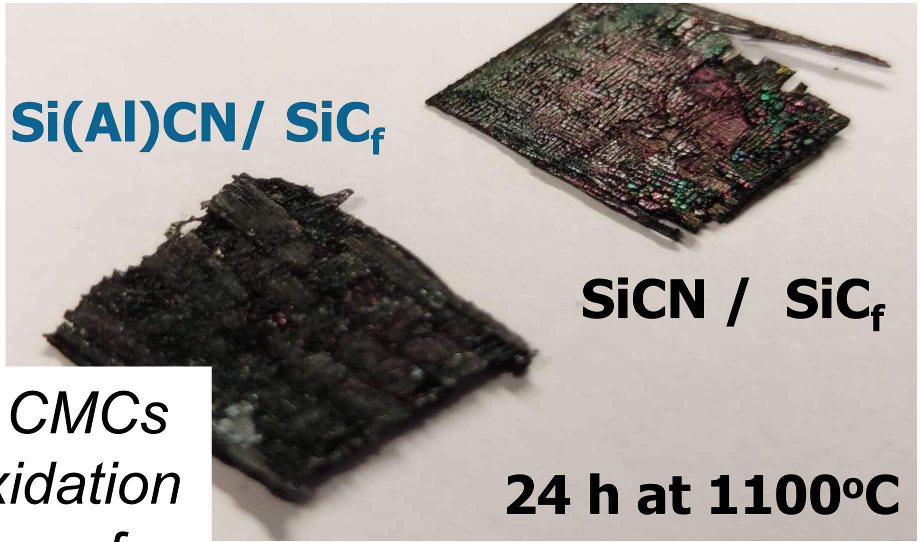
Al modification occurs at both the Si-H and N-H bonds

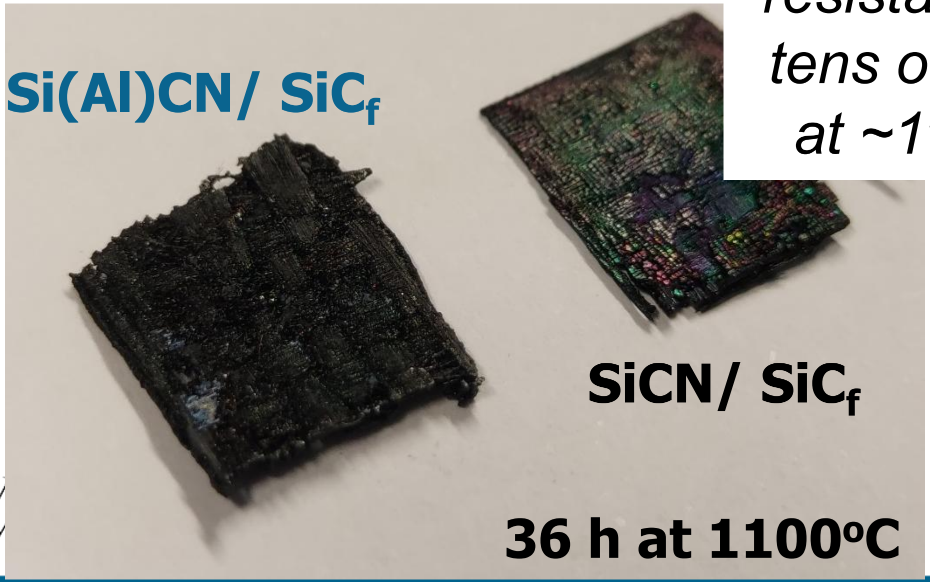


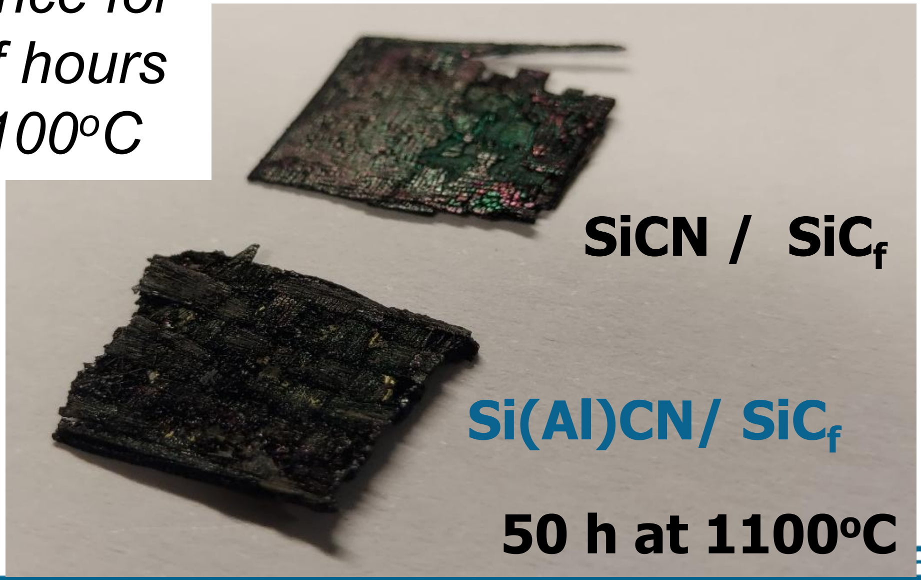
SEM image of the Si(Al)CN ceramic showing Al is atomically distributed

High Temperature Oxidation Tests









These CMCs offer oxidation resistance for tens of hours at ~1100ºC

Advantages and Challenges

➕

Use of PDCs to make fibre reinforced CMCs offers:

➖

- Lower processing temperatures.
- Fine microstructure tuning with functionalisation & processing conditions, e.g. doping.
- Almost certainly applicable to AM processing.

- Limited material selection and handleability with regards to toxicity and air sensitivity of certain preceramic polymers.
- Multiple PIP cycles required (increases time and cost).
- Limit to maximum density achievable.

Joining and Repair

Dr James Alexander & Dr Leyla Yanmaz

Question: *How well can we join ceramics & CMCs and can we repair them?*

Approach: Ceramic / CMC components are rarely used on their own, what are the pros and cons of different joining techniques? Also, can we repair them, either to salvage a component during manufacture or to extend service life?

Activities include:

- Benchmark commercial adhesive offerings.
- Investigate other joining approaches, e.g. brazing, transient liquid phase bonding (TLBP), etc.
- Determine the state of the art for the repair of both monolithic and composite ceramics.

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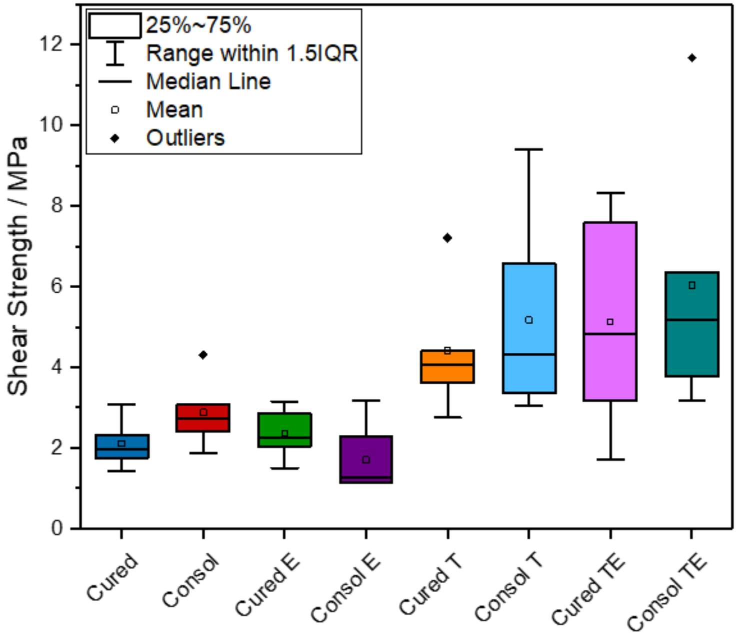
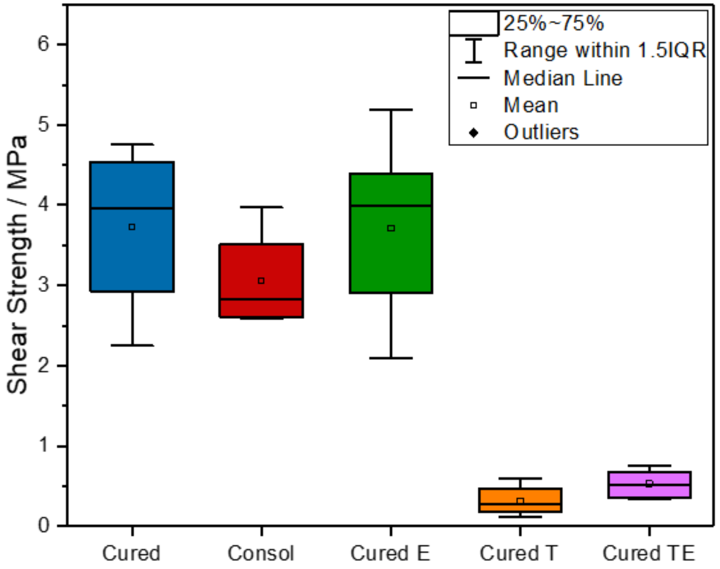
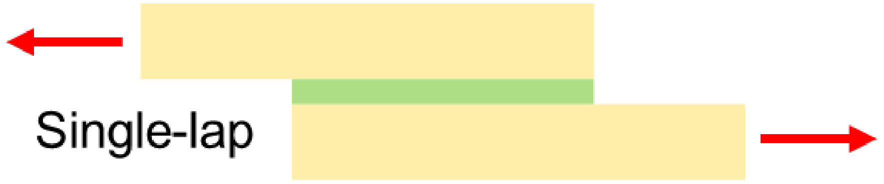
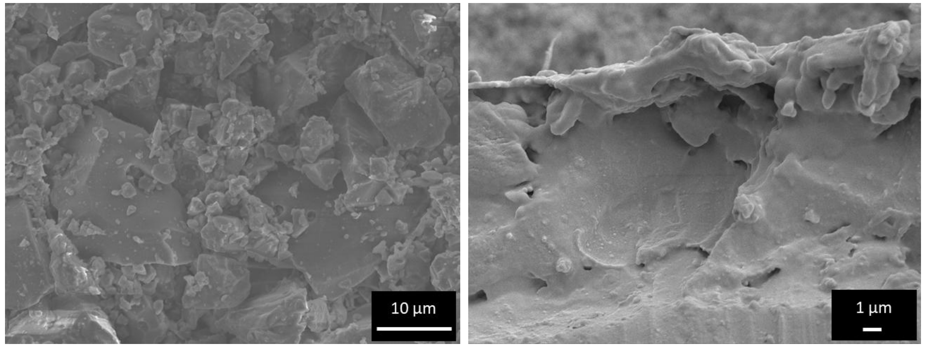
Joining

- ☐ Very large number of commercial adhesives investigated
- ☐ Alumina-alumina monolithics mainly tested to date
- ☐ Influence of humidity and thermal cycling investigated







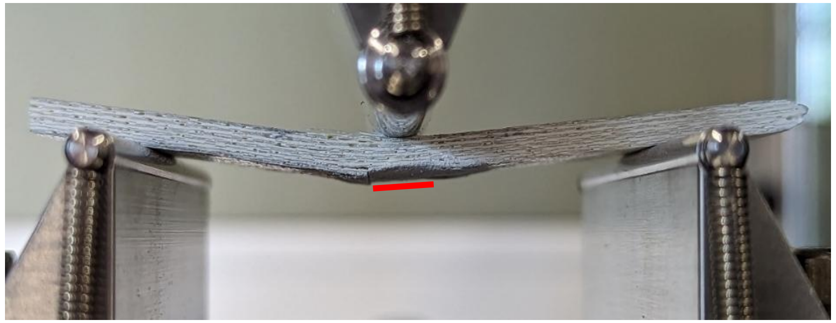


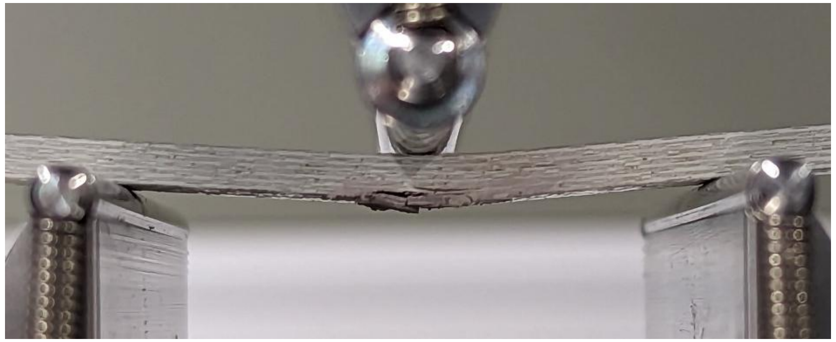
In general, commercial ceramic adhesives found to be very disappointing

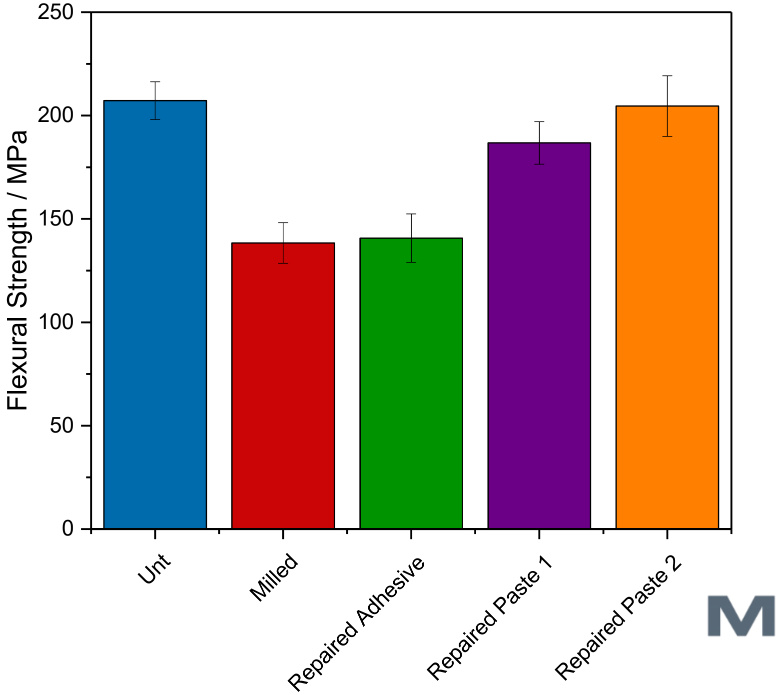
Repair

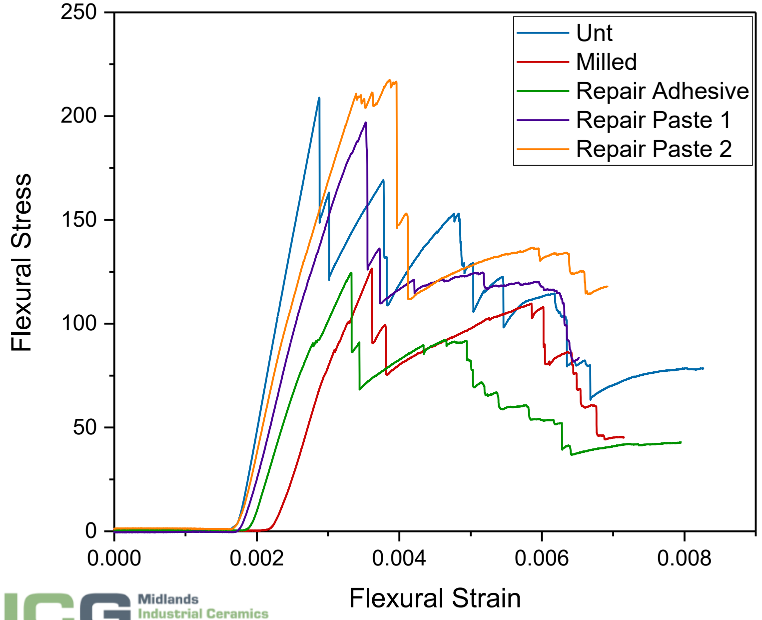
- ☐ Original strength: ~210 MPa
- ☐ Commercial adhesive: ~140 MPa
- ☐ UoB paste #1: ~190 MPa
- ☐ UoB paste #2: ~205 MPa

Approx. full strength restored









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Advantages and Challenges

Early perspectives on
joining & repair:

- Joining is definitely needed for a wide range of ceramics and to a diverse range of materials!
- Some success being found in terms of repair of ox-ox CMCs.

- Commercial ceramic adhesives don’t seem to be very good.
- Considerable further work needed; we are just scratching the surface.

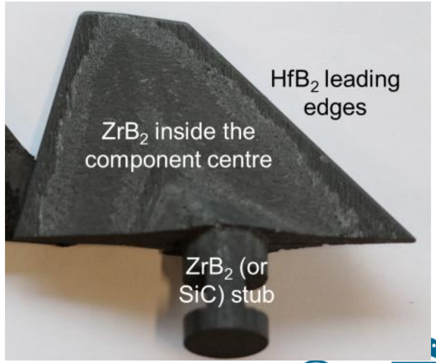
Conclusions

- CMCs are increasing significantly in their use in a diverse range of applications, from around 1100 – 1200^{o}C for ox-ox up to 2500 – 3000^{o}C (*combined* with multiple Mach gas flows & very high heat fluxes) for UHTCMCs.
- They can be made by a variety of different manufacturing routes, with different processes being suitable for different compositions and structures.
- We have an increased opportunity to *design* compositions and manufacturing routes that yield improved properties (and greater control of them) and hence superior performance.

Ox-ox diffuser

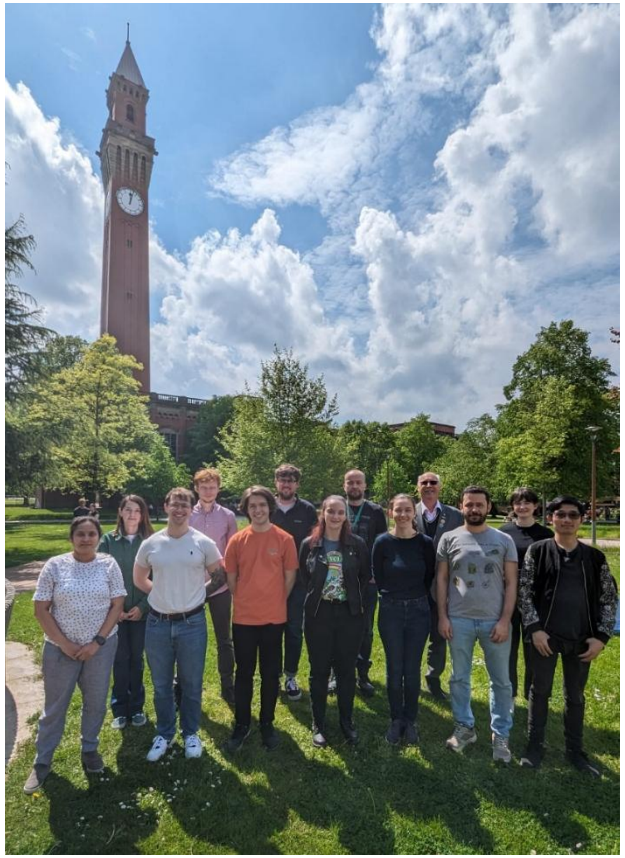
SiC-SiC tubes

Graded or ungraded UHTCMC jet vanes



The buffet table is growing!

Thank you for your attention



Thanks to my research team, especially:

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Dr Leyla Yanmaz

Dolly Ye

Dr Mohammed Younas

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And, of course, our sponsors!