SiOC- und SiC-Faserverbundwerkstoffe für thermisch und tribologisch hochbelastete Leichtbaustrukturen

Rainer Gadow und Patrick Weichand

Outline:

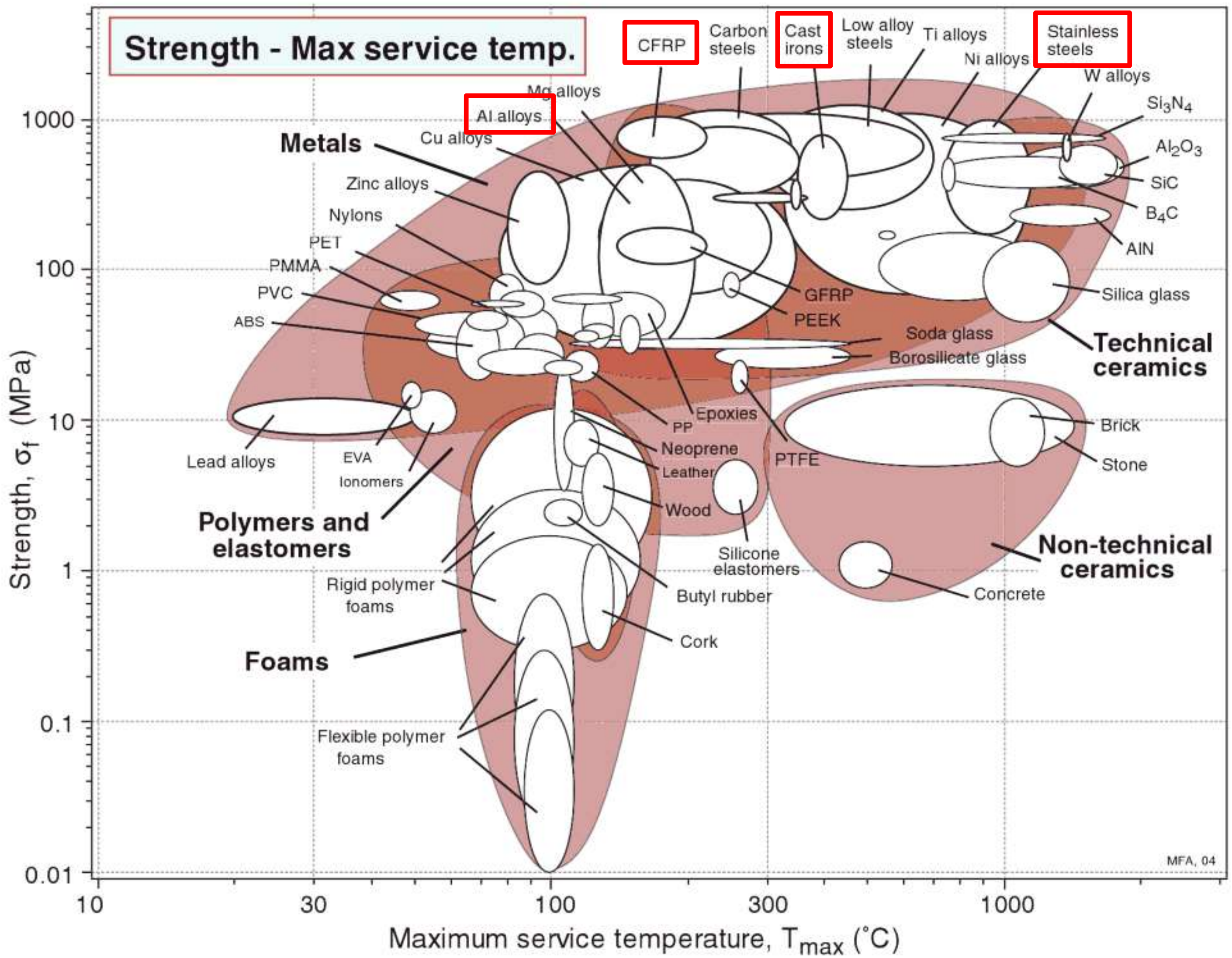
- Introduction: Review on PMC and CMC
- Processing and Manufacturing of CMC
- Liquid Precursor Infiltration (LPI)
- PDC and SiOC Ceramics
- SiOC-Composite Properties
- Thermal resistivity
- Tribological evaluation
- Summary and conclusions

Heraeus Holding GmbH, Hanau 22.01.2015

Hochtemperatur - Verbundwerkstoffe für den Leichtbau

materials valley

Strength and Maximum Service Temperature of various Materials



source: Ashby, M. F.: *Materials Selection in Mechanical Design, 3rd Edition (2005)*

PMC – Polymer Matrix Composites

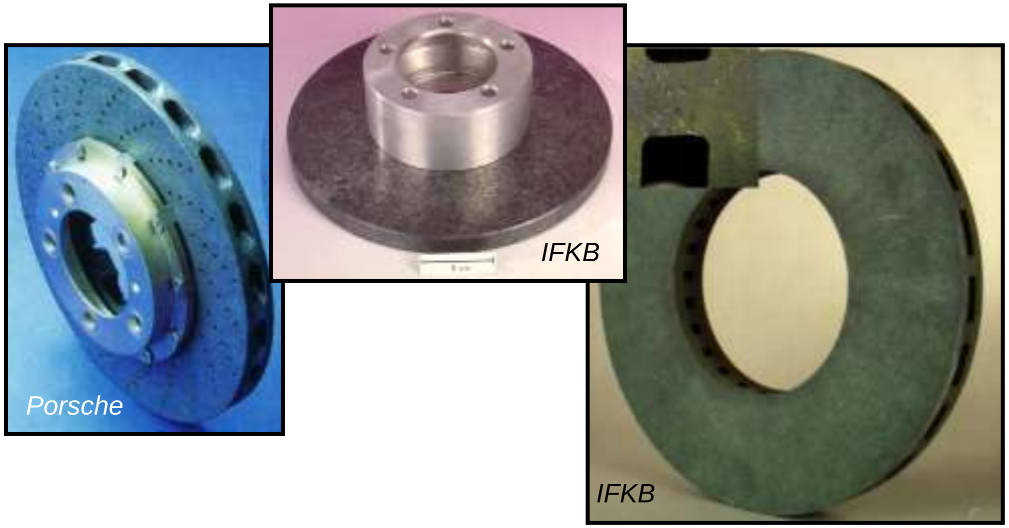
Advantages:

- ✓ excellent proportion strength/density
- ✓ fully developed manufacturing technologies
- ✓ relative cost-efficient
- ✓ small-scale / serial production

Disadvantages:

– tribological properties
– limited temperature resistivity (<<250 °C)
– 350 °C PEEK, PI, cyanate ester (>>60 $/kg)

CMC – Ceramic Matrix Composites



Rolls-Royce jet engine (RR-Derby)

Advantages:

- ✓ good mechanical properties
- ✓ service temperatures up to over 1800 °C
- ✓ quasi-elastic failure behavior
- ✓ excellent wear resistance

Disadvantages:

– very complex manufacturing processes
– very expensive raw material base (ceramic-fibers)
– adjusted fiber-matrix-interface essential

→ for special applications

Manufacturing Scheme for Fiber Reinforced Composites

SiC- and C-Matrices

Raw Materials

Filler (graphite, SiC, …)
Fibers
Carbon Precursors (thermoplastic: pitch, PAM-precursors; thermoset: phenolic-, epoxy-, furan-resins)
Metal-organic ceramic Precursors (Silane, Siloxane, Silazanes)

↓

Incorporation and Alignment of Fibers / Matrix Consolidation and Preform Manufacturing

CFRP

Low Pressure Processes (< 10 bar)

*simultaneous fiber impregnation and forming process (resin transfer molding-**RTM**)*

*prepreg lamination and subsequent thermosetting (**Autoclave**)*

Warm Pressure Molding

controlled die filling with prepregs or granulates
*(**granulation, extrusion, milling**)*

↓

Pyrolysis and Controlled Thermal Transformation

CFC

thermal degradation of the thermosetting resin system
-> carbon fiber reinforced carbonaceous preform with well defined porosity

CMC

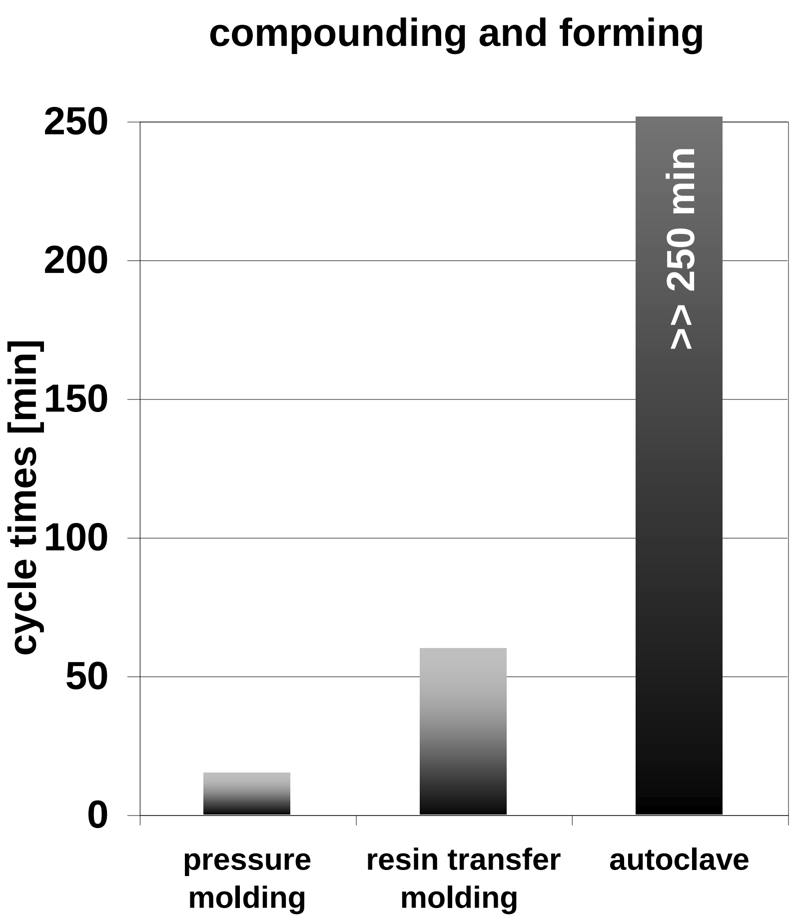
Chemical Vapor Infiltration (CVI)
repeated densification steps via chemical vapor deposition

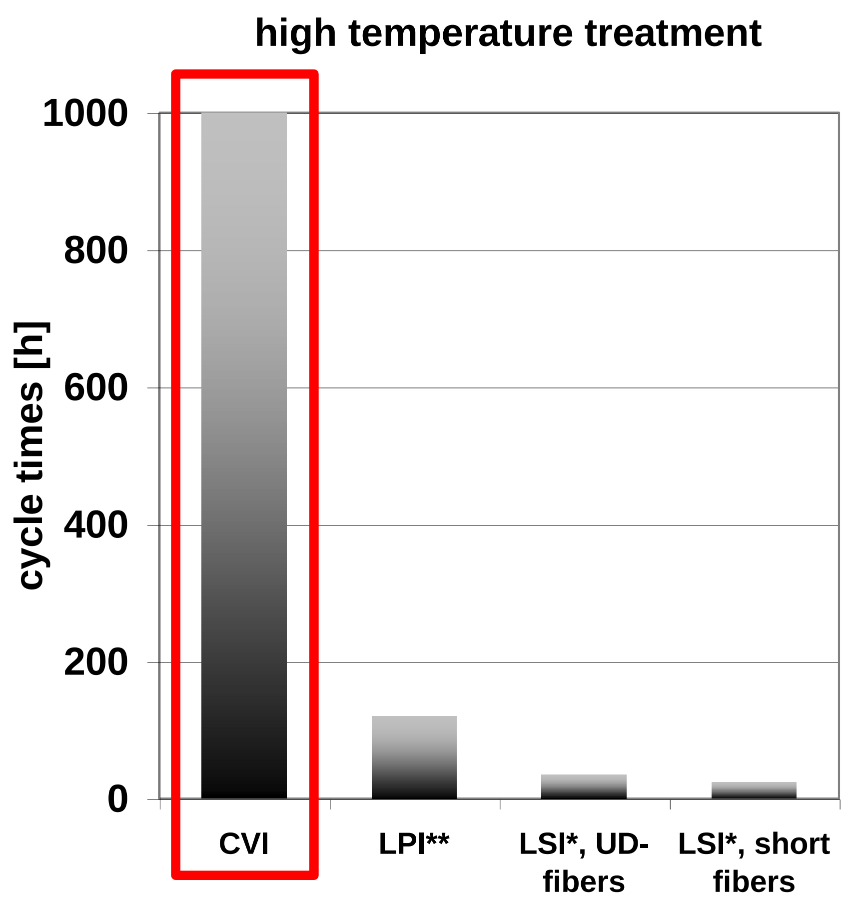
Silicon Infiltration
ceramization and densification via liquid silicon infiltration and simultaneous reaction bonding (**RB**) to SiC

Liquid Precursor Infiltration – LPI
repeated densification steps via pitch or (metal-) organic precursors and subsequent pyrolysis

Production Cycle Times of Different Processing Techniques

appropriate manufacturing technologies for fiber reinforced ceramics





***LPI-Liquid Precursor Infiltration* **LSI-Liquid Silicon Infiltration*

Problems occurring during Chemical Reaction and Reaction Bonding of SiC

- incomplete metal impregnation and chemical transformation caused by pore neck closure or insufficient metal melt excess
- inhibition on internal surface by formation of wetting effective undesired byproducts (SiO etc.)
- excessive free silicon content in the CMC caused by exaggerated original compact porosity with a resulting decrease in mechanical properties

➢ **risk of fiber damage by micromechanical effects and chemical interaction during harsh transformation reaction conditions**

fiber protection during liquid silicon infiltration

inner surface coating of CFC preform

coating deposition on the inner surface of CFC preform via CVI- or LPI-processes

fiber monofilament coating

coating deposition on each fiber monofilament via LPI-process

optimized CFC preform design (SMC - „sandwich structure“)

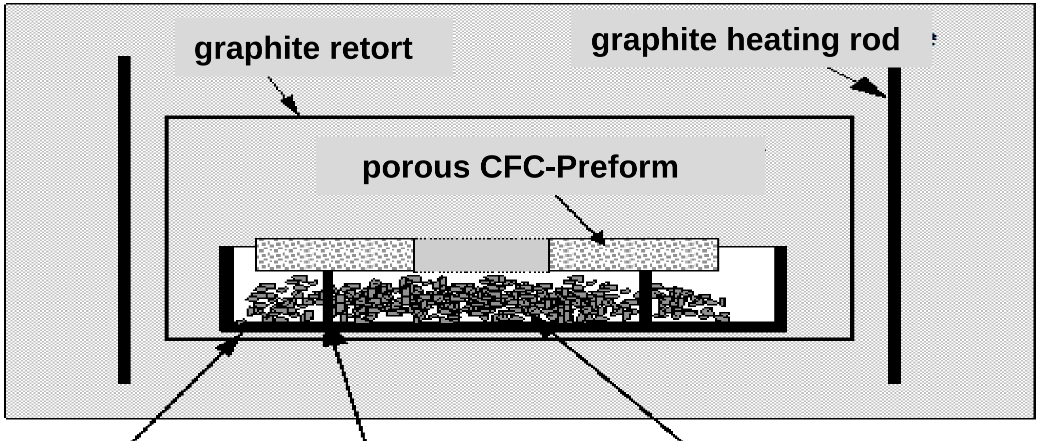
CFC preform with reduced open porosity on selected areas prevent silicon infiltration and carbon fiber damage

CMC - High-Temperature-Techniques for Matrix Consolidation

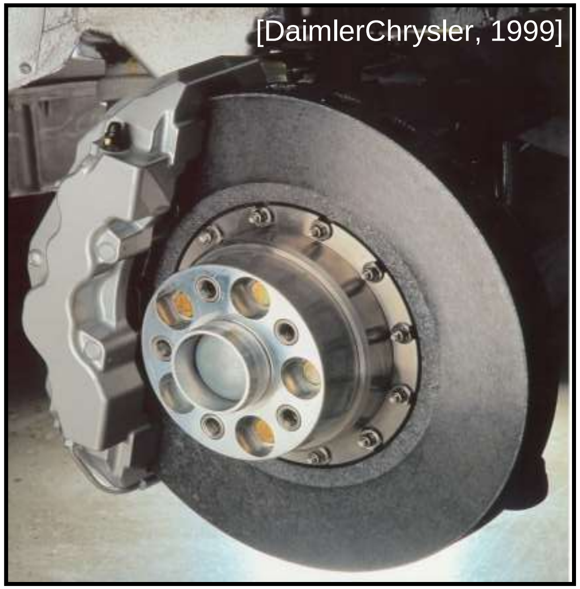
***Siliconizing** of carbonaceous, porous preforms*

liquid silicon impregnation method for the fabrication of SiC composite materials by **reaction bonding** of porous fiber preforms with additional carbon matrix

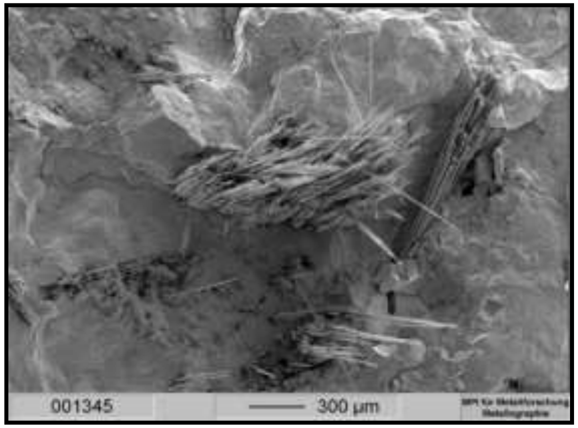
→ selective conversion of a porous carbon binder and filler matrix to SiC, while the reinforcement fiber is not or only slightly attacked by the Si melt



Schematic layout of RB Siliconizing Process



C_f-RB-SiC CMC-Brake Disk



SEM fracture surface of FeSi75SiC

C_f/Si(RB)SiC-Brake rotors for passenger cars

source: ADACMotorwelt

Essentials of SiC and SiOC composites in comparison

Fundamentals of chemical transformation reaction to SiSiC composites

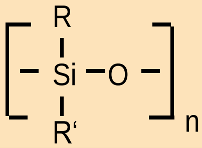
- Heterogeneous chemical reaction of carbon with Si liquid or vapor impregnation at high temperatures (1600 – 2000 °C)
- Hot pressing of powder compacts at high temperatures under protective atmosphere
- Harsh conditions for the fiber component during processing
- Protective interlayers and fiber coatings required to control CMC fracture toughness
- Extremely high investment cost in HT vacuum furnaces and instrumentation
- Complex and cost intensive total manufacturing chain

Advantages of PDC in processing and manufacturing engineering

- Viscous flow behavior of matrix precursors used for forming processes
- Reduced process temperatures and thermochemical load for the fiber component during processing
- Fast and effective forming processes as established for polymers and plastics
- High surface quality depending on tool or die geometry and surface quality
- Cheap thermal treatment under atmospheric conditions

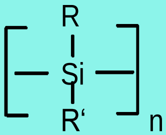
Selection of Precursor Materials for Si-O-C-Ceramics

Si-O-C

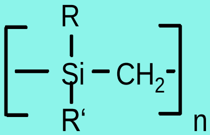


Polysiloxane

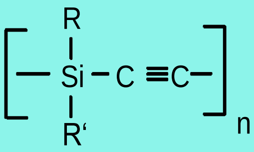
SiC (C)



Polysilane

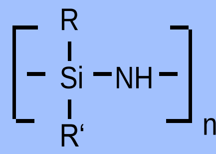


Polycarbosilane

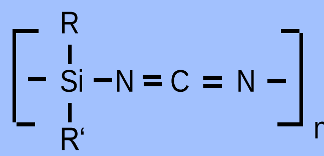


Polyethynylsilane

Si-C-N; Si_3N_4/SiC



Polysilazane



Polysilylcarbo-diimide

Requirements:

- Low viscosity, good wetting behavior
- Polymerization by thermal, chemical or photochemical activation
- Pyrolysis mainly in solid state
- High yield of amorphous ceramics with defined composition
- Thermochemical and phase stability at high temperatures
- Easy handling
- Low cost material

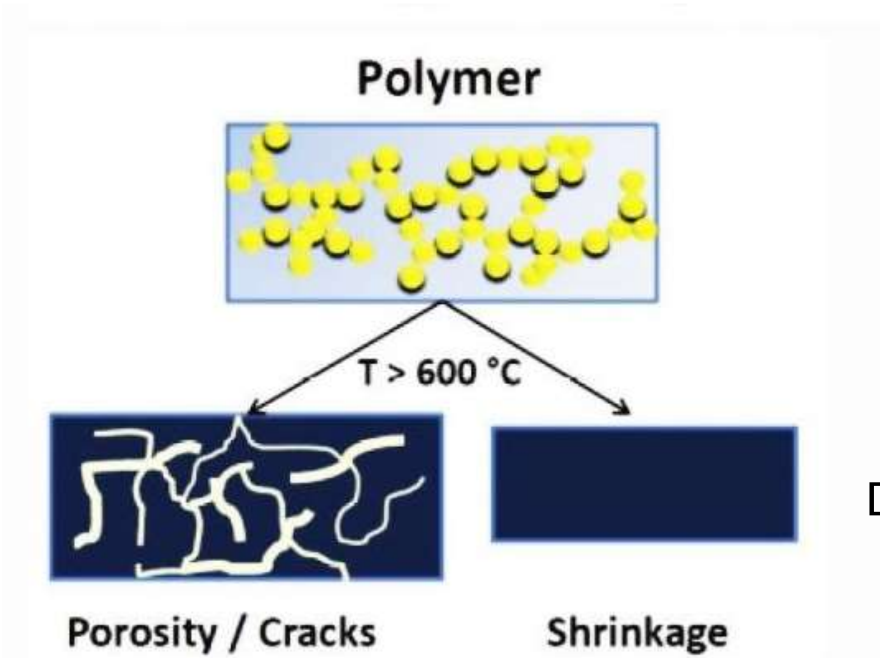
1. Low cost Matrix
2. Low cost reinforcement
3. Inexpensive Manufacturing Process

→ Intermediate temperature Composite Materials with decent mechanical properties

High-Temperature-Techniques for Matrix Consolidation

Liquid Precursor Infiltration – LPI and controlled pyrolization

- ✓ Low processing temperatures
- ✓ Adaption to Polymer techniques possible
- ✓ Possibility of manufacturing porous Materials



Polymer to Ceramic transformation

source: Colombo, P.; Mera, G.; Riedel, R.: Polymer-Derived-Ceramics: 40 Years of Research and Innovation in Advanced Ceramics. (2010)

- **High volume shrinkage** (up to 50 %), drawback for net shape manufacturing
- Low mechanical properties as monolithic ceramic
- High filler contents needed for adequate low shrinkage

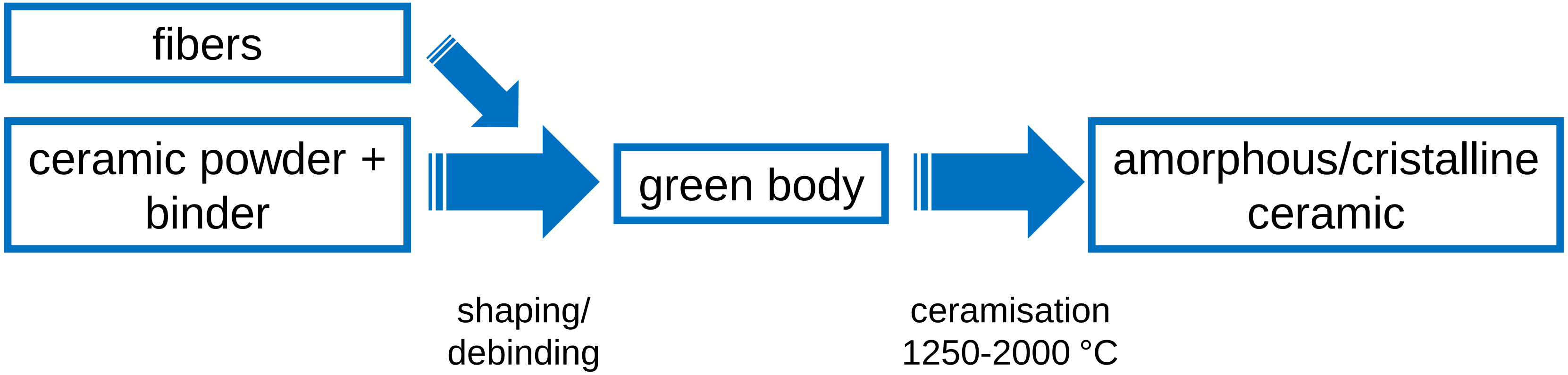
Drawback for **bulk ceramic** manufacturing

⬇

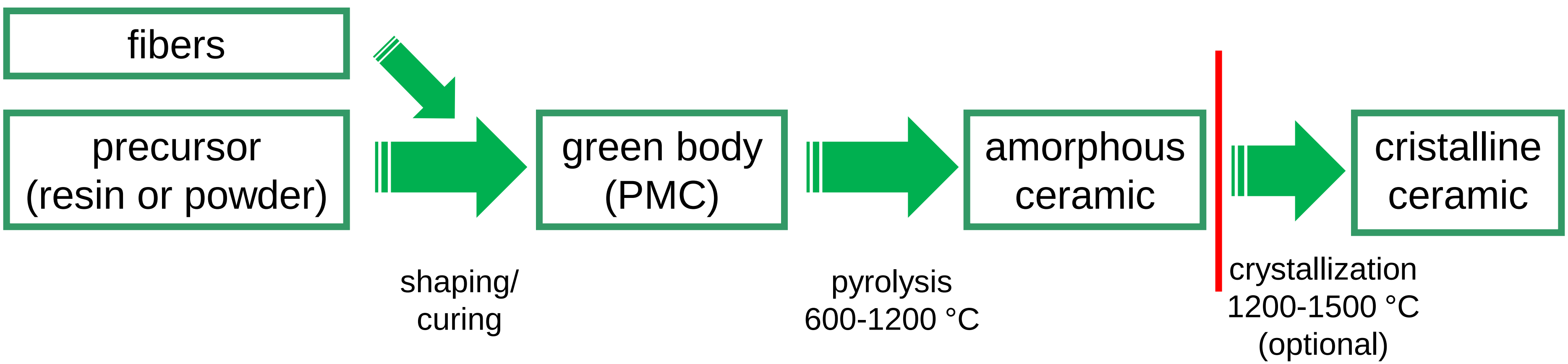
Interesting for **composite** manufacturing

Precursor and conventional ceramic manufacturing routes

Classic CMC-Manufacturing (simplified):



Precursor-route (Adaption of PMC-techniques):



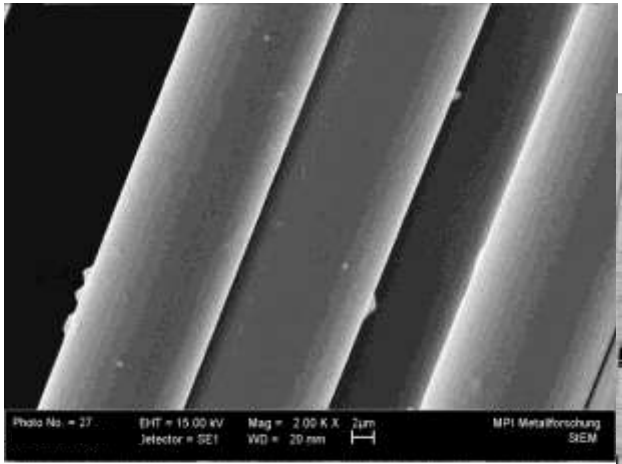
➡ Lower process temperatures => new reinforcement materials possible ?!?

Basalt Fiber

- principal properties -

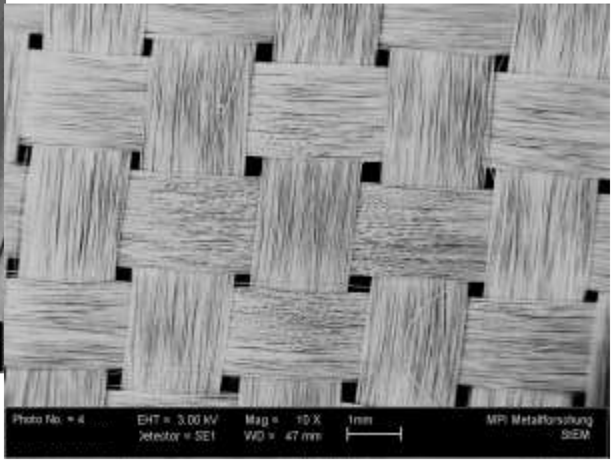
- **Mineral fiber (aluminosilicate)**
- **Green-brown coloured**
- **Amorphous microstructure**
- **Conventional application comparable to glass fiber**
- **Mainly produced in Russia, Austria, China, Ukraine**

Basic raw material: basaltic stone



SEM-picture of basalt fiber surface

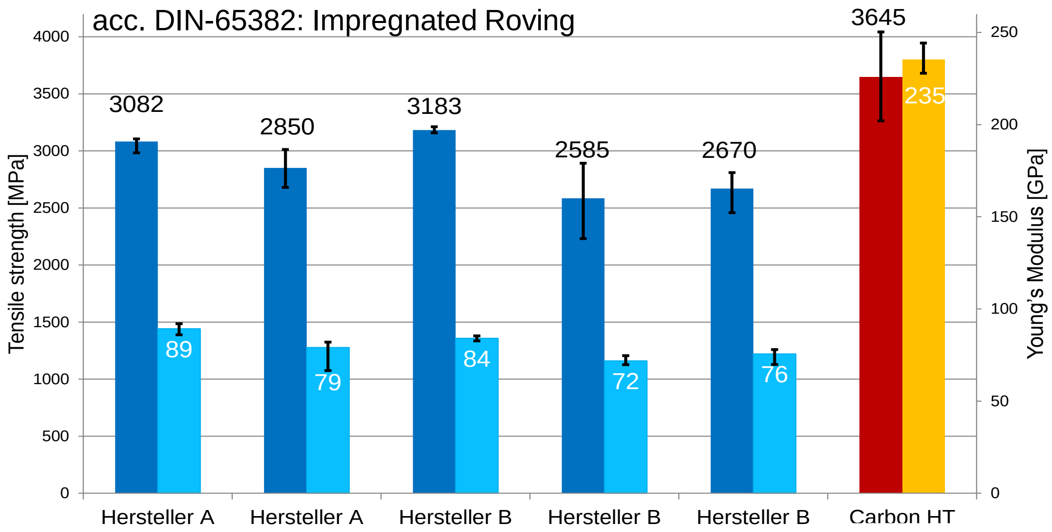
Basalt-fiber roving



Basalt fabric plain weave

Basalt Fiber

- correlation between chemical composition and mechanical properties -

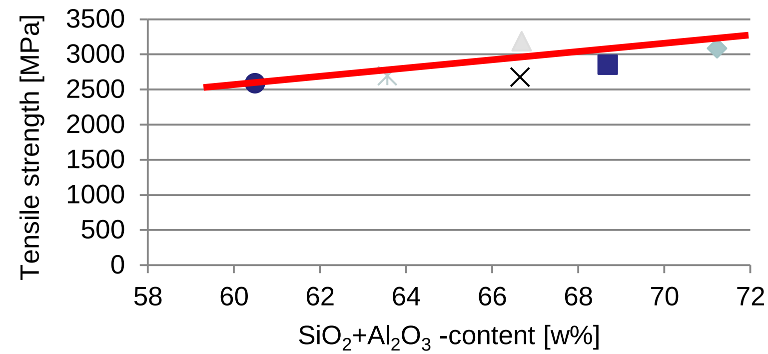


Composition depends on:

- <u>geology of stone quarry !</u>
- manufacturing lot
- process parameters

	A Lot1	A Lot2	B Lot1	B Lot2	C Lot1	D Lot1	E Lot1
Oxide	[w%]	[w%]	[w%]	[w%]	[w%]	[w%]	[w%]
Na_2O							
MgO							
Al_2O_3							
SiO_2							
K_2O							
CaO							
TiO_2							
FeO							

Chemical composition of actual manufacturing lots (EDX)

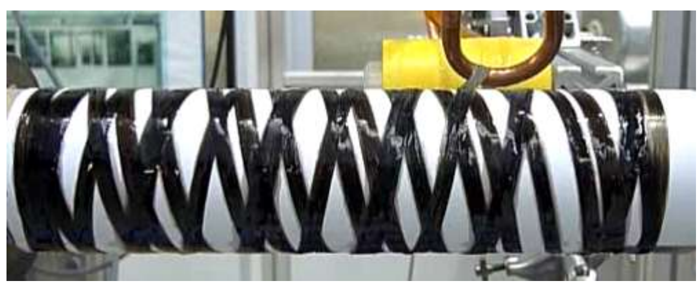


➡ constant quality:
by blending of oxides

Adaption of PMC-Manufacturing

Uniaxial Warm Press Molding

Resin-Transfer-Moulding



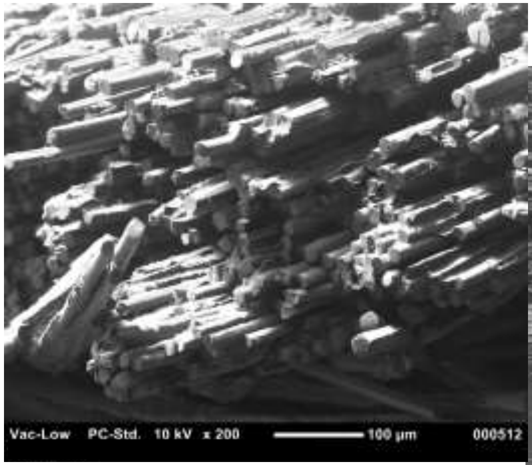
Filament-Wet-Winding

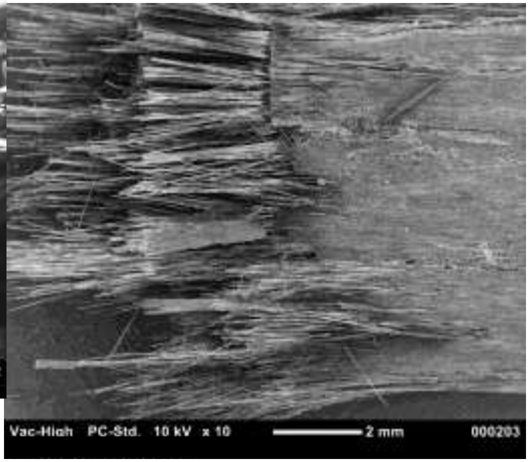
Injection-Moulding

Properties of SiOC-Hybrid-Composite

polished surface with reinforcement structure R_a=0,19

- Density: 2,1-2,5 g/cm³
- Max. service temperature: 600 °C
- Short term stability: 1000 °C
- CTE: ~ 5 ppm (V2A: >18; Al-alloys: >23)
- High wear resistivity
- **Non flammable**
- Very attractive price level





SEM fracture surfaces with fiber-pull-out

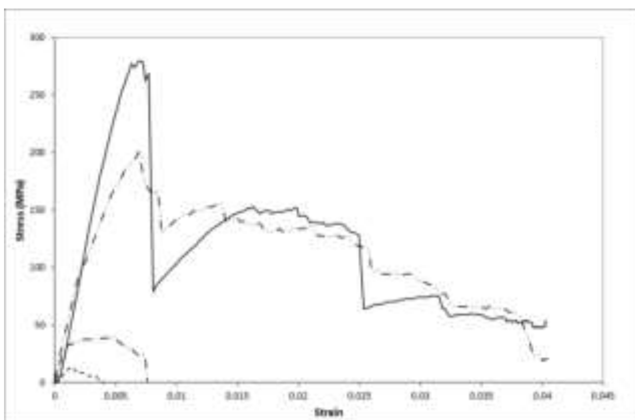
$B50_f$/SiOC turbine blade

Bending strength at elevated temperatures

*– 3 point-bending at **500 and 600 °C** in air –*

Rolls-Royce University Technology Centre (UTC) in Materials, Swansea (UK)

	V1 (UD)		V2 (UD)		V3 (2D)	
Temp.	UTS [MPa]	E_{fail}	UTS [MPa]	E_{fail}	UTS [MPa]	E_{fail}
RT	321	0,042	446	0,038	158	0,028
500 °C	280	0,040	201	0,041	40	0,008
600 °C	155	0,038	155	0,041	71	0,019



stress-strain diagramm at 500 °C

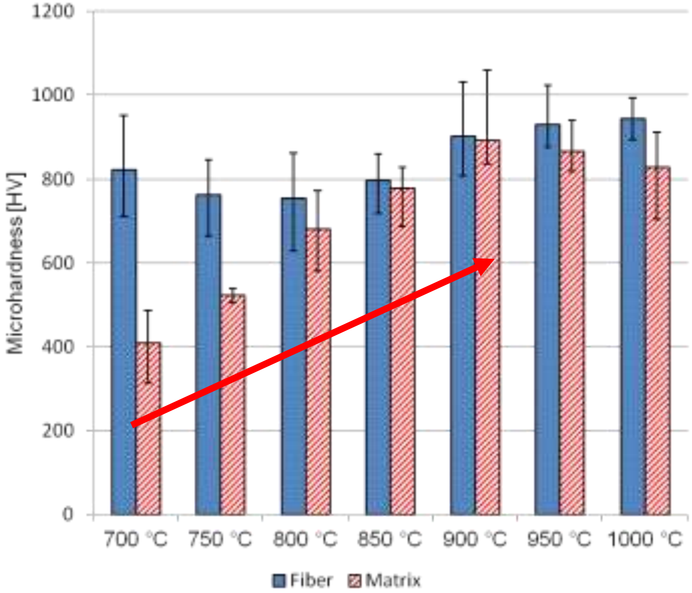
Swansea University
Prifysgol Abertawe

Rolls-Royce

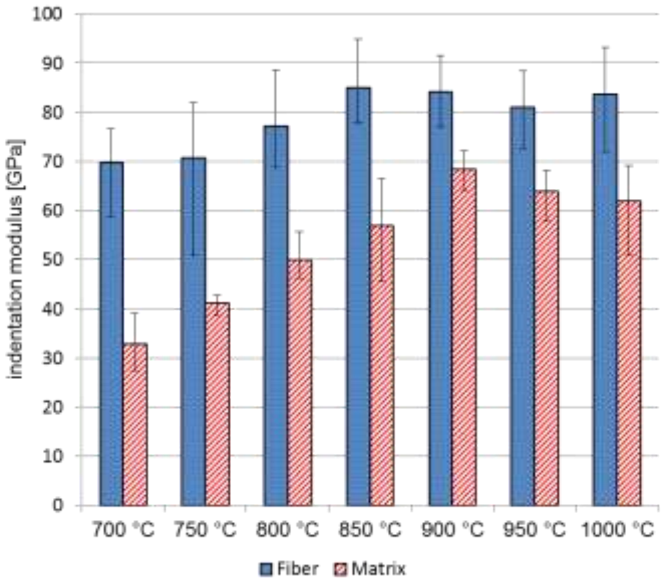
IFKB University of Stuttgart

Bache, M.; Gadow, R.; Newton, C.; Weichand, P.:
Mechanical Assessment of a Basalt Based Ceramic Matrix Composite,
14th European Inter-Regional Conference on Ceramics,
Hrsg. Gadow, R.; Kern, F., Stuttgart, (2014)

Hardness evolution of SiOC matrix and Basalt fibers

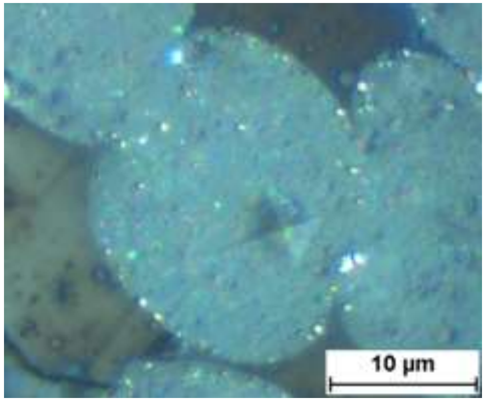


Micro hardness $HV_{0,1}$ of the matrix and $HV_{0,03}$ of the fibers after different pyrolysis temperatures



Indentation modulus of matrix and fibers after different pyrolysis temperatures

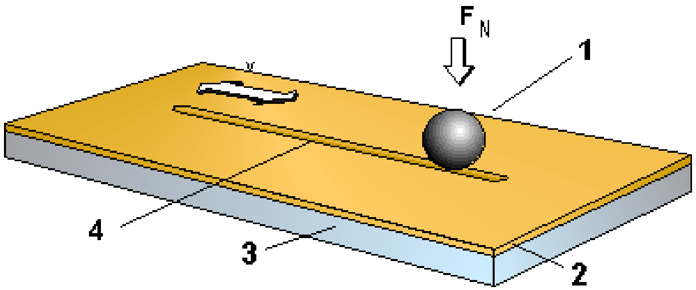
	HV	maximum force
Fiber	$HV_{0,03}$	294.199 mN
Matrix	$HV_{0,1}$	980.665 mN



Vickers indentation on basalt filament

Characterization – Tribological Properties (Wear Behavior)

Reversive-Oscillation Tribology:



1. counterpart (ball)
2. sample surface
3. (substrate)
4. wear track

$$F_R = \mu * F_N$$

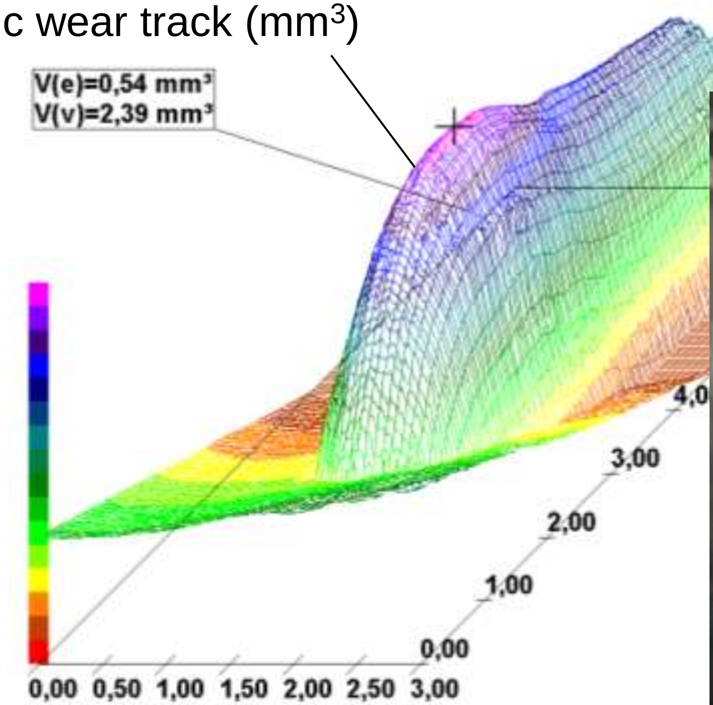
Wear coefficient:

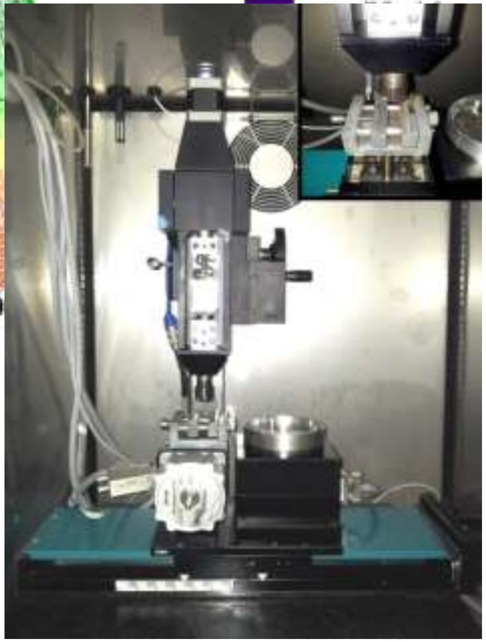
$$K = \frac{V(mm^3)}{F_n(N) \times wearpath(m)}$$

➩ *measure for wear resistance*

V - wear volume; measured by tactile surface metrology:

volumetric wear track (mm³)





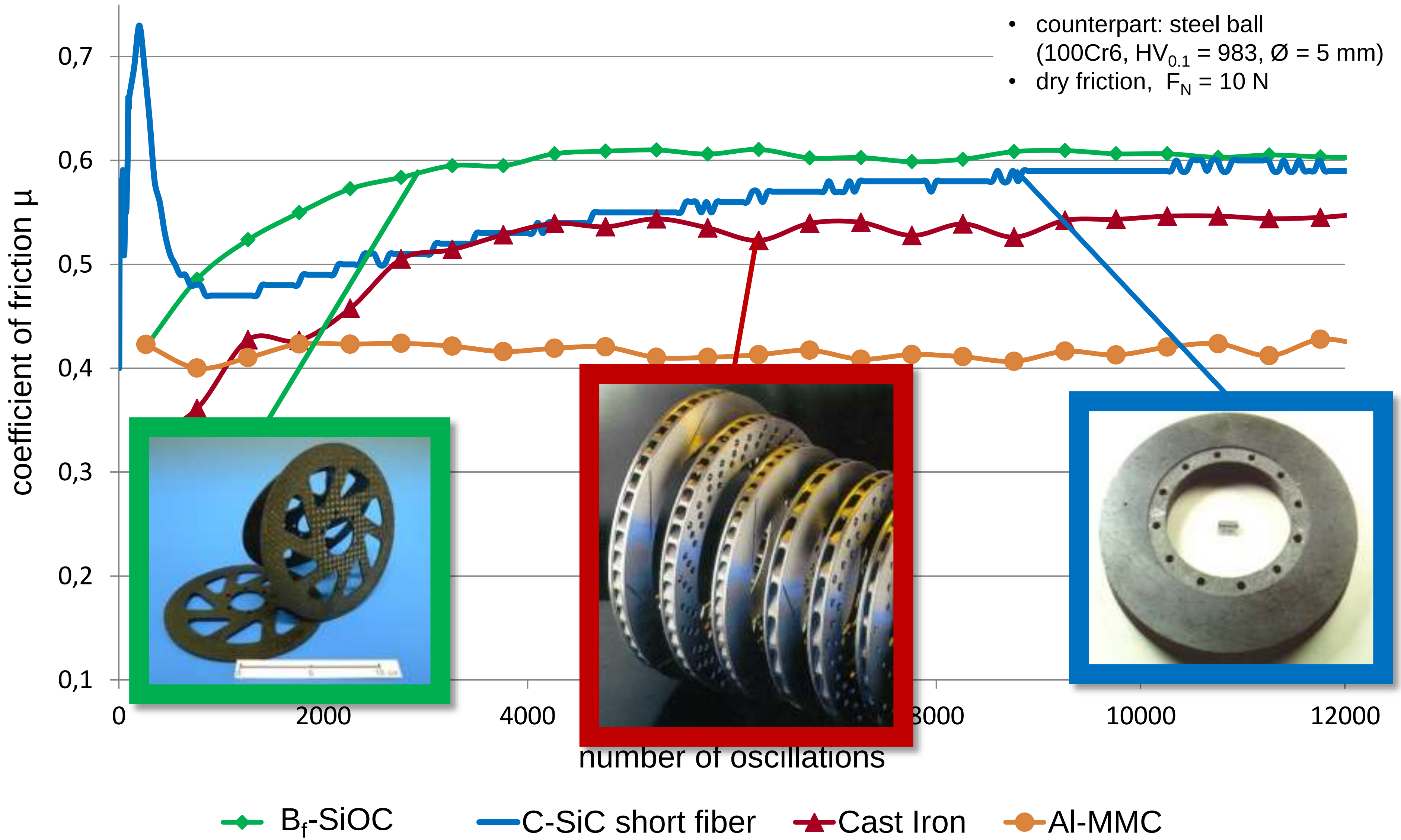
Test characteristics:

- counterpart: steel ball (100Cr6, $HV_{0.1}$ = 983, Ø = 5 mm)
- dry friction
- normal force: F_N = 10 N
- stroke length: 10 mm
- stroke speed: 12 mm/s
- number of strokes: 20,000

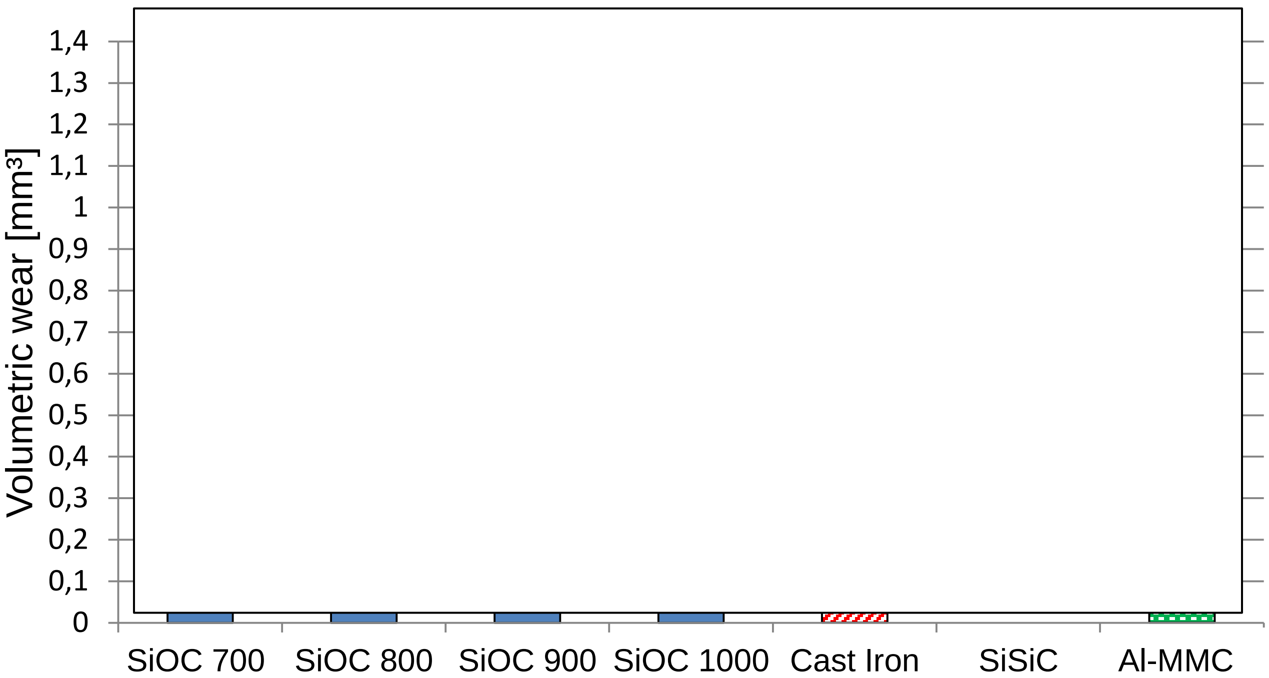
Tribological Behavior of Different Brake Rotor Materials

Testparameter:

- counterpart: steel ball ($100Cr6$, $HV_{0.1}$ = 983, Ø = 5 mm)
- dry friction, F_N = 10 N

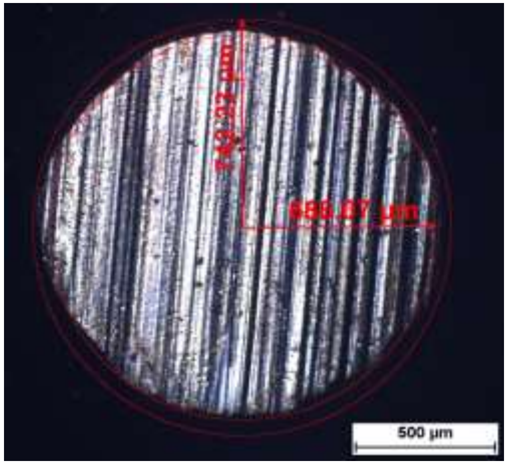


Volumetric wear of various brake rotor materials

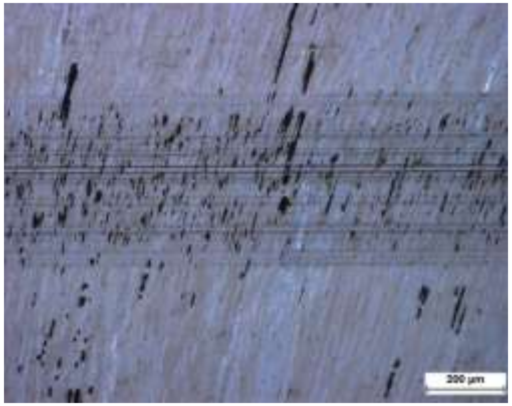


10 mm

Volumetric wear track on
B_f/SiOC 1000 °C specimen



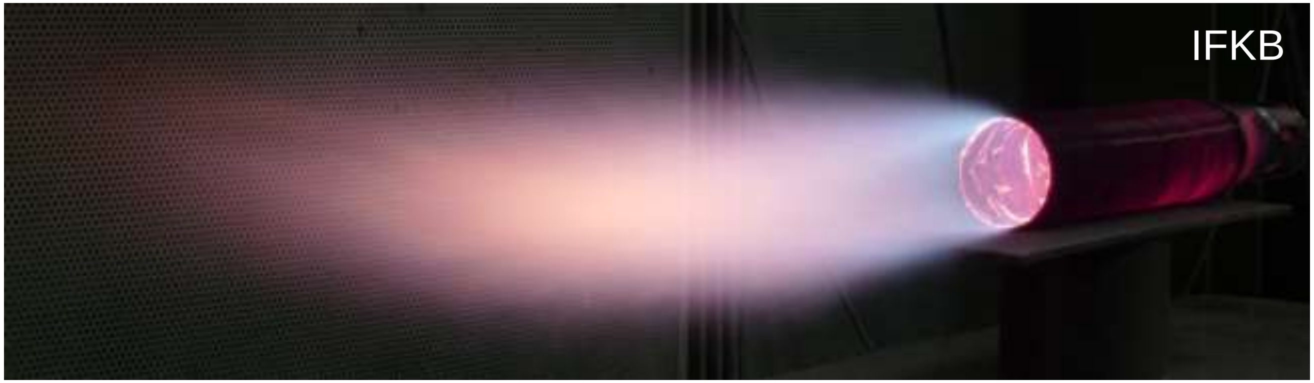
Wear on counter part
(100Cr6)



*„Wear“ on C_f/SiSiC sample

Application– Composite Exhaust System

- competitive alternative up to 1000 °C short term application -



Manufacturing of the whole structure in one step without insulation needed

Exhaust silencer demonstrator:
weight saving >65 % vs. stainless steel

Materials for exhaust systems:

(limiting factor)

- steel/stainless steel (high weight)
- Inconel (Ni-alloys) (Formula 1)
- titanium (high price)
- aluminum (limited service temperature)
- CFRP (limited service temperature)
- CMC (SiC/SiC) (exorbitant price)

→ Hybrid Composite

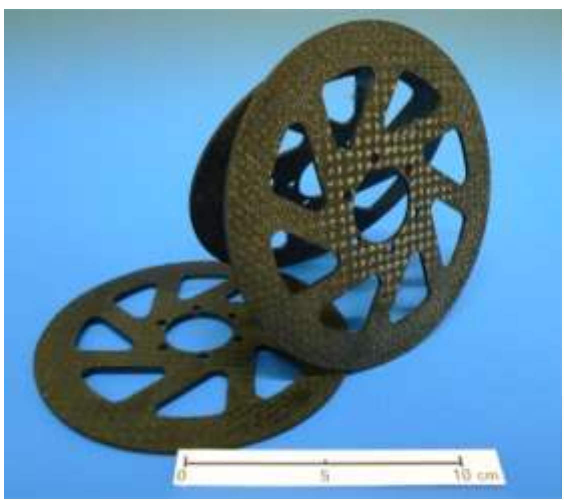
Application – Composite Brake Rotor Disk

- adjustable friction properties-

Brake rotor for bicycles after 150 km test run

- **B_f- and C_f-SiOC composites**, a competitive **alternative to C/SiC or CFC** materials for friction applications in e-mobility, (motor-)cycles
- Full composite material rotor and brake pad design for maximum weight saving

organic brake pad after 150 km test run with B_f/SiOC rotor



Gen2 brake rotors

full composite brake pad design (CF)

Tribological Properties of different Brake Disk Materials

	Cast Iron	C/C	SiSiC	FeSi75SiC	B_f-SiOC
density [g/cm³]	7,25	1,85	2,79-2,99	3,12	2,1-2,5
HV_{01} [kg/mm²]	715	69	SiC 2428 Si 1345	SiC 2428 Si 1345 $FeSi_2$ 753	300-1000
coefficient of friction µ	0.30-0.50	0.25-0.35	0.45-0.55	0.55-0.6	0.41-0.6
max. application temperature [°C]	700	500-600 in air	1350	1350	600

Summary

- "True" SiC composites need expensive HT process chains with additional fiber coatings and controlled interfaces to match the mechanical properties
- High temperatures during Si liquid or vapor impregnation are a strong limitation for the fiber selection
- Extremely high investment cost in HT vacuum furnaces and instrumentation
- Hot pressing at high temperatures under protective atmosphere means harsh conditions for the fiber component during processing

- **Intermediate temperature composites** like SiOC enable the adapation of **cheap and effective forming and shaping techniques** as established for polymers and plastics
- Thermal treatment can be made under atmospheric conditions
- **Basalt fibers** are a **cost effective alternative to carbon and ceramic fibers** for **intermediate temperature** applications and superior to glass fibers
- **SiOC composites meet the technical <u>and</u> economic requirements of the automotive industry**

Institut für Fertigungstechnologie keramischer Bauteile

Tel: +49 711 / 685-68301

Fax: +49 711 / 685-68299

E-mail: ifkb@ifkb.uni-stuttgart.de

URL: www.ifkb.uni-stuttgart.de

Diese Arbeit wurde unterstützt von:
- *Ministerium für Wissenschaft, Forschung und Kunst, Baden-Württemberg*
- *Stiftung Industrieforschung, Köln*
- *Deutsche Forschungsgesellschaft(DFG).*