Interface Challenges in Dense Oxide as well as Non-oxide CMCs for Long-Term Applications

Precursor Derived Ceramics and Advanced Hybrid Materials
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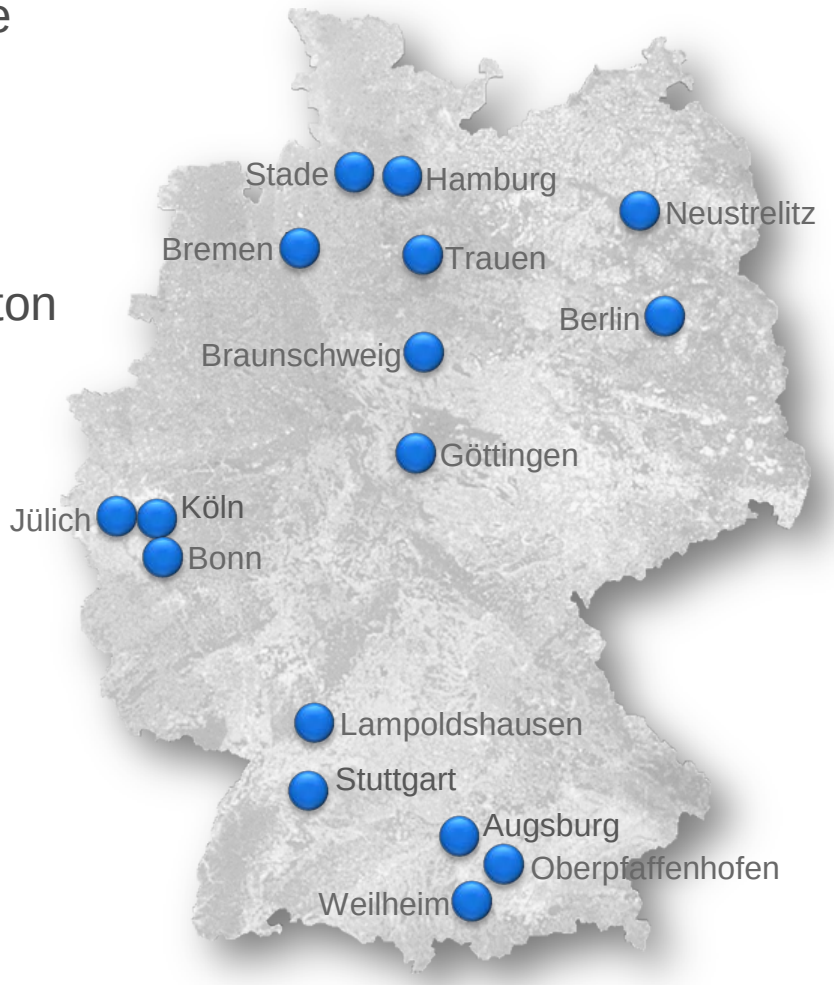
The German Aerospace Center (DLR)

Largest aerospace research facility in Europe

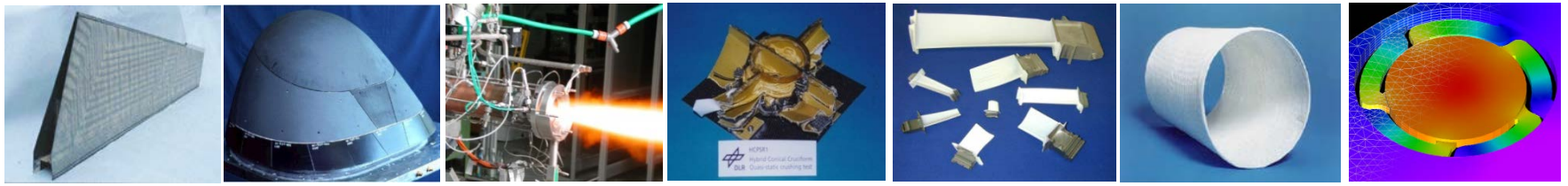
- 7800 employees
- 32 institutes
- 16 sites in Germany
- Offices in Brussels, Paris, Tokio, Washington

- Turn over: 1769 M€

- Space program 971 M€
- Research 798 M€
  - Space 50%
  - Aeronautics 34%
  - Transport 7%
  - Energy 9%



Mission in Research and Education



Research

- High performance materials and structures and relevant processes
- Virtual tools for computational materials engineering and structural design
- Complete engineering chain - from material to automated production

Transfer

- Application focused and close to industry

Education

- Professor chairs and lectures at universities
- Under-graduate and doctoral students

Consulting

- Politics and industry

Outline and Motivation

- Short review on classical CMC manufacturing methods
- Interfaces (interphases) in oxide and non-oxide fibre-reinforced CMCs
- Monazite fibre coating process in principle
- Variation of coating parameters
- Manufacture of CMCs (SiC/SiCN) using PIP and monazite coating
- Physical and mechanical properties of CMCs (SiC/SiCN) and OXIPOL
- HVOF-test and microstructural characterisation of CMCs (SiC/SiCN) before and thereafter
- Summary and outlook

Classic methods to manufacture SiC/SiC(N) composites

CVI

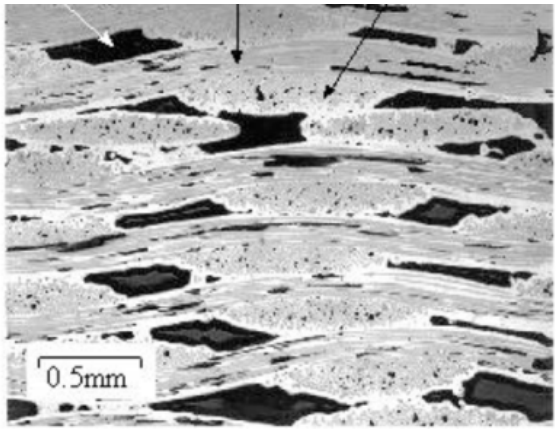
Chemical Vapour Infiltration

Advantages:

- comparably low process temperatures (≈ 1100 ˚C)
- stoichiometric process is feasible to SiC composites
- fibre coating can be / is part of CMC manufacture

Disadvantages:

- high matrix porosity, large voids in gussets
- release of partly aggressive reaction products
- time-consuming processing to decrease porosity
- Difficulty to process thick-walled parts



Jacques Lamon, 2005

PIP

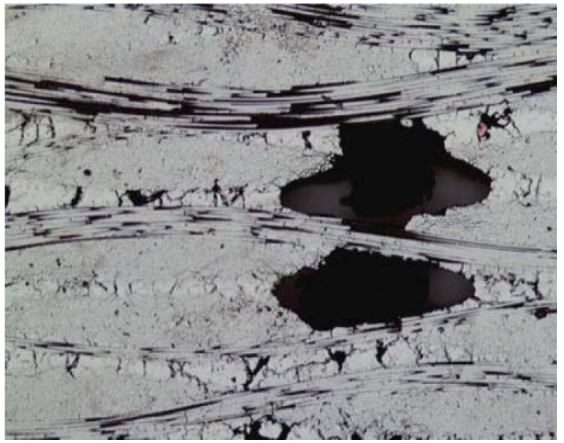
Polymer Infiltration & Pyrolysis

Advantages:

- comparably low process temperatures (≈ 1100 ˚C)
- matrix composition can be easily influenced by chosen polymer (SiC, SiCN, SiBCN, etc.)

Disadvantages:

- high porosity by loss of mass and increase of density of the matrix during pyrolysis in gussets: in advantage are amorphous matrices (e.g.: SiCN and SiBCN)
- time-consuming processing to decrease porosity



Kazuaki Nishiyabu, 2007

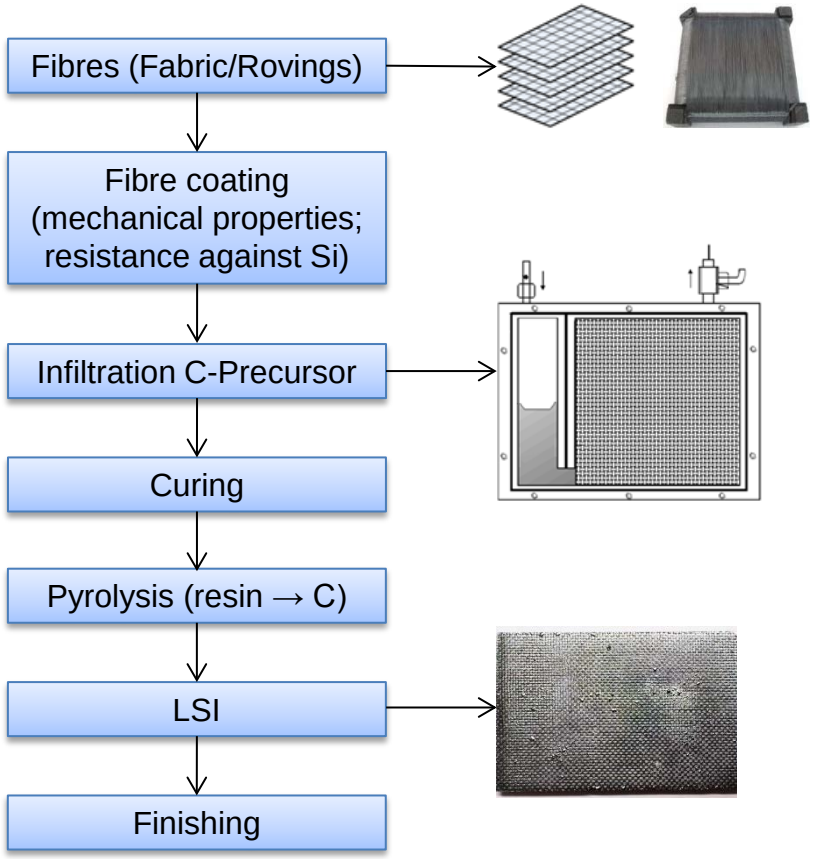
Liquid Silicon Infiltration Process (LSI) at DLR

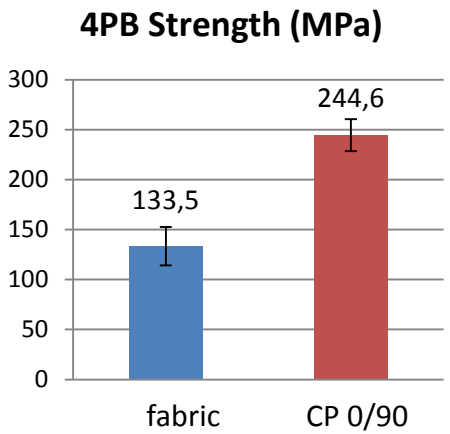
Advantages and requirements for processing

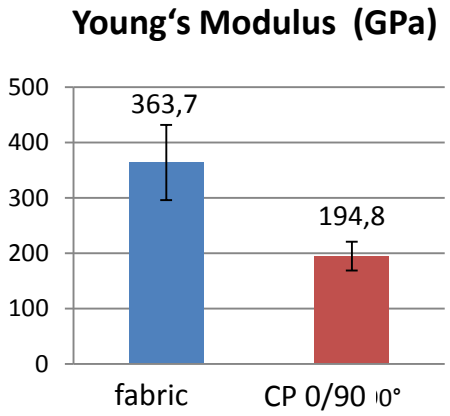
- feasibility of manufacture of shapes and geometries (no limitation to thickness of parts)
- no fibre coating necessary for achievement of damage tolerant behaviour
- intermediate processing (easy machining and substance joining) feasible
- short processing time
- “dense” matrix

Requirements for future $SiC_f/SiC(N)$ composites

- (near) no porosity
- stoichiometric SiC matrix (no excess of C)
- resistance to corrosion at high temperatures
- necessity of coatings for fibre protection versus chemical attack by liquid Si (or metals)







uncoated SiC fibers

Interfaces in Oxide and Non-oxide Fibre-reinforced CMCs

Interphases based on pyrolytic carbon or boron nitride and dense matrix

- o.k. for short term applications

Interfaces based on porous matrices with no coating

- o.k. for low gas flow and low requirement for gas tightness

Interphases based on fugitive coating and dense matrix

- o.k. for short term applications

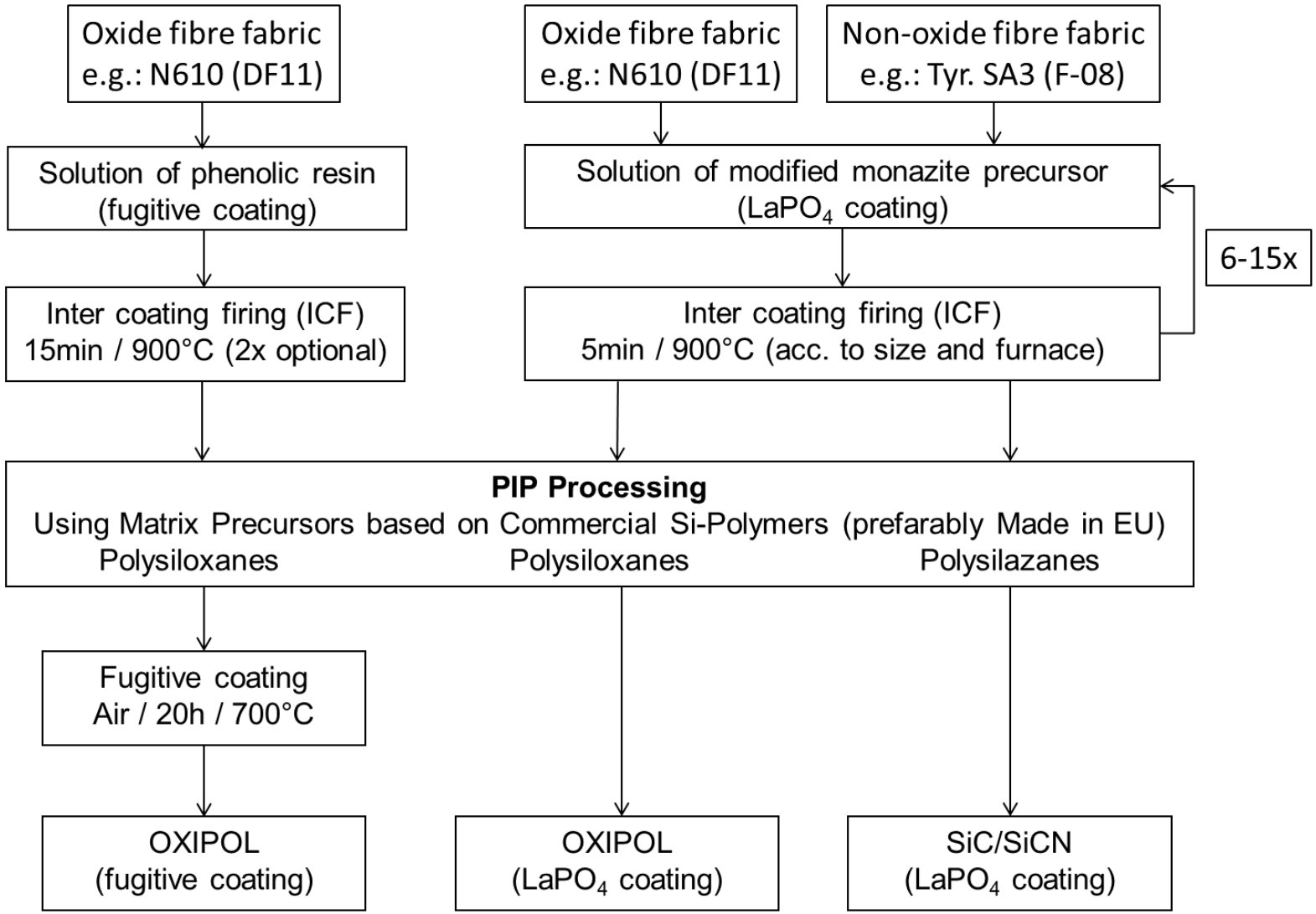
All interphases above suffer from:

- severe attack on matrix and fibre in agressive chemical environment
- intensive protective coatings necessary (EBC, TBC)

➢ **CMCs based on stable interphase and dense matrix are mandatory**

➢ **Monazite (lanthanum phosphate, $LaPO_4$) as a model candidate**

Manufacture of OXIPOL and SiC/SiCN Using PIP-Processing



Polymer Infiltration and Pyrolysis

SiC-fabric
Tyranno SA3
(0|90° plain weave)

PyC fibre coating
(via CVI) or $LaPO_4$ (via DC)

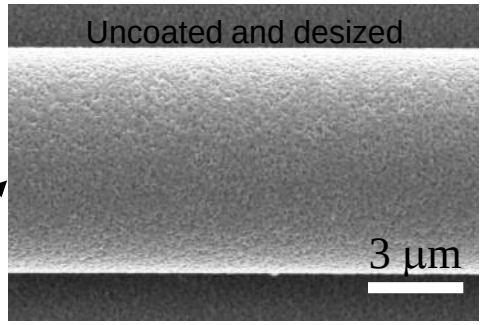
infiltration with
polysilazane precursor
via RTM-process

pyrolysis
(polysilazane → SiCN-matrix)

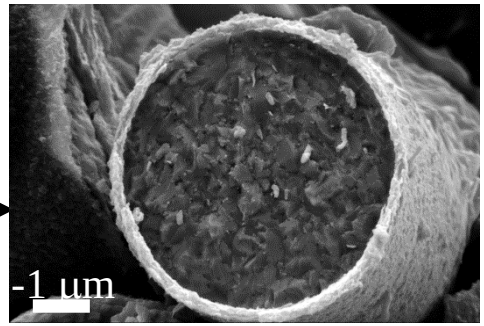
finishing

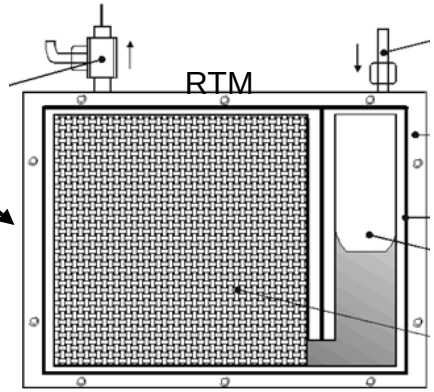
6 times
to decrease
porosity

SA3-I16:



PyC coated SA3-I16





Final CMC
plate
(300x90x2mm)

Monazite Fiber Coating Process in Principle

Monazite as oxidation resistant fibre coating for dense CMCs:

- high melting point: 2073 ˚C
- low modulus: ≈ 130 GPa
- thermodynamically stable and chemically inert to many materials
- low bonding strength to common oxide fibres

Precursor solution made of $La(NO_3)_3$, citric (H_3Cit) and phosphoric acid (H_3PO_4)

Stabilisation and inhibition of reaction by citric acid via complex formation:

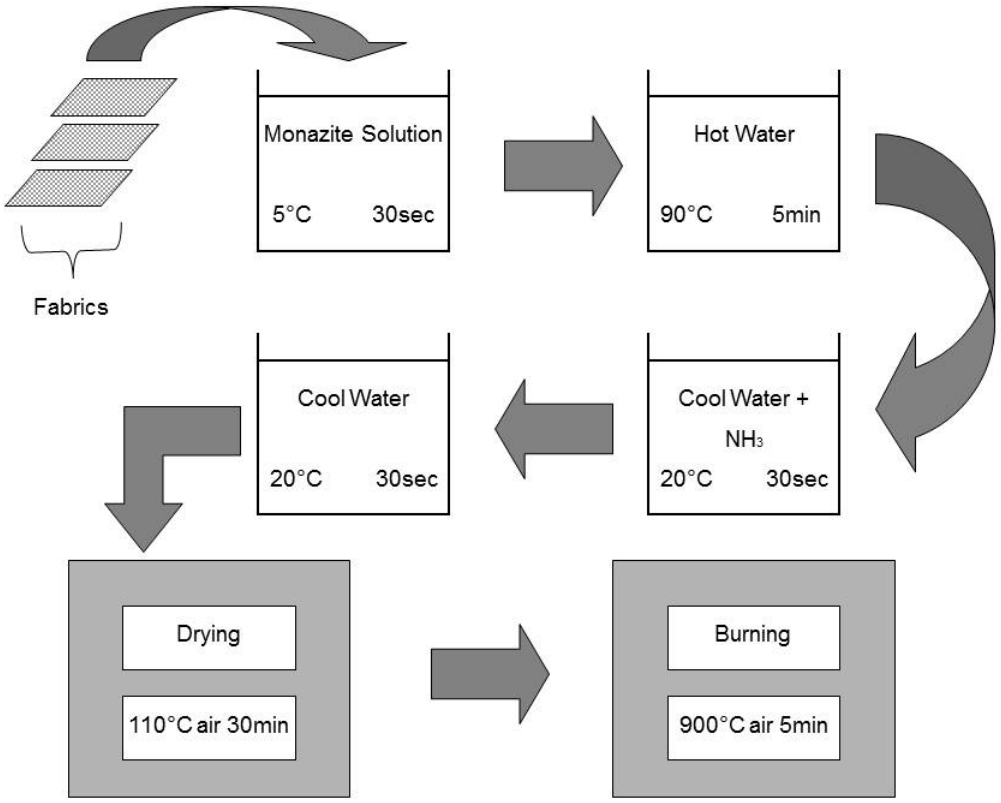
$$La(NO_3)_3 + H_3Cit \rightarrow La\text{-}Cit + 3HNO_3$$

The precipitation reaction in the precursor solution only depends on temperature and concentration, and therefore, can be controlled: **heterogeneous nucleation**

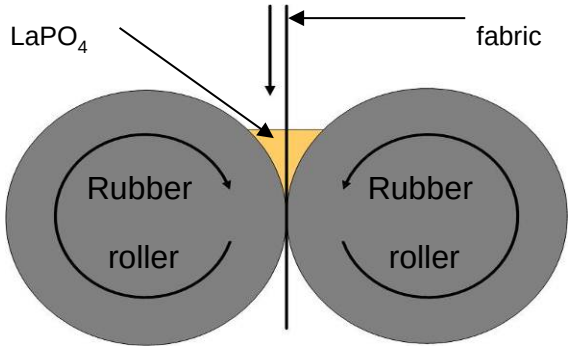
$$La\text{-}Cit + H_3PO_4 \rightarrow LaPO_4 + H_3Cit$$

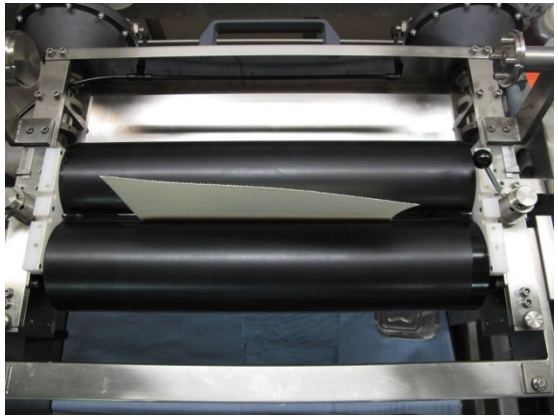
Coating Methods:

Dip coating (classic)

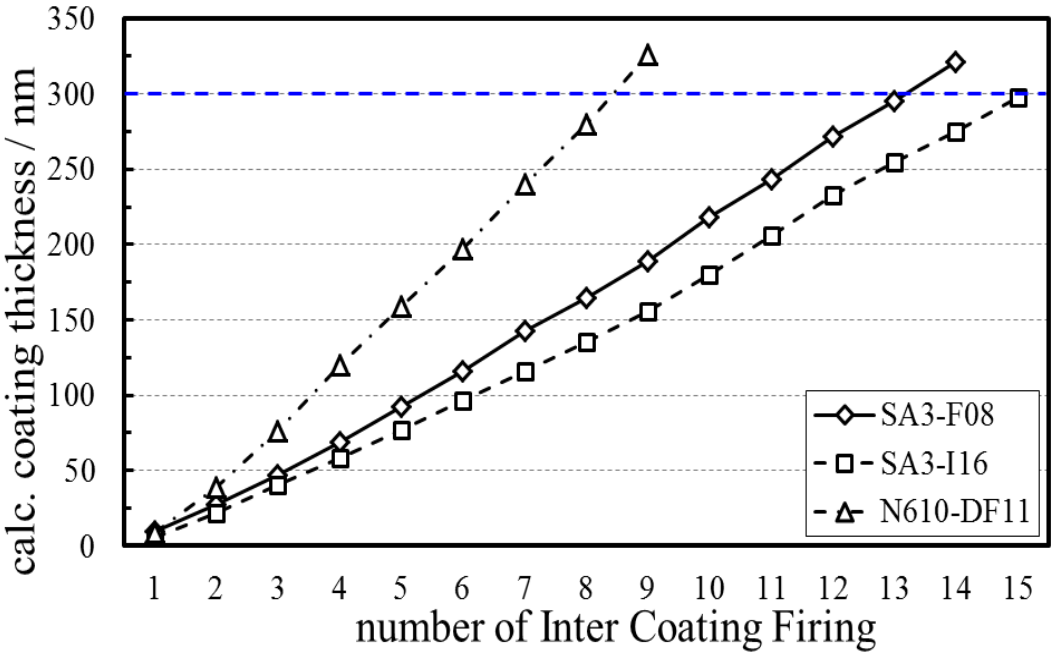


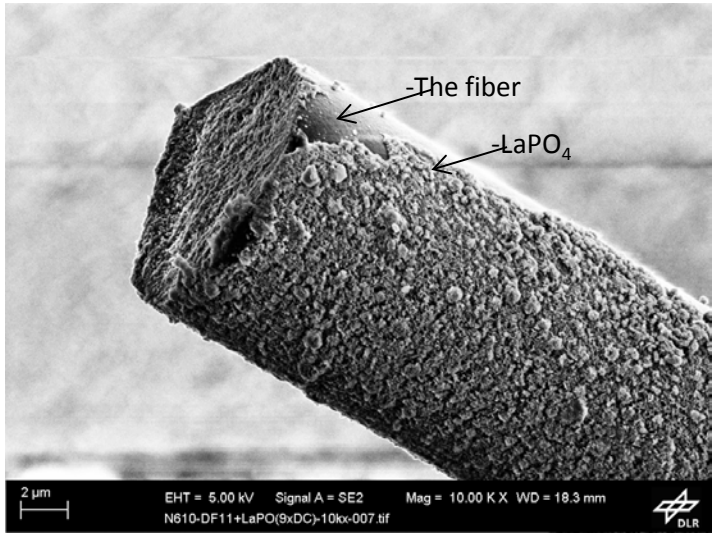
Foulard Coating (advanced)





Variation of Coating Parameters (1):
DC results



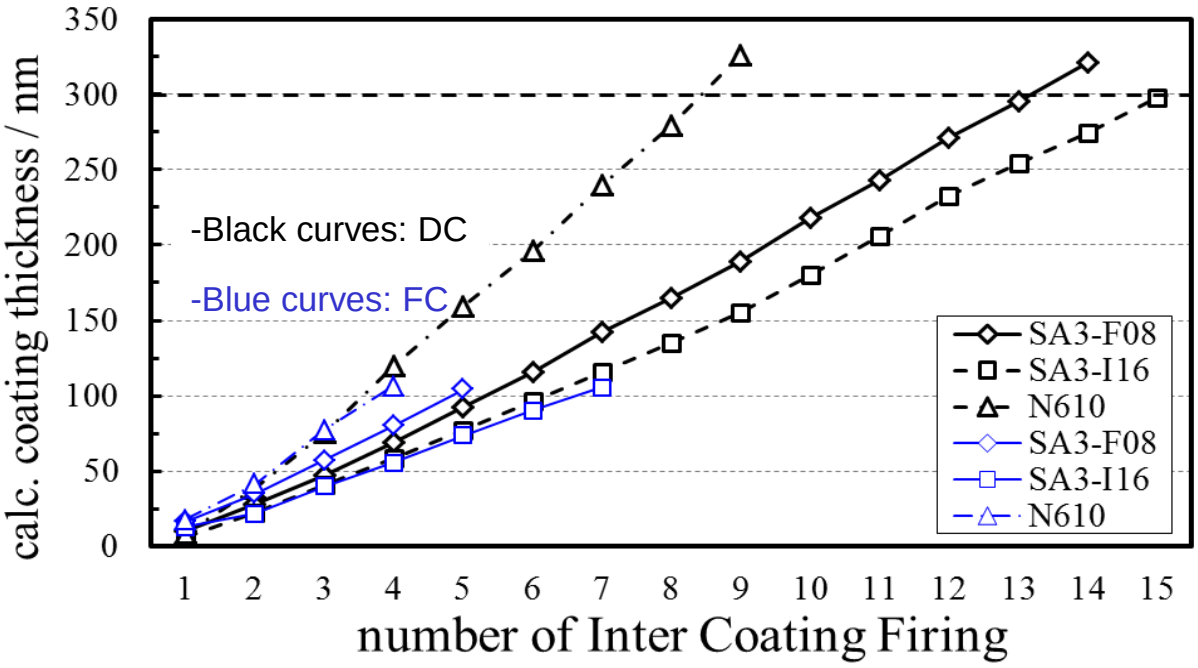


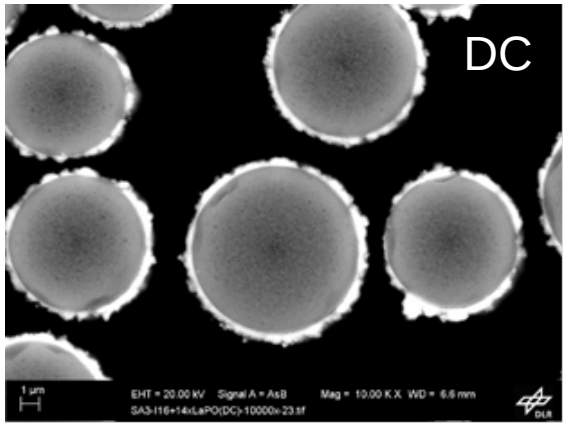
SEM picture of Nextel610 fibre after 9 loops

	Fibre diameter	No. of filaments
SA3-I16	7.5	1600
SA3-F08	10	800
N610-DF11	12	400

conclusions:
- the thicker the fibre diameter, the thicker the coating
- the smaller the number of filaments/roving, the thicker the coating

Variation of Coating Parameters (2):
Comparison between DC and FC





- DC target: 300nm
- FC target: 100nm

- DC and FC (needs 2 coating cycles) are very similar w.r.t. coating thickness!!!
- FC provides a more homogeneous coating than DC!

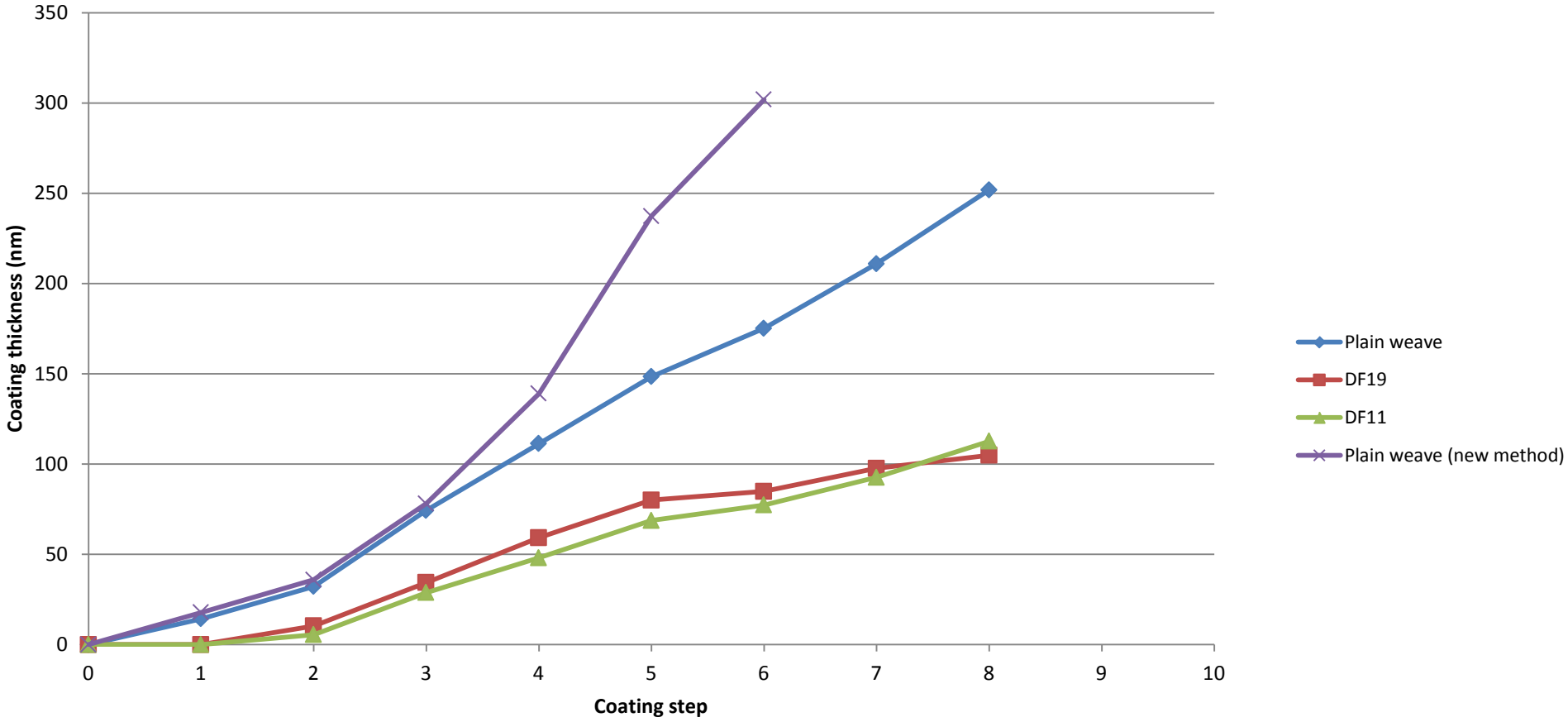
Improved fibre coating processing for fabric types Al_2O_3 (Nextel 610) and SiC (Tyranno SA3)

- State-of-the-art: dilute solutions in order to achieve homogeneous coatings:
  disadvantage: many time and cost consuming cycles needed for thick coatings

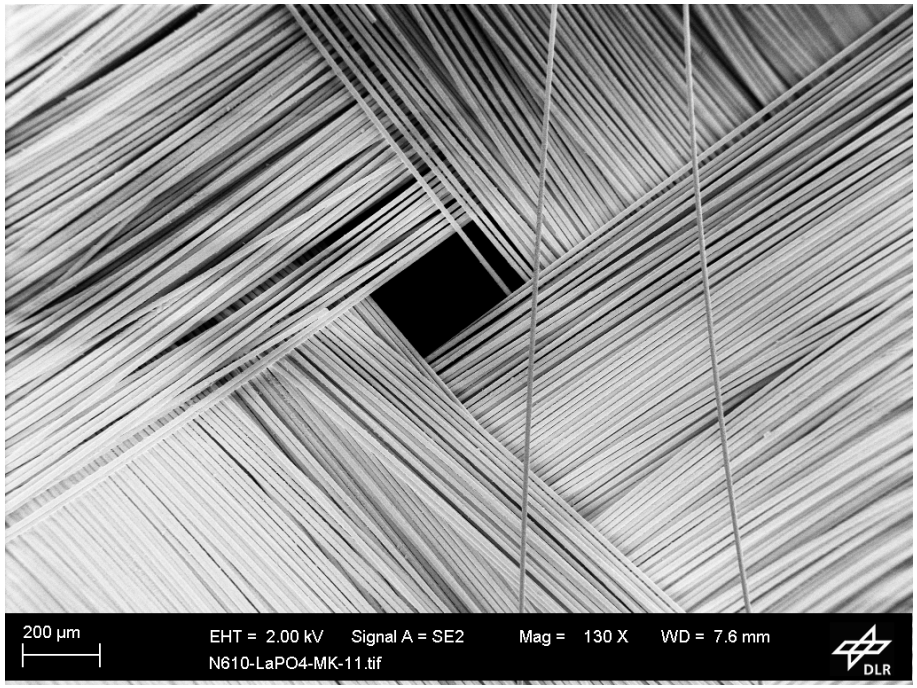
- Further development at DLR by applying more concentrated solutions via Foulard technique

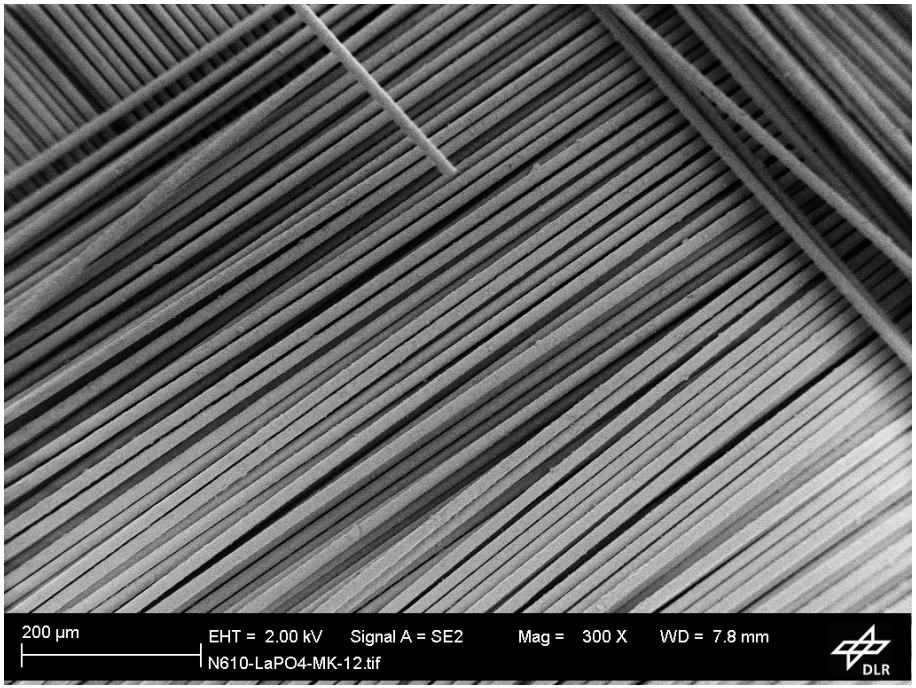
- This work shows that Foulard technique using almost saturated solutions is feasible and provides promising results as well as potential:
  - homogeneous fibre coatings with very low fibre bridging
  - Thick fibre coating steps achievable by low number of cycles
  - Foulard technique has potential for cost-effective fibre coating

Calculated coating evolution from mass gain with respect to fabric type (Al_2O_3)



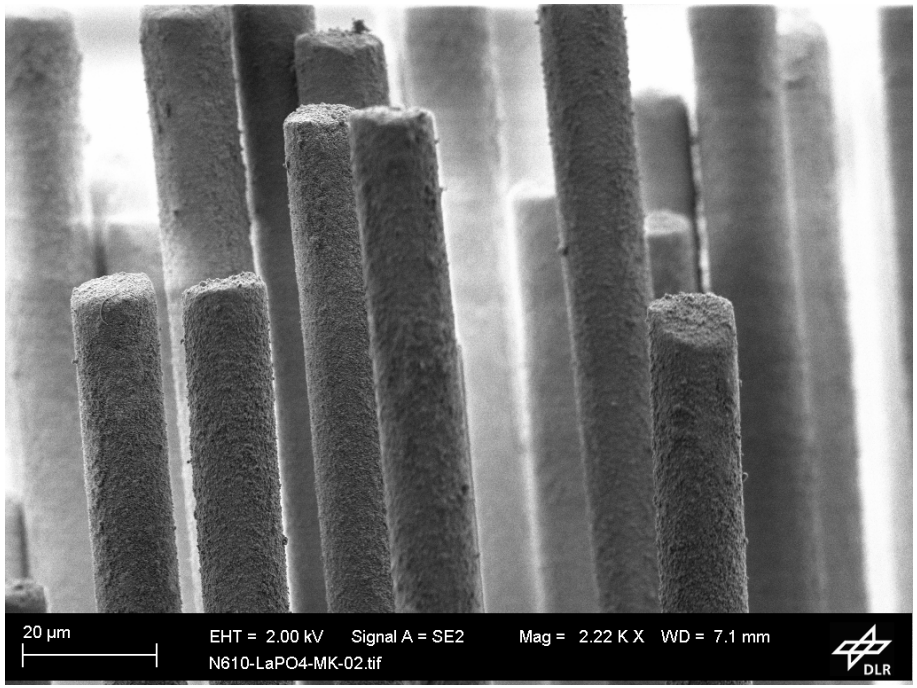
$LaPO_4$ fibre coating on Al_2O_3 (Nextel 610) I

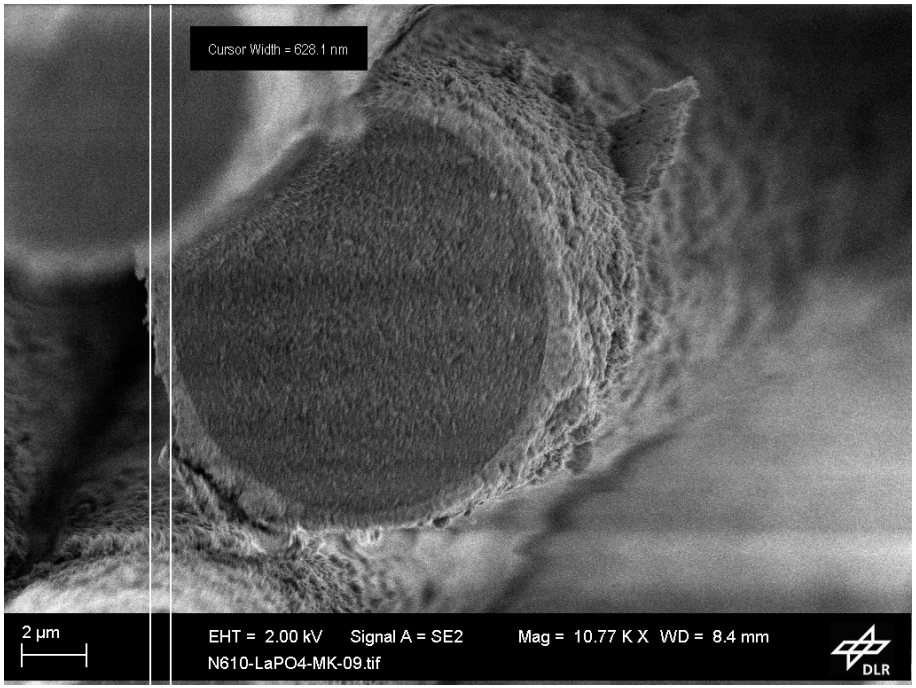




- **No bridging by fibre coating**
- **Single fibre coating**

$LaPO_4$ fibre coating on Al_2O_3 (Nextel 610) II





-Thick homogeneous fibre coatings (628 nm) with six cycles!

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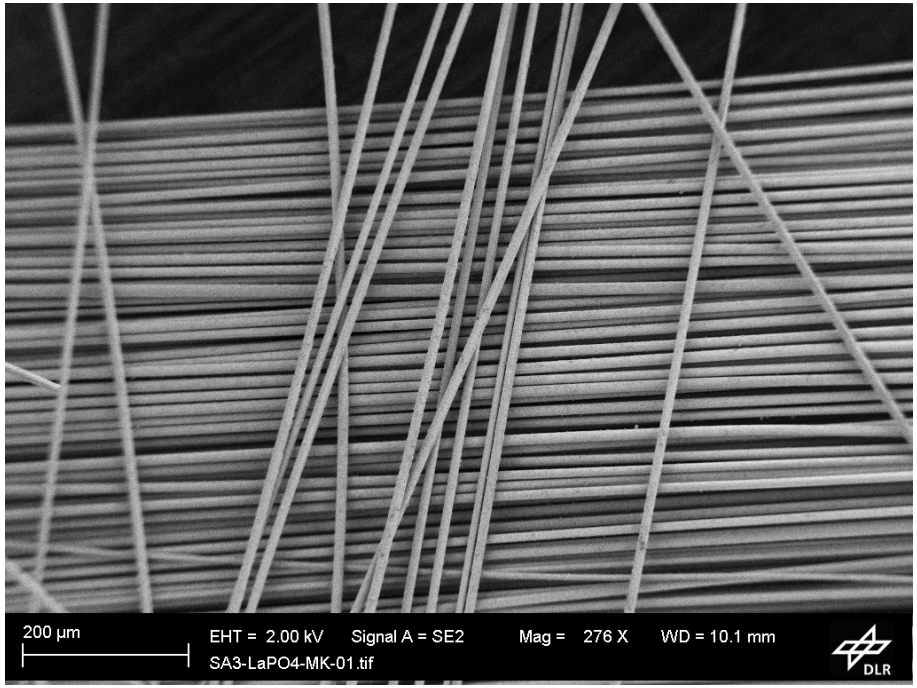
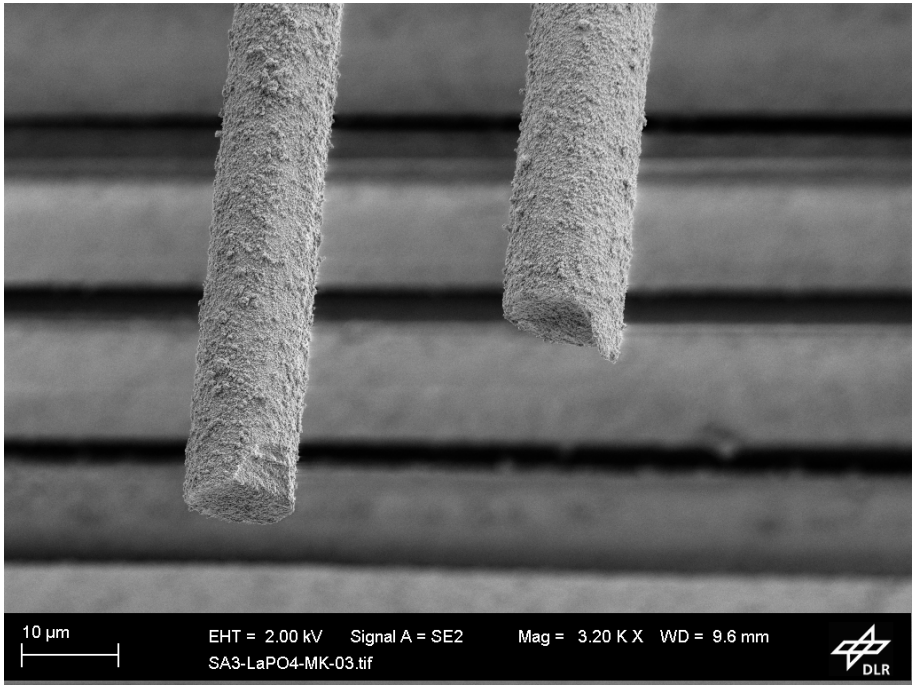
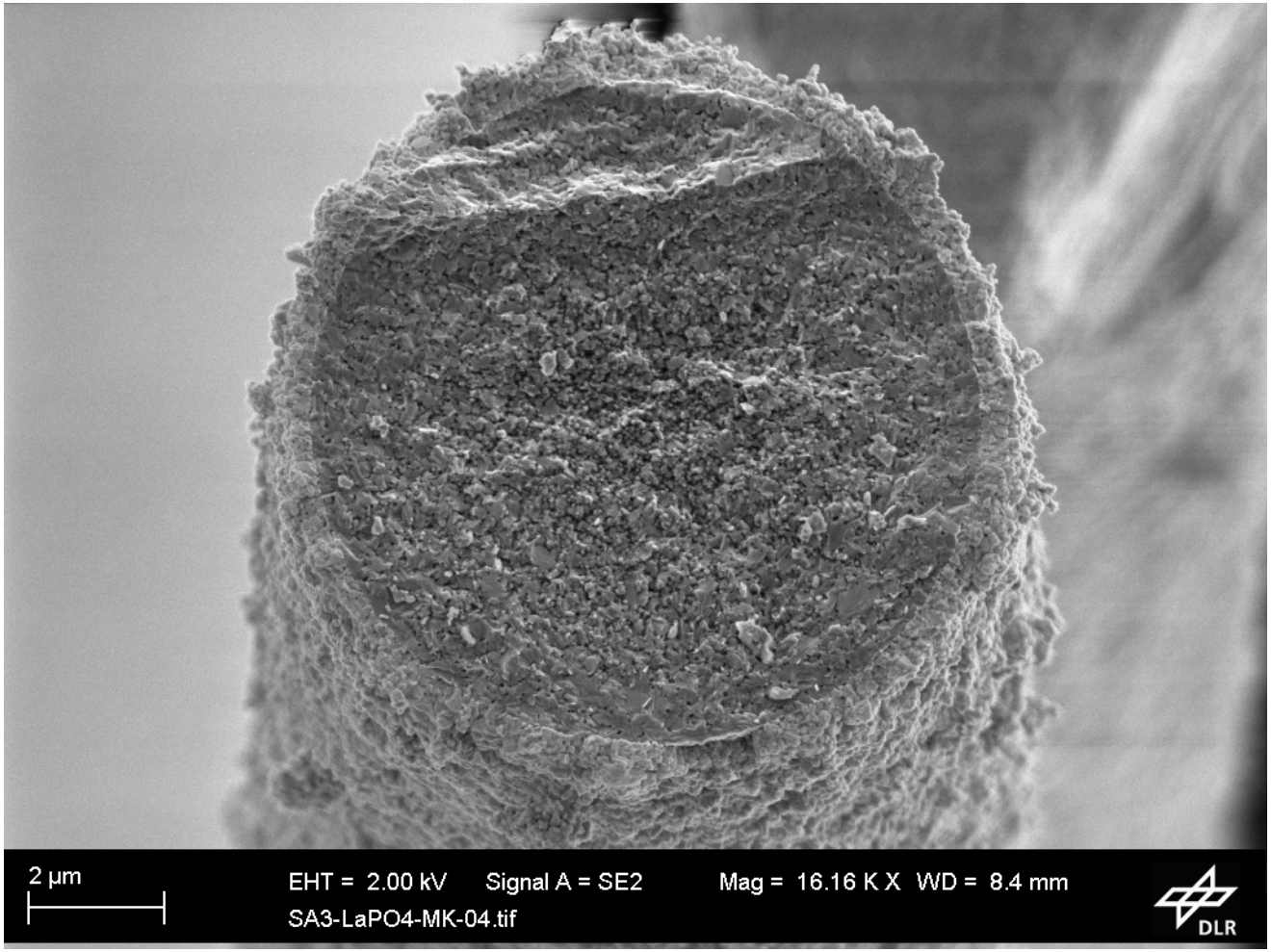
$LaPO_4$ fibre coating on SiC fabrics (SA3) I





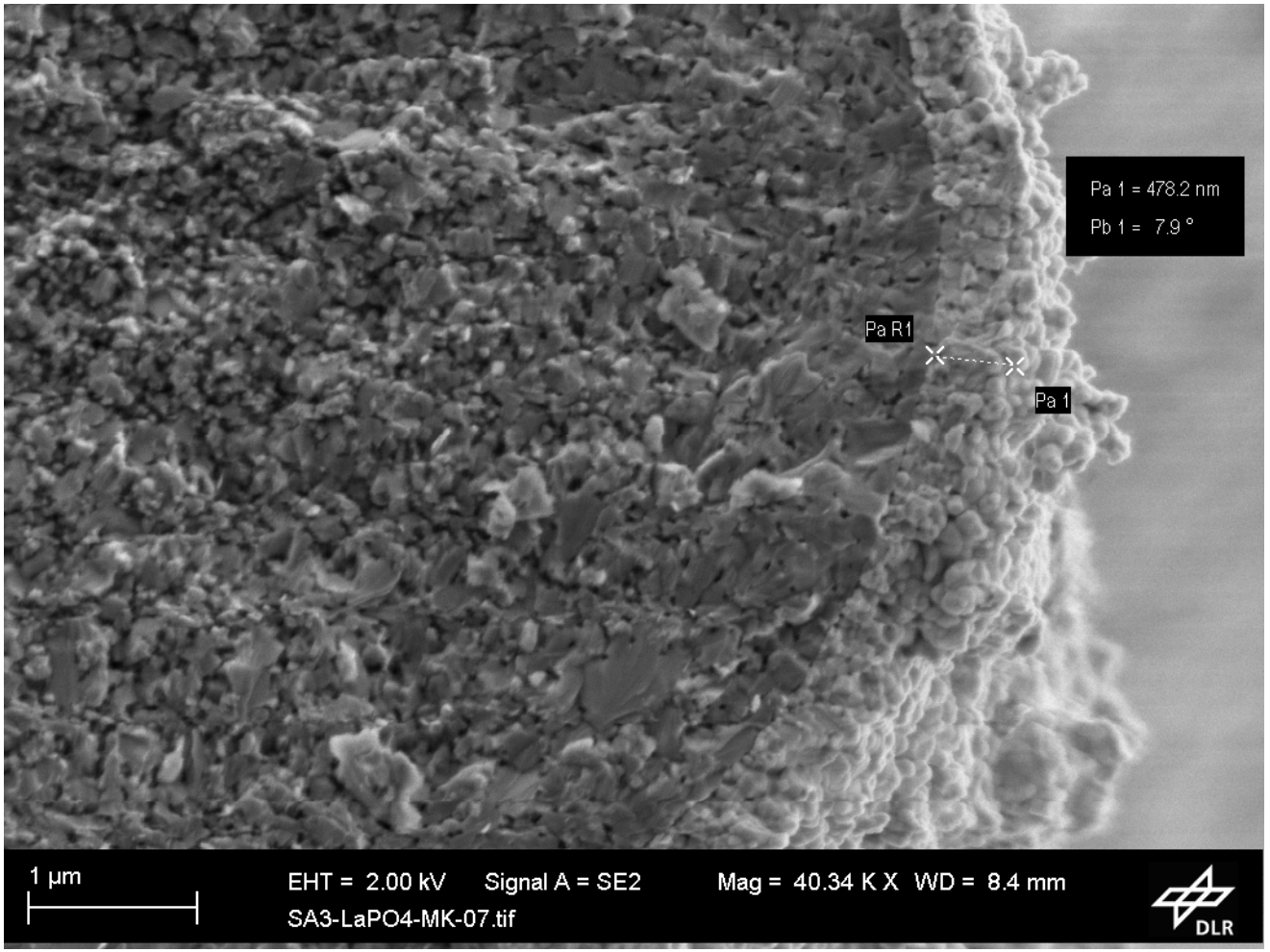
- **No bridging by fibre coating**
- **Single fibre coating**

$LaPO_4$ fibre coating on SiC fabrics (SA3) II



- **Homogeneous fibre coating**

$LaPO_4$ fibre coating on SiC fabrics (SA3) III



-Thick homogeneous fibre coatings (478 nm) with six cycles!

Properties of OXIPOL (A-D) and SiC/SiCN (E)

Specimen	A	B*	C	D*	E**
Coating type	$LaPO_4$	$LaPO_4$	-	fugitive	$LaPO_4$
Coating loops [-]	9	4	0	2	9
Coating thickness [nm]	300	100	0	<100	300
Fibre volume content [%]	43	45	42	51	45
Fabric type (Nextel 610 fibre) (Tyranno SA3) Aerial weight [g/m²]	DF11 - 373	DF11 - 373	DF11 - 373	DF19 - 654	- F-08 240
Density [g/cm³]	2.77	n.d.	2.88	2.76	2.51
Open porosity [%]	7.0	16.6	6.1	11.7	6.3
Flexural strength (3-point) before exposure [MPa]	132.4	169.5	87.4	197.9	167***
Flexural strength (3-point) after exposure (1100˚C, air, 20h) [MPa]	≥ 98.3	≥ 73.3	94.3	117.0	129***
Failure mode after exposure	shear	shear	tensile	tensile	tensile

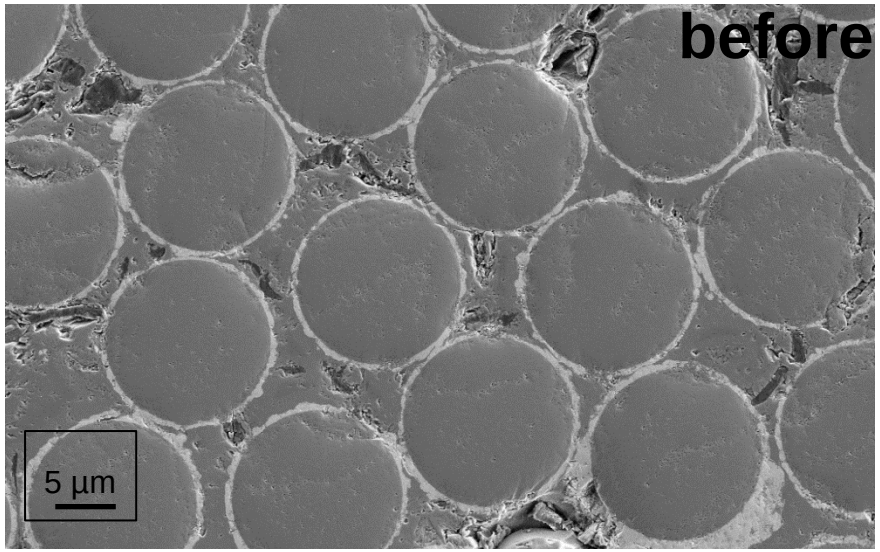
*S. Hönig et al.: 36th Int. Conf. on Advanced Ceramics and Composites (ICACC) 2012.

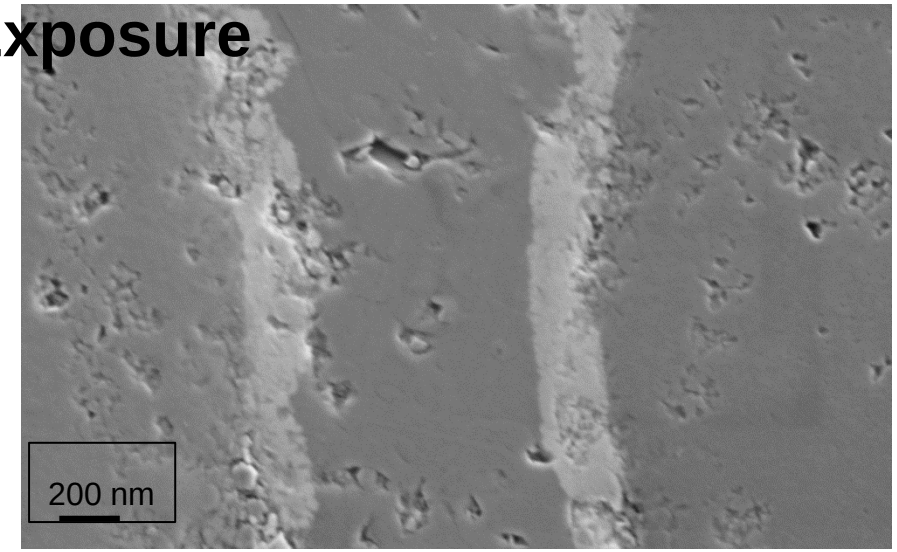
**E. Klatt: PhD Thesis DLR Stuttgart 2013

***measured according DIN ENV 658-3 (l/d=20)

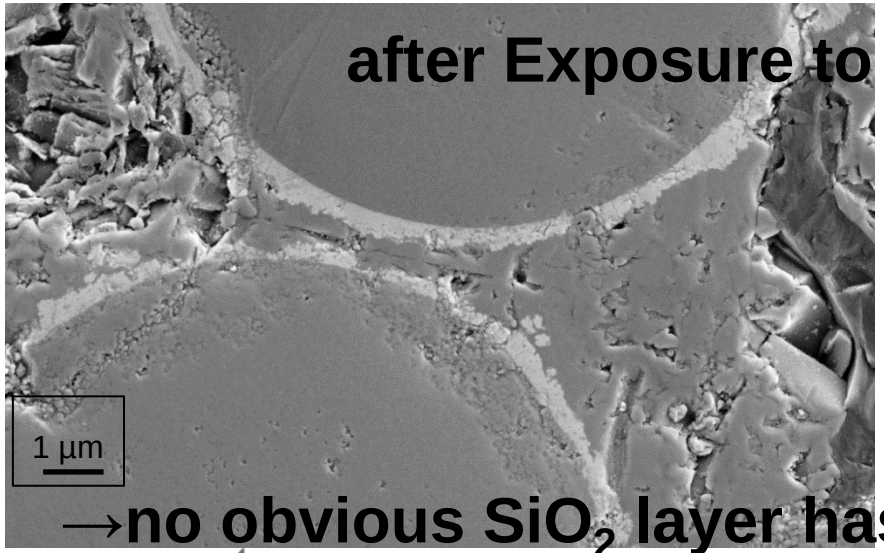
SEM of Polished Surface of OXIPOL with $LaPO_4$ coating

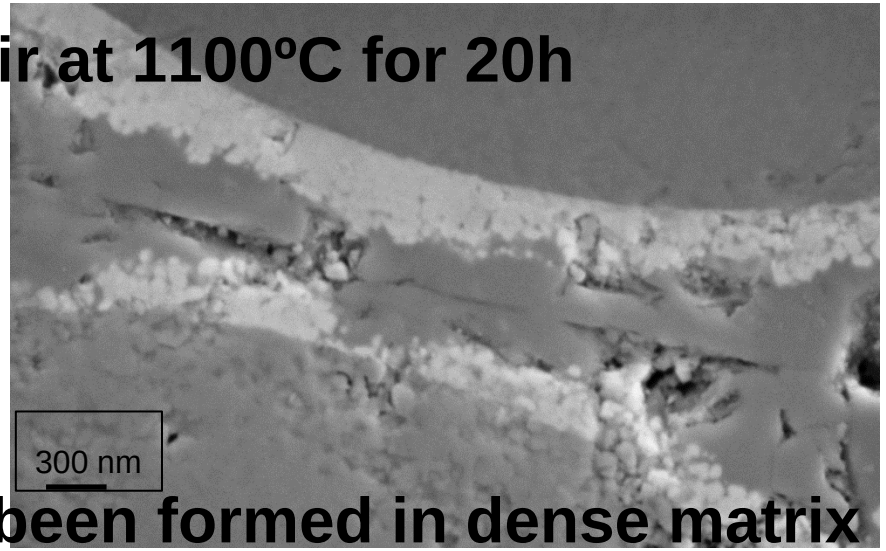
before Exposure





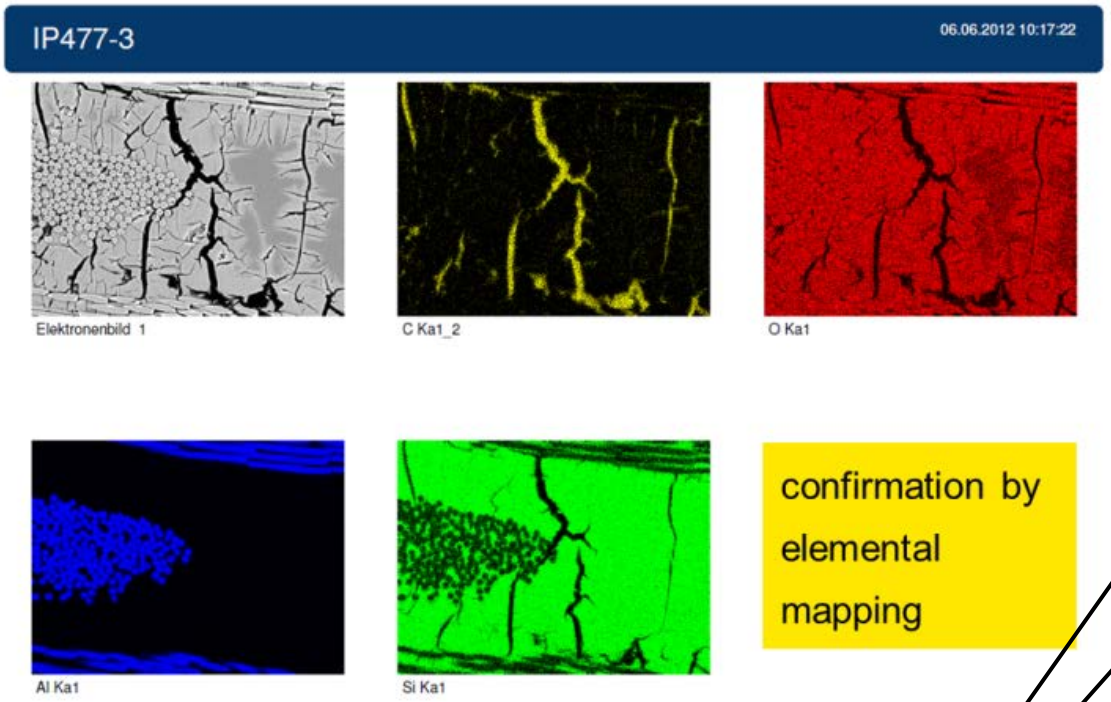
after Exposure to Air at 1100ºC for 20h



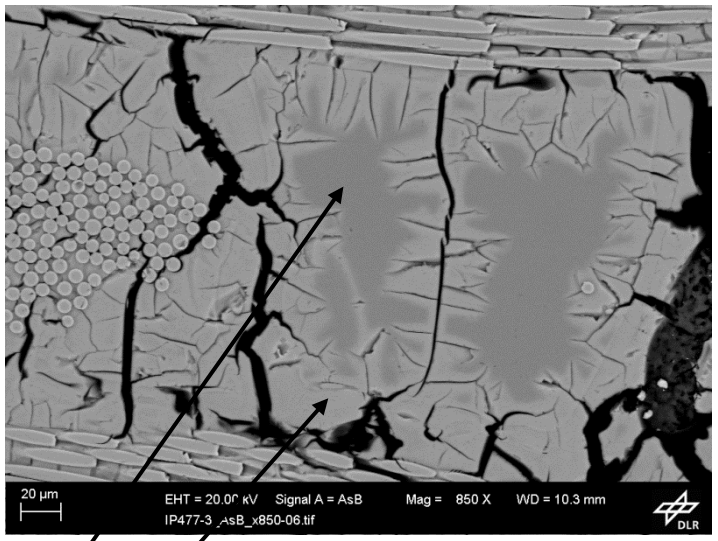


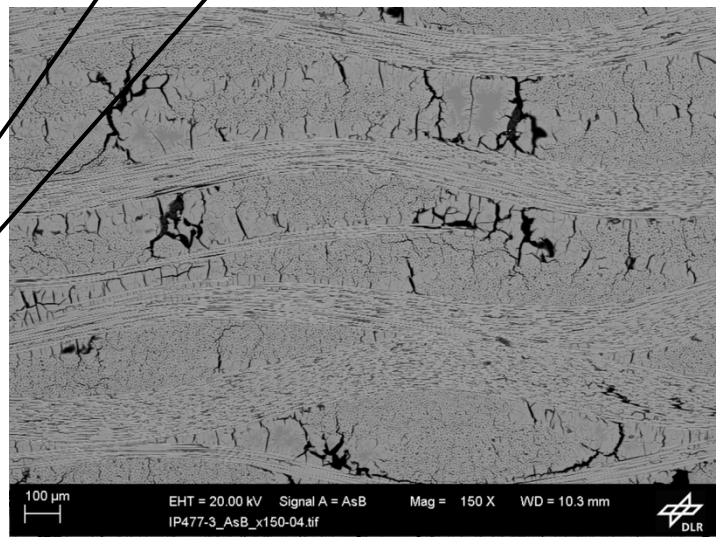
→no obvious SiO_2 layer has been formed in dense matrix

EDX-Analysis of Oxidized OXIPOL @ 1100˚C for 20 h in Air



confirmation by elemental mapping





- matrix composition w.r.t. EDX: → „SiO2C“
- oxidized matrix composition w.r.t. EDX: → „SiO2“

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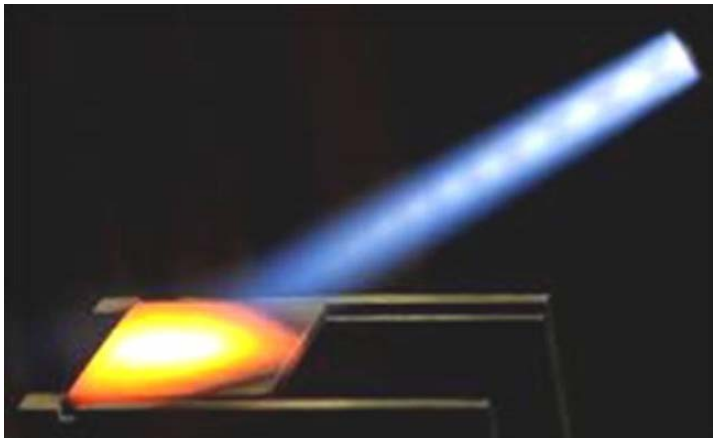
HVOF-Test in combustion environment



-HVOF-Test
-(**H**igh **V**elocity **O**xygen **F**uel)

-by EADS Astrium
(ATLLAS II-project)

- represents combustion typical conditions like combustion chemistry / combustion products, temperature, gas velocity
- test conditions in a temperature range of 1000 ˚C up to 2050 ˚C possible
- the HVOF-flame was fueled by Kerosene/Oxygen

Microstructural Characterisation of uncoated C/C-SiC @ T

-C/C-SiC, uncoated, untested

-1500 ˚C, 1h

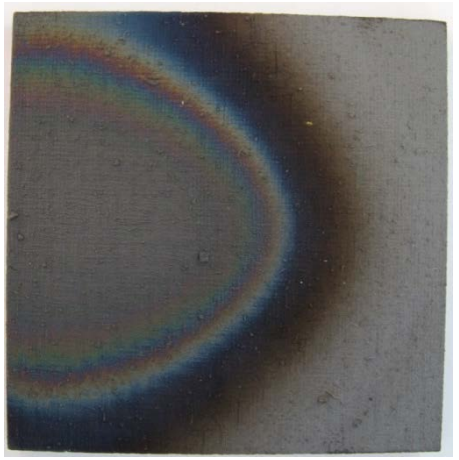
-1700 ˚C, 1h

- **both tested samples are very brittle after exposure**
- **heavy degradation of the sample tested at 1700 ˚C**

Visual Characterisation of CVD-SiC coated C/C-SiC @ T

-C/C-SiC, SiC-coated, untested

-1500 ˚C, 4h



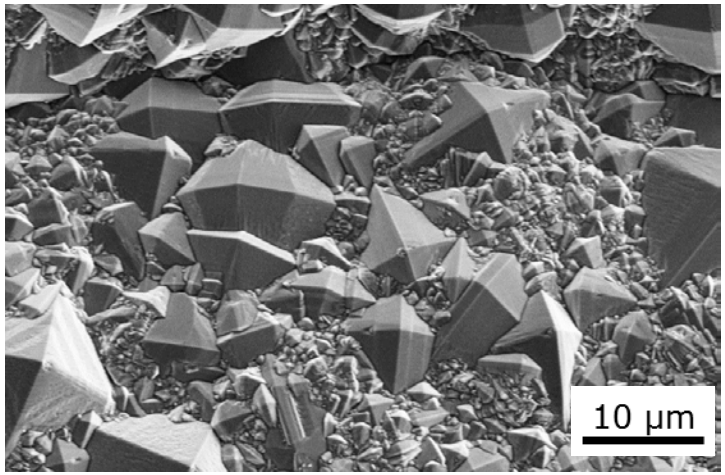
-1700 ˚C, 1h

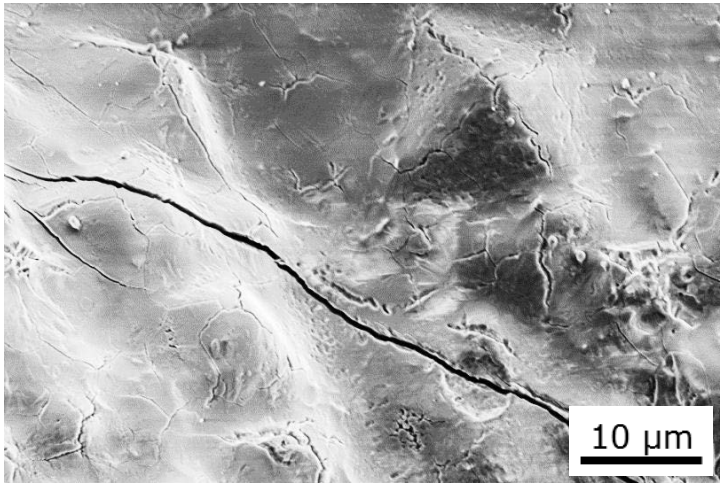
- **the SiC-coated samples stay intact even at 1700 ˚C**
- **some degraded spots can be observed**

Microstructural Characterisation of C/C-SiC @ 1500 ˚C

-1500 °C, 4h,

-surface, top view



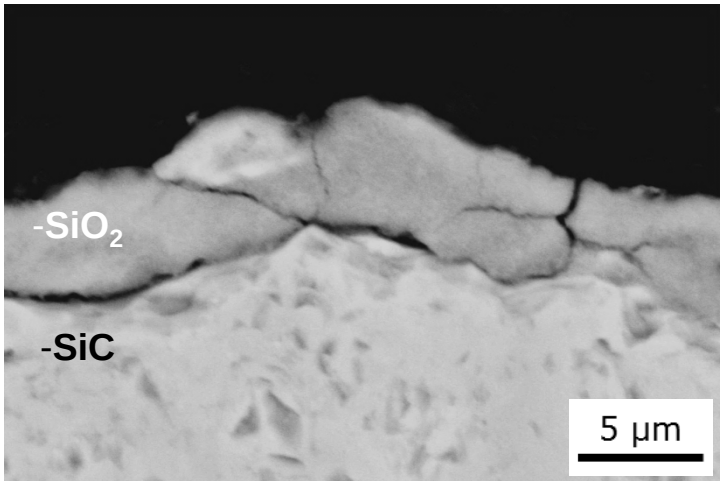


-C/C-SiC, SiC_{CVD} coating

-(untested sample)

-1500 °C, 4h,

-surface, side view



⇒ **Formation of a 5 µm SiO_2-scale**

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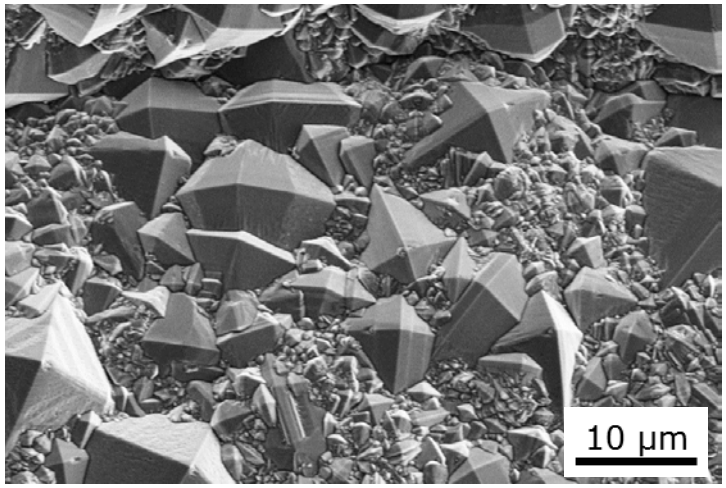
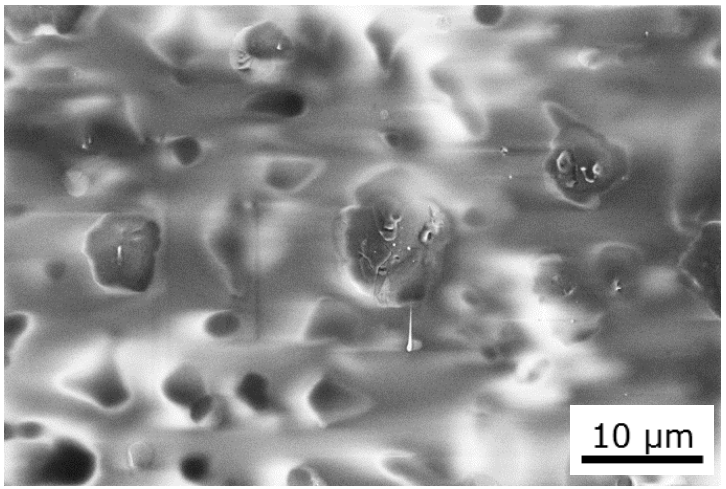
Microstructural Characterisation of C/C-SiC @ 1700 ˚C

-1700 °C, 1h,

-surface, top view



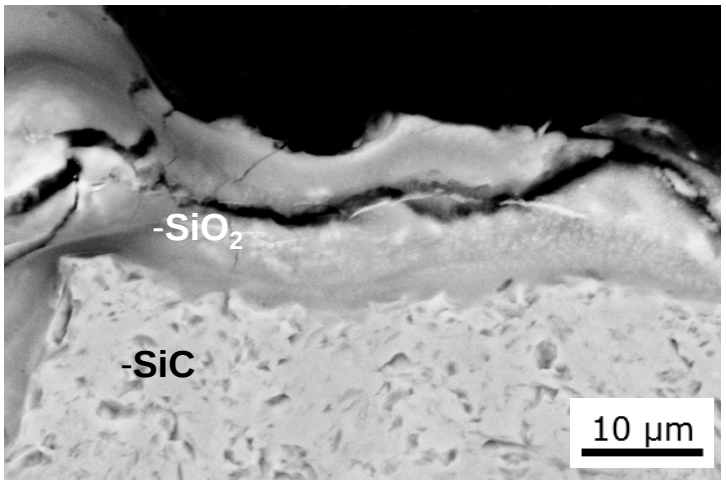


-C/C-SiC, SiC_{CVD} coating,

-(untested sample)

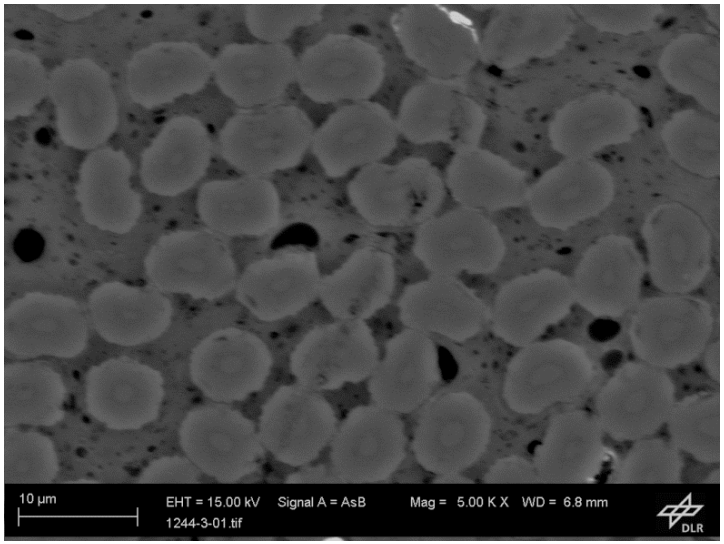
-1700 °C, 1h,

-surface, side view



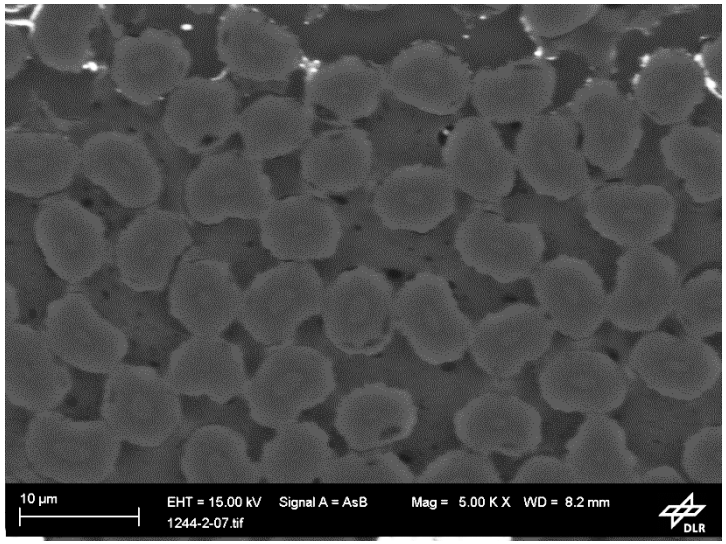
⇒ **Formation of a 10-20 µm SiO_2-scale**

Microstructural Characterisation of C/C-SiC @ T



-C/C-SiC, SiC_{CVD} coating,

-(untested sample)



-C/C-SiC, SiC_{CVD} coating,

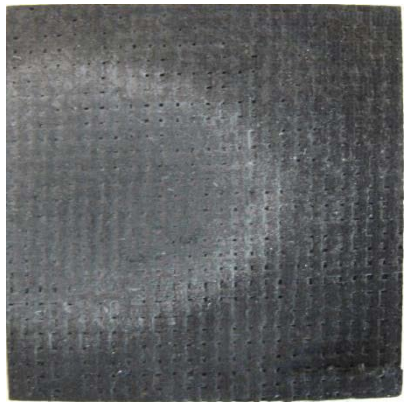
-1700 °C, 1h

⇒ **C-matrix is not affected**

Visual Characterisation of SiC_{pyC}/SiCN @ T

-untested

-1300 ˚C, 4h



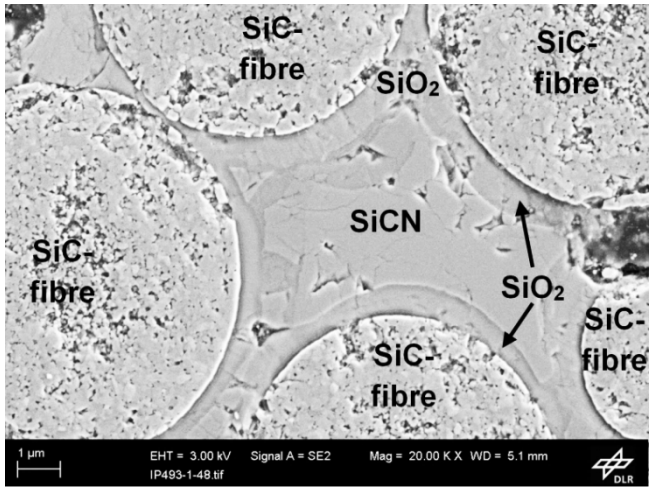
-1500 ˚C, 4h

-1700 ˚C, 4h

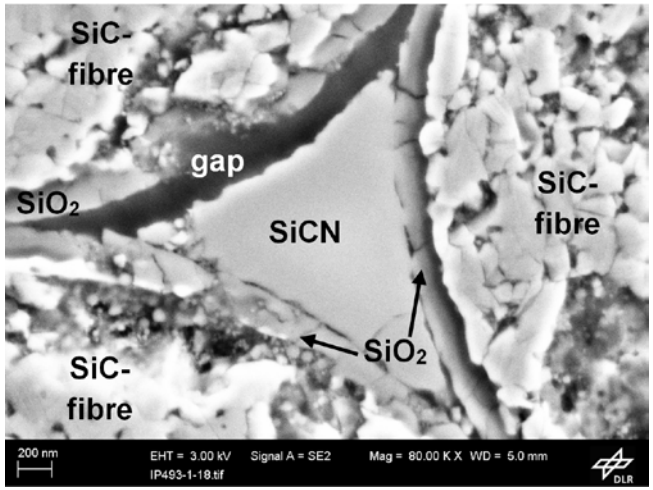
e‘ before exposure [%]	7.04	6.08	6.06
e‘ after exposure [%]	11.26	11.74	11.31
Δm/m [%]	-2.8	-3.3	-3.3

- **Increased porosity after exposure (independent from test temperature)**
- **no spallation of the surface**

Microstructural Characterisation of SiC_{pyC}/SiCN @ 1300 ˚C



- **Close to surface**
  - ➢ **PyC coating was removed due to active oxidation**
  - ➢ **Occurring gaps were completely filled by SiO_2**



- **Center of sample**
  - ➢ **PyC coating also was removed**
  - ➢ **Occurring gaps were starting to get filled by SiO_2**
  - ➢ **@ higher T similar microstructure in center of composite like on surface**

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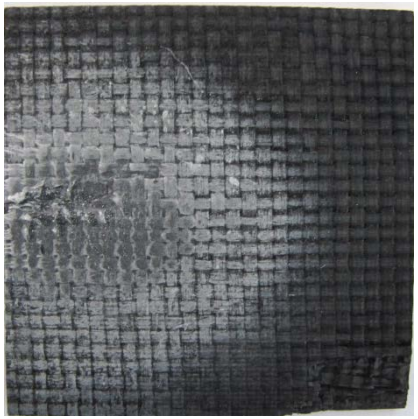
Visual Characterisation of SiC_{LaPO4}/SiCN @ T

-untested

-1300 ˚C, 4h

-1500 ˚C, 4h

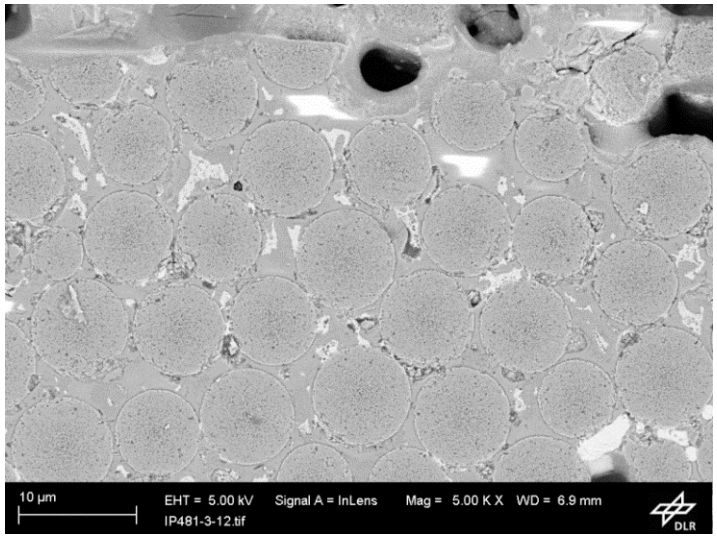


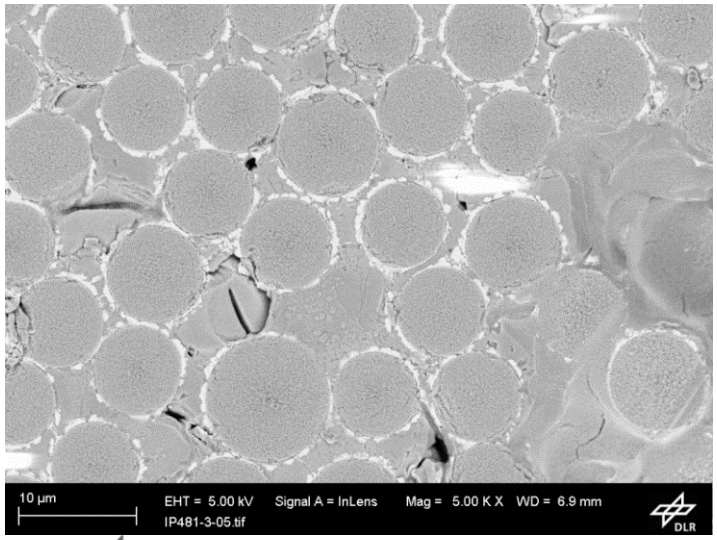
-1700 ˚C, 1.5h

e‘ before exposure [%]	11.16	12.12	12.24
e‘ after exposure [%]	13.21	16.97	16.47
Δm/m [%]	-1.8	-2.4	-2.7

- **only slight increase of porosity at 1300 ˚C**
- **strong increase of porosities at 1500 ˚C and above**
- **1700 ˚C test aborted after 1.5 hours due to spallation of the surface**

Microstructural Characterisation of SiC_{LaPO4}/SiCN @ 1700 ˚C



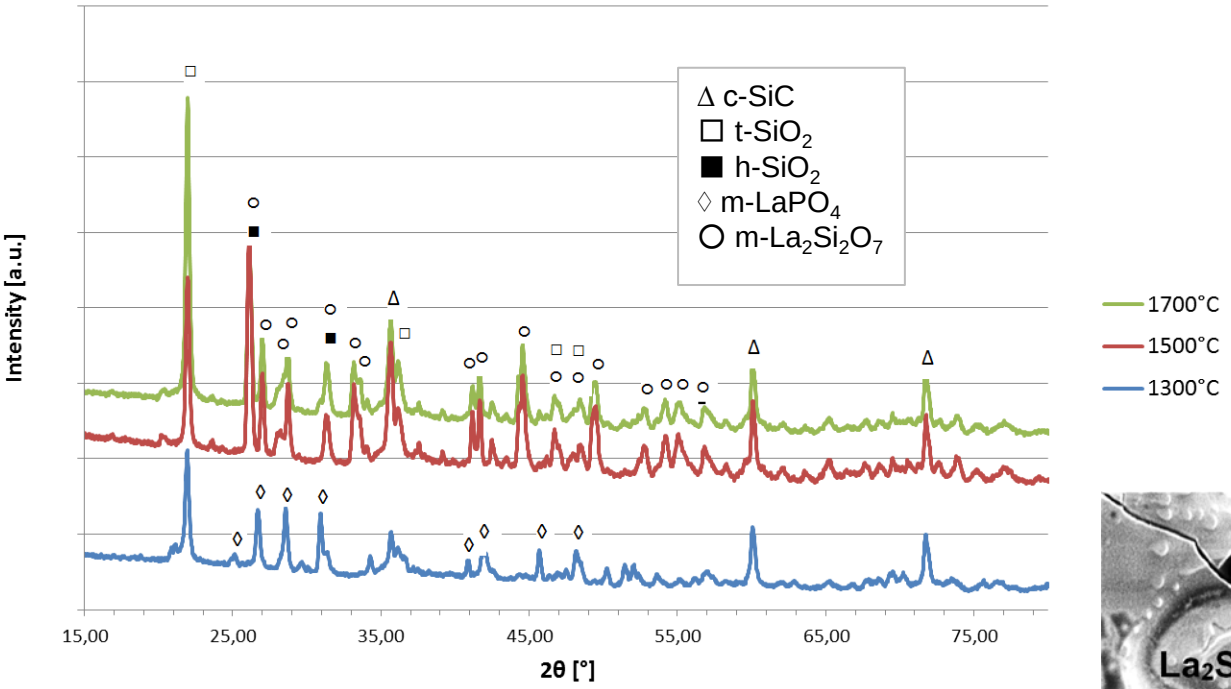


-Shown is sample tested at 1700 ˚C, close to surface

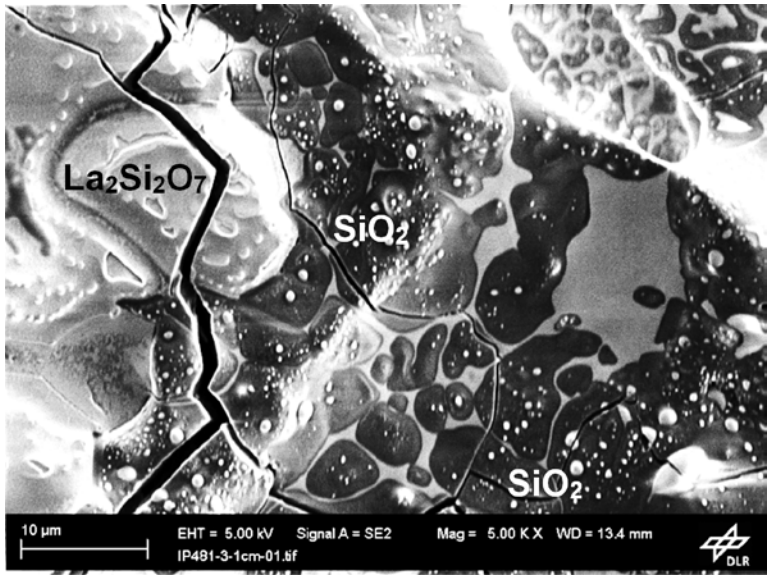
- **Close to the surface: degradation of coating already can be detected at 1300 ˚C**

- **At the center of the samples the coating stayed intact at 1700 ˚C (1.5h)**
- **Samples tested at lower temperatures (4h) showed growth of SiO_2 between fiber and coating**

Microstructural Characterisation of SiC_{LaPO4}/SiCN @ 1700 ˚C



- Top view on sample with $LaPO_4$-coated fibres
  dark phase (SiO_2)
  bright phase ($La_2Si_2O_7$)



- **formation of $La_2Si_2O_7$ at 1500 ˚C and 1700 ˚C detected via XRD on the samples surfaces**
- **Necessity for EBC-protection of structure**

Potential Hydrothermal Decomposition of Monazite

Although, reaction of $LaPO_4$ with SiO_2 is thermodynamically unfavorable

$$4\ LaPO_{4(s)} + 4\ SiO_{2(s)} \rightarrow 2\ La_2Si_2O_{7(s)} + P_4O_{10(g)} \qquad \Delta G > 0$$

However, decomposition of $LaPO_4$ at T > 1300˚C in the **presence of excess water vapor (jet stream) and SiO_2** is feasible due to enforced decomposition reactions. XRD and SEM/EDX of first test samples and thermodynamical calculations reveal:

$$4\ LaPO_{4(s)} + 6\ H_2O_{(g)} + 4\ SiO_{2(s)} \rightarrow 2\ La_2Si_2O_{7(s)} + 4\ H_3PO_{4(g)} \qquad \Delta G < 0$$
$$4\ H_3PO_{4(g)} \rightarrow P_4O_{10(g)} + 6\ H_2O_{(g)} \qquad \Delta G < 0$$

in total:

$$4\ LaPO_{4(s)} + 4\ SiO_{2(s)} \rightarrow \langle H_2O_{(g)} \rangle \rightarrow 2\ La_2Si_2O_{7(s)} + P_4O_{10(g)} \qquad \Delta G < 0$$

Summary

Monazite ($LaPO_4$) fibre coatings have been successfully applied for

- Oxide (OXIPOL) as well as non-oxide CMCs (SiC/SiCN)

Influences of coating parameters have been demonstrated:

- fibre type and diameter as well as surface roughness
- Foulard (FC) and dip (DC) coating
- Further improvement of coating process w.r.t. coating efficiency

CMC behaviour before and after exposure in hot gas environment (HVOF-Test)

- Potentials and limits of $LaPO_4$-coating were demonstrated
- SiO_2 formation observed on outer and crack surface by SEM
- Potential of CVD-SiC as EBC-coating was demonstrated even with oxidation sensitive C/C-SiC
- Hypothesis of potential decomposition of $LaPO_4$ in water vapor and presence of SiO_2

Outlook

- Further densification of composite (porosity < 5%) may improve composite properties such as strength level before and after exposure to oxidation
- Implementation of fillers serving for „self healing“ properties are in our focus
- Development of EBC/TBC coatings for both type of composites (OXIPOL and SiC/SiCN) are necessary and in development (e.g.Y_2SiO_5/$Y_2Si_2O_7$)
- Mid-term research targets are fibre coatings for CMCs (reaction barrier, low fibre-matrix bonding) suitable for melt-infiltration („dense matrix“)
  - Development of fibre coatings for LSI-processing based on Y_2O_3, Si_3N_4 and TiB_2 are in progress in collaboration with special partners (Technical University of Chemnitz)
  - Development of fibre coatings for LSI-processing based on polymer-derived ceramics are in progress in collaboration with special partners (Technical University of Darmstadt and University of Stuttgart)

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