Mo- and W-Fiber Reinforced SiCN Ceramic Matrix Composites based on PIP process

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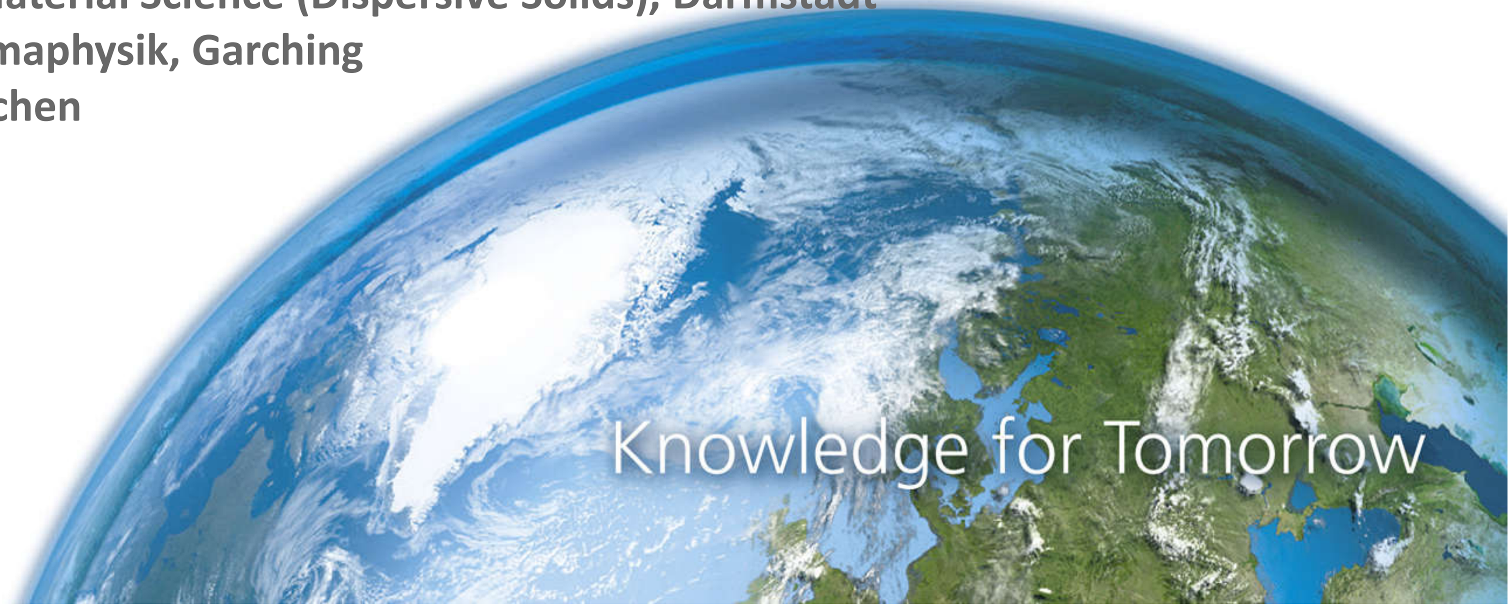

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Overview

- Introduction and motivation
- Properties of Mo- and W-fibers
- Manufacture of Mo/SiCN and W/SiCN composites
- Mechanical properties of composites
- Microstructure and phase analysis of composites
- Summary and outlook

Introduction and motivation

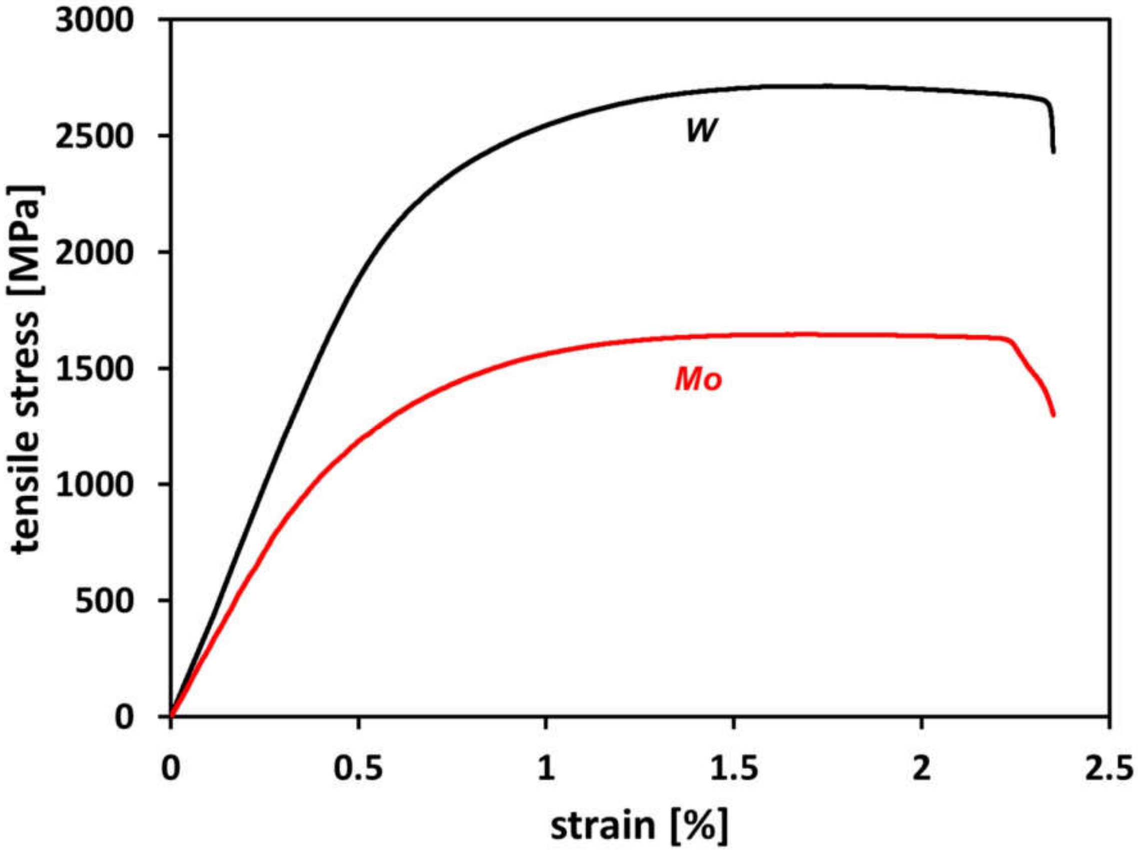
- Monolithic ceramics are brittle, have high stiffness and low fracture strain, but show catastrophic failure when overloaded
- Ceramic fiber reinforced ceramic matrix composites show graceful failure when overloaded, but still have low fracture strain (compared to metals)
- Metal fiber reinforced ceramic matrix composites are very little known, however, could be interesting due to higher fracture strain of metallic fibers
- Ceramic matrices are more oxidation and corrosion resistant as well as light-weight compared to molybdenum and tungsten

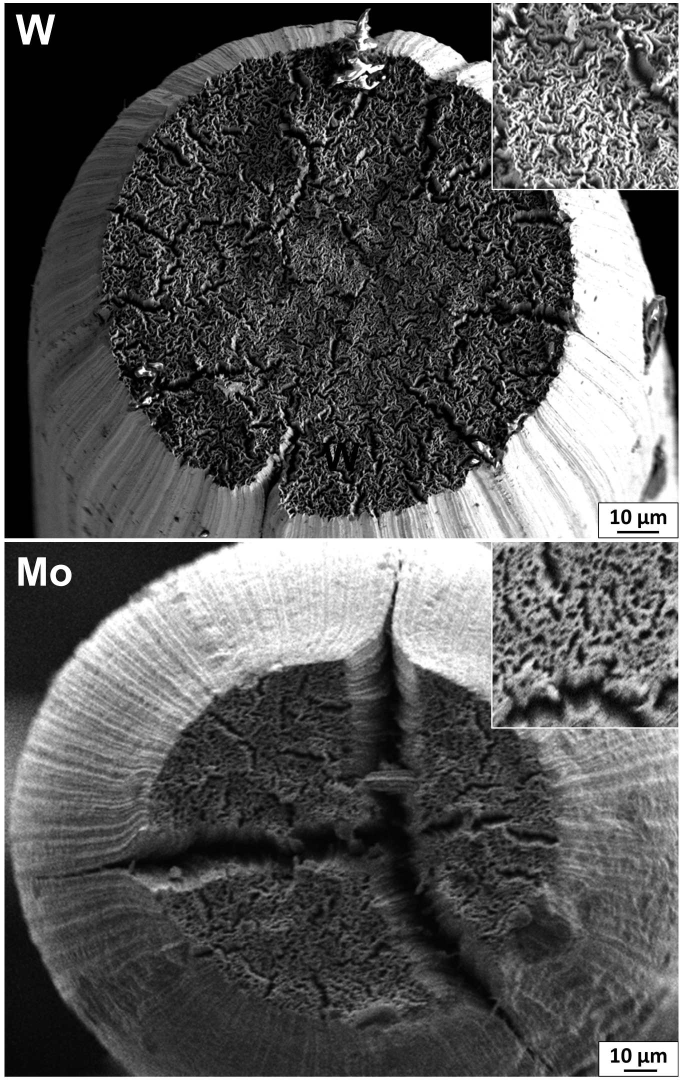
Physical and mechanical properties of Mo- and W-fibers

Fiber type		**Tungsten** **BSD-OG-102045280100**	**Molybdenum** **MOA-B6144601XX42**
Manufacturer		Osram	Osram
Diameter	µm	150	200
Density	g/cm^3	19.250	10.220
Yield strength	MPa	1855±18	1207±5
Tensile strength	MPa	2780±27	1647±1
Tensile modulus	GPa	(400)*	287±2
Fracture strain	%	1.85±0.05	1.9±0.1
Reduction in area	%	38.5±0.7	70.2±0.2
K content	ppm	70-80	150-200

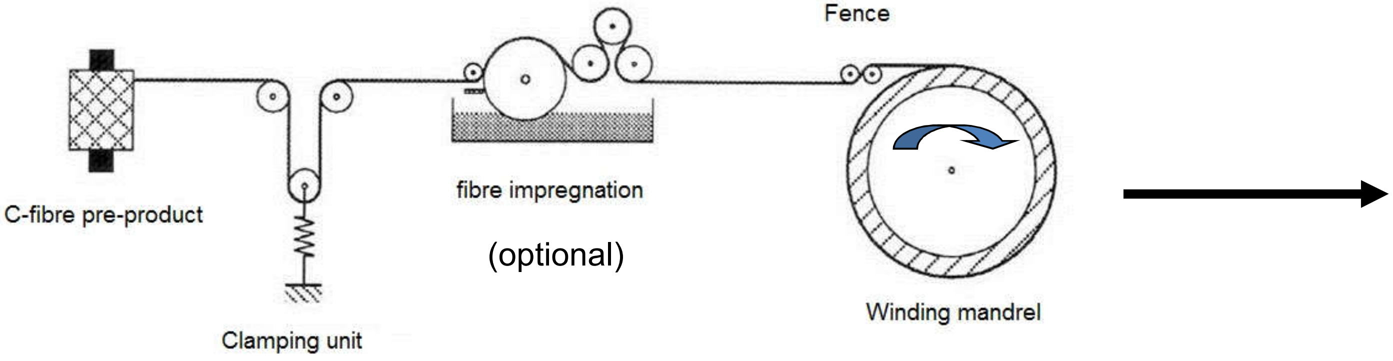
*) The measurements of the W wire were normalized to a Young’s modulus of 400 GPa to allow comparability

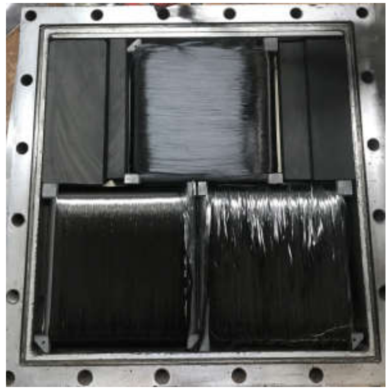
Tensile testing of single Mo- and W-fibers

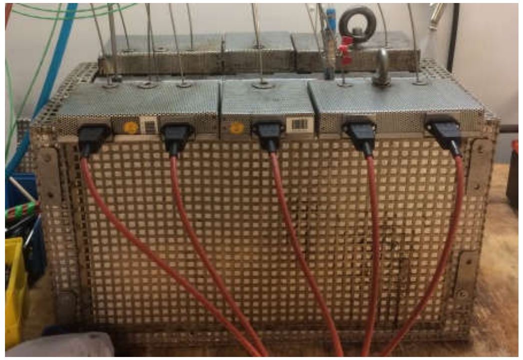




Preform manufacture – dry filament winding



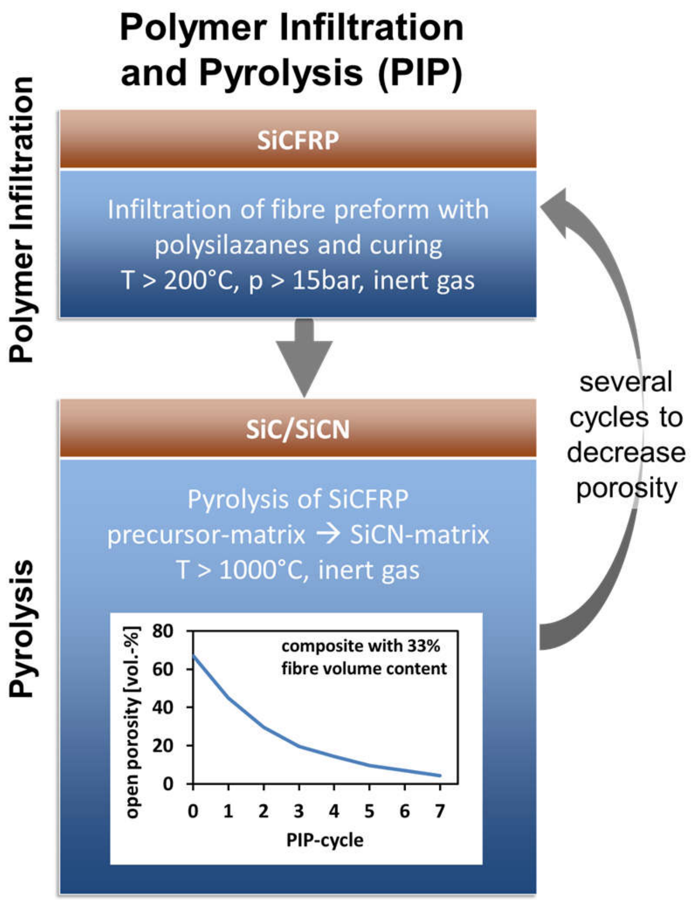


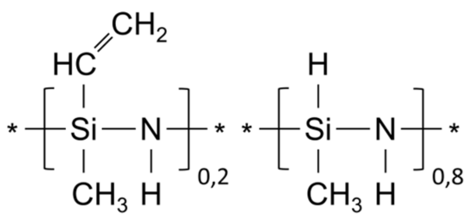


Raw materials and equipment:

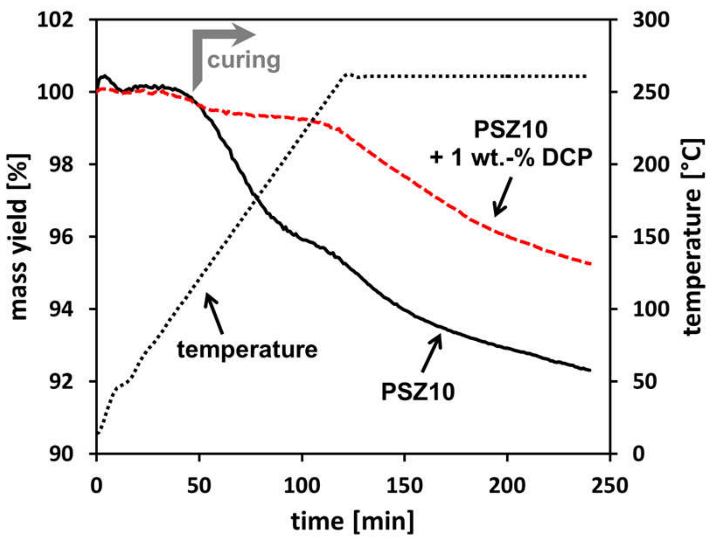
- Mo- or W-fibers
- Filament winding machine controlling winding speed and angle
- Graphite mandrel equipped with Teflon tape
- Precursor PSZ10 (polysilazane resin) for RTM infiltration and curing
- Steel mould for RTM infiltration and curing under pressure

Manufacture of Mo- and W-fiber ceramic matrix composites





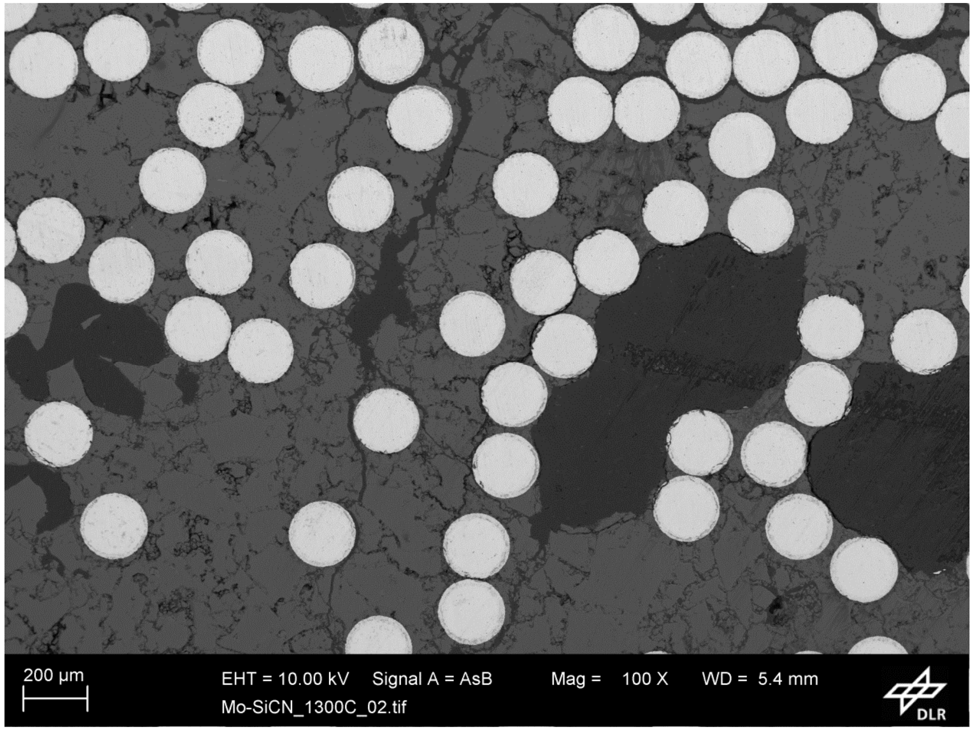
Clariant PSZ10

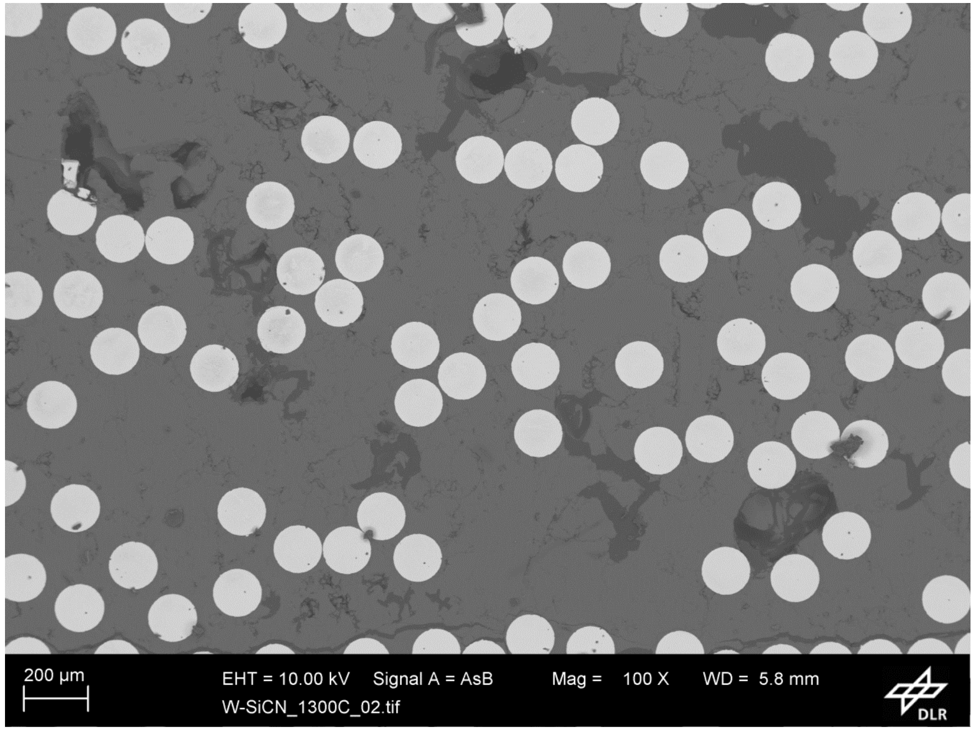


- Experimental polysilazane
- Low viscosity
- high mass yield

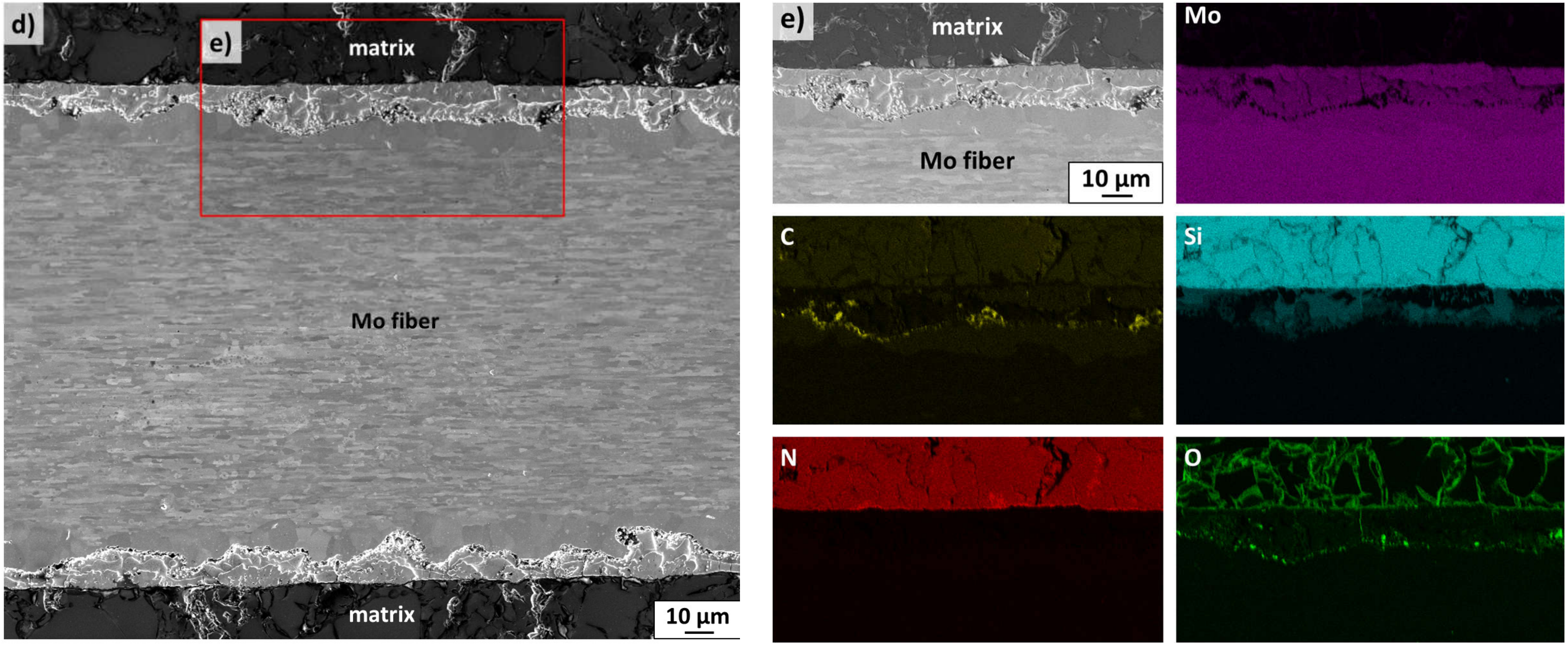
- Reduced mass loss by applying a catalyst (DCP) in curing step

Microstructure of Mo/SiCN (le.) and W/SiCN (ri.) after pyrolysis at 1300°C

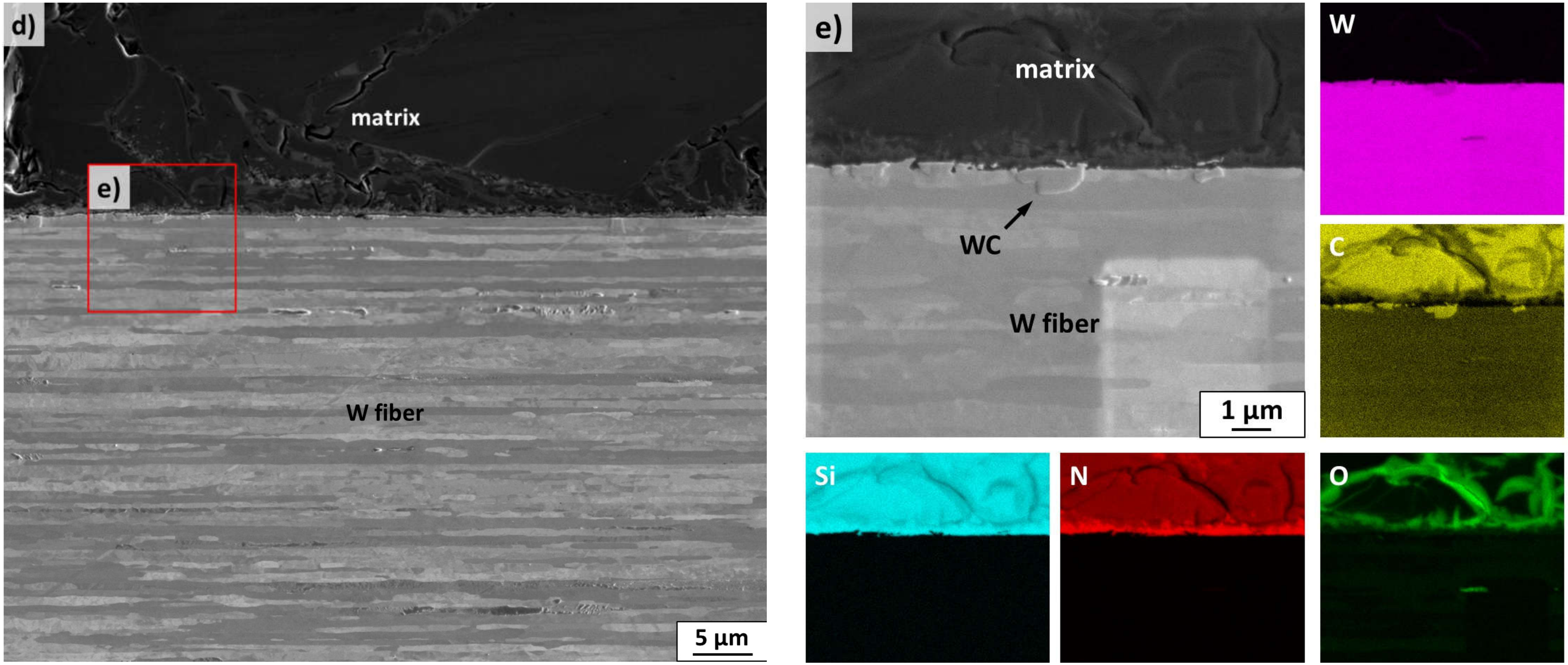




Microstructure of Mo/SiCN



Microstructure of W/SiCN

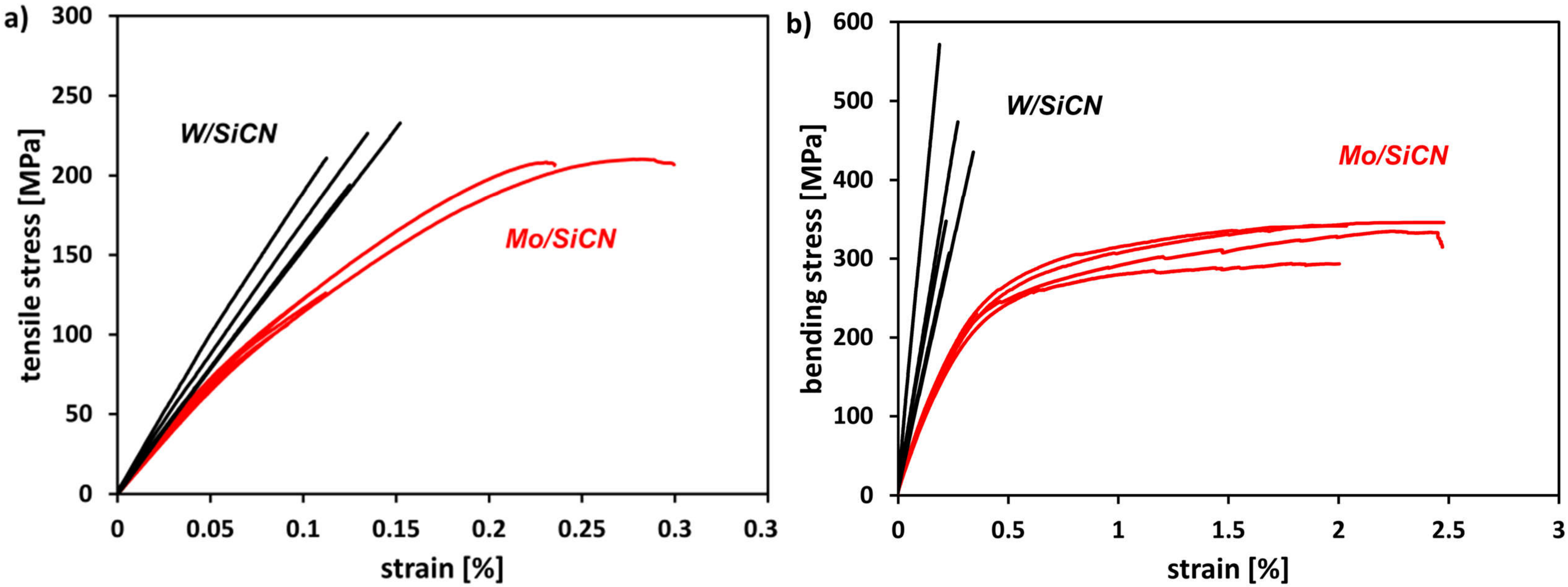


Properties of Mo/SiCN and W/SiCN composites

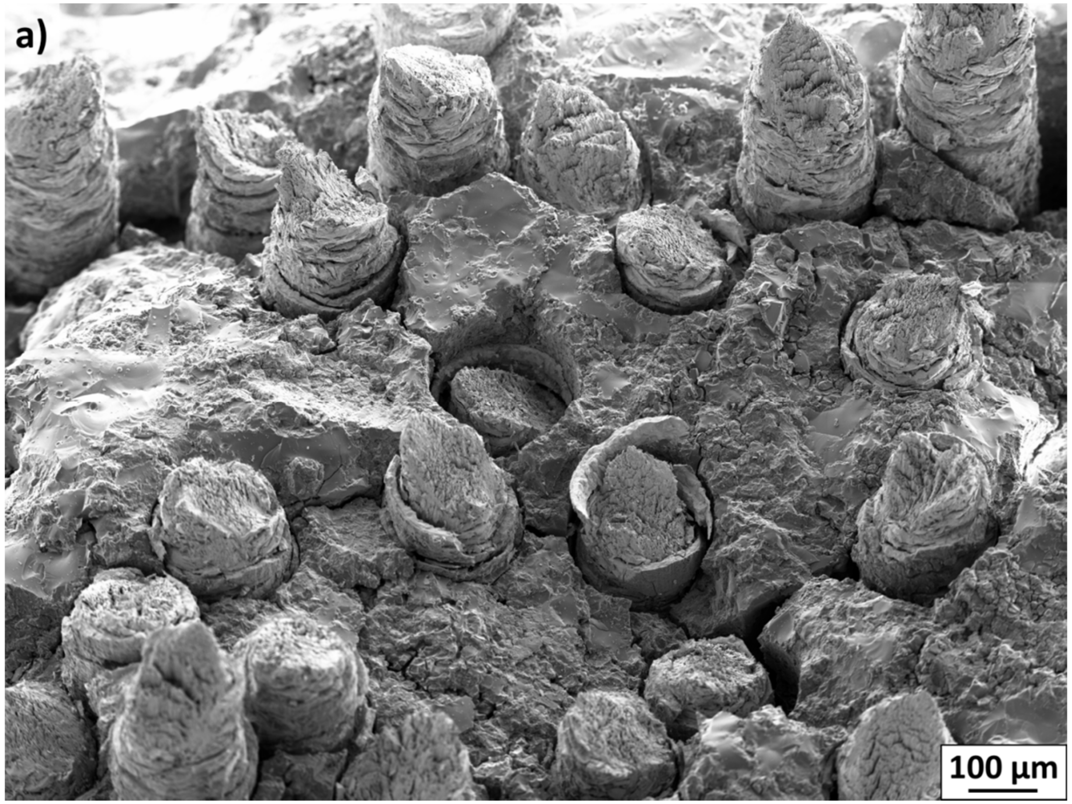
Composite type		W/SiCN	Mo/SiCN
Fiber volume content	%	25 (33*)	30
Tensile strength	MPa	206±27	156±50
Tensile modulus	GPa	172±19	144±7
Tensile fracture strain	%	0.126±0.018	0.164±0.086
Bending strength	MPa	427±105	312±50
Bending modulus	GPa	193±89	90±6
Bending fracture strain	%	0.24±0.08	2.02±0.93
Density	g/cm^3	7.72	4.44
Porosity	Vol.-%	6.86	10.07
Density (calculated)	g/cm^3	6.38 (7.74)	4.44

*calculated by asuming 2.30 g/cm^3 for density of SiCN

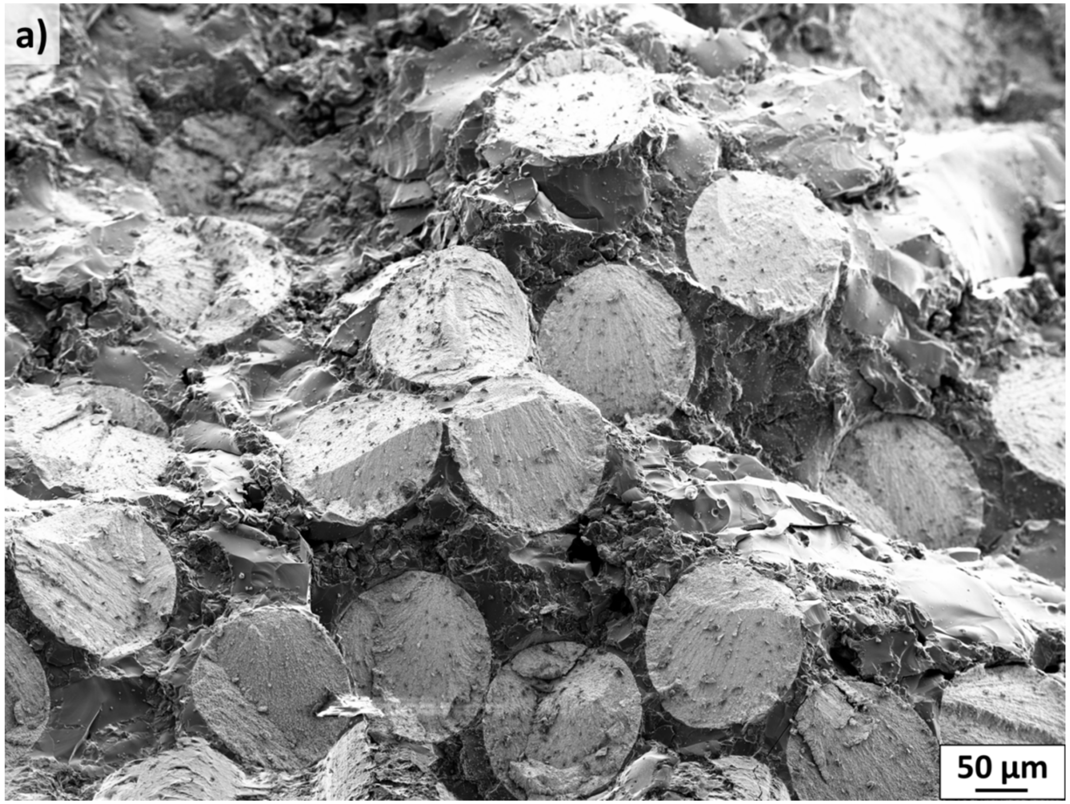
Tensile and bending testing of Mo/SiCN and W/SiCN



Fracture surface of Mo/SiCN (le.) and W/SiCN (ri.)



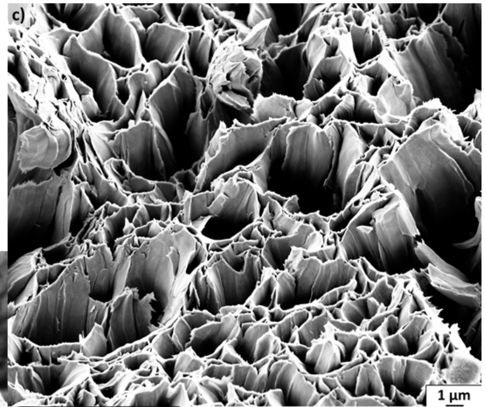
„ductile“ fracture



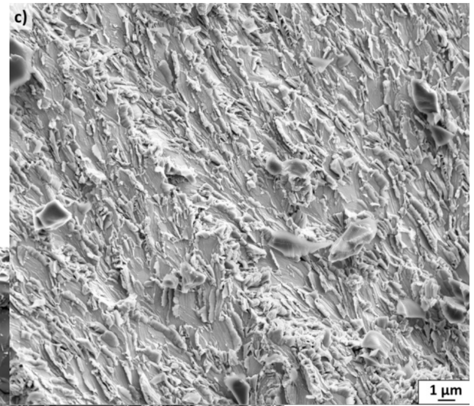
„brittle“ fracture

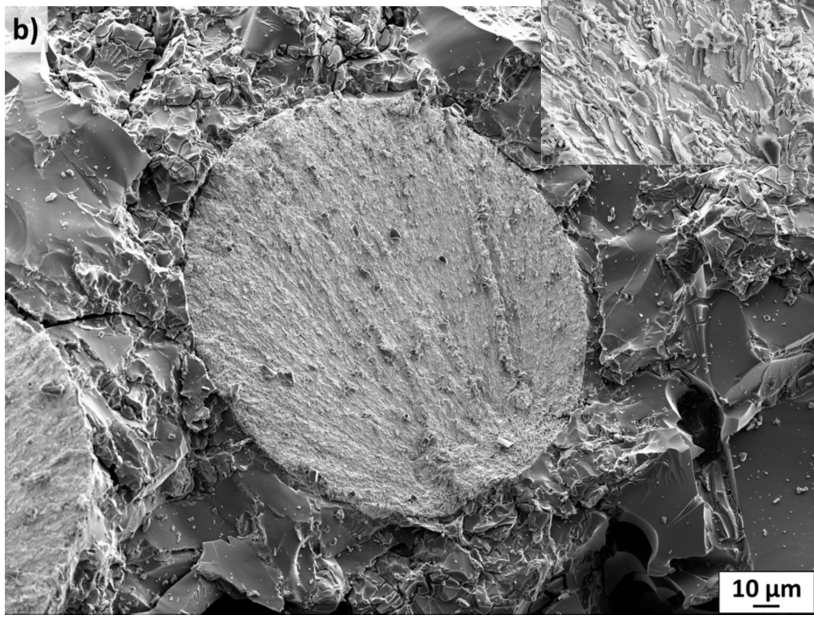
Fracture surface of Mo/SiCN (le.) and W/SiCN (ri.)

„ductile“ fracture

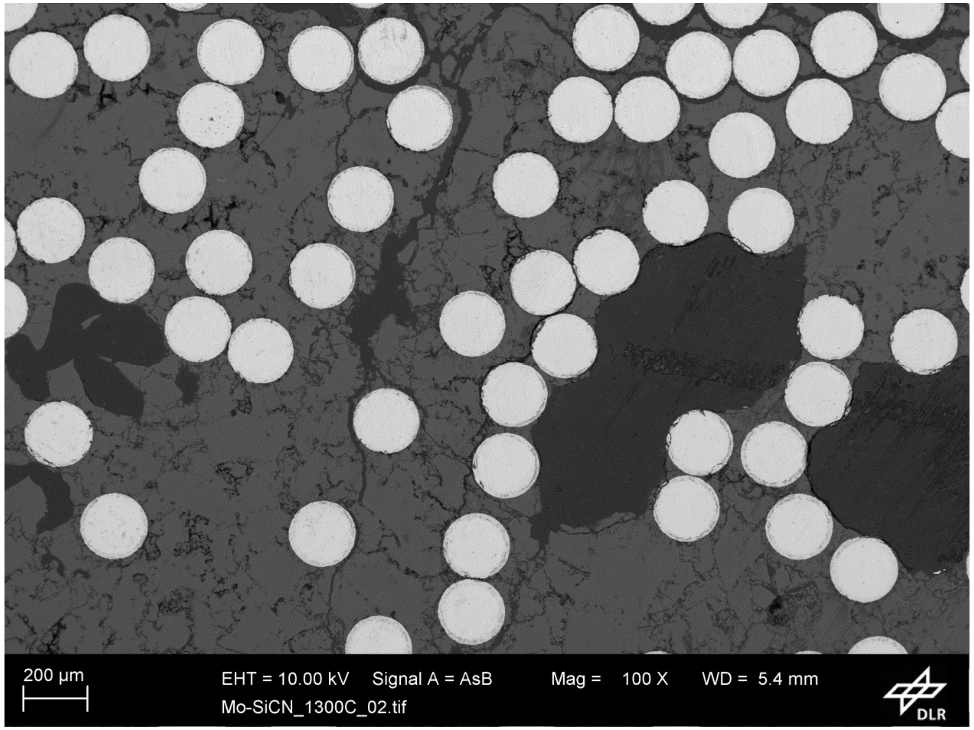


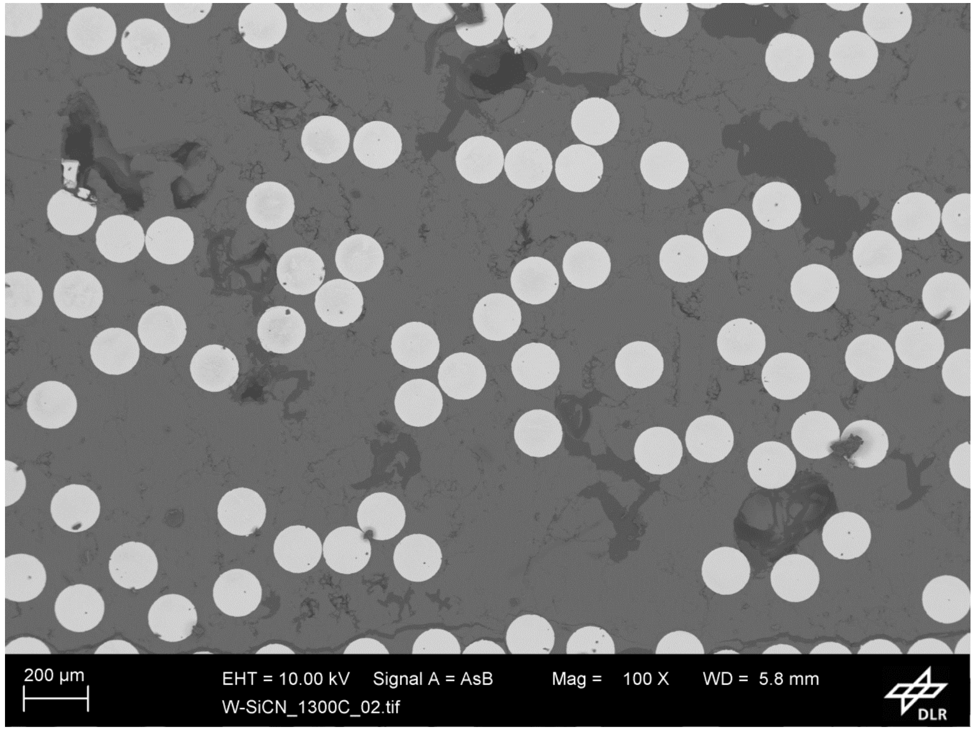
„brittle“ fracture



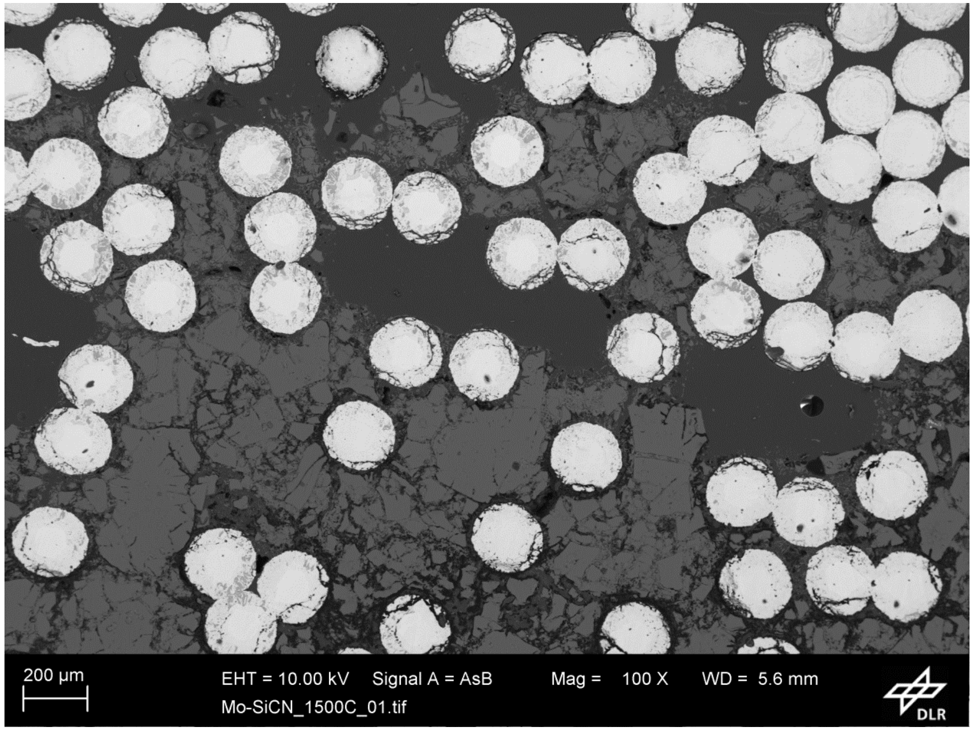


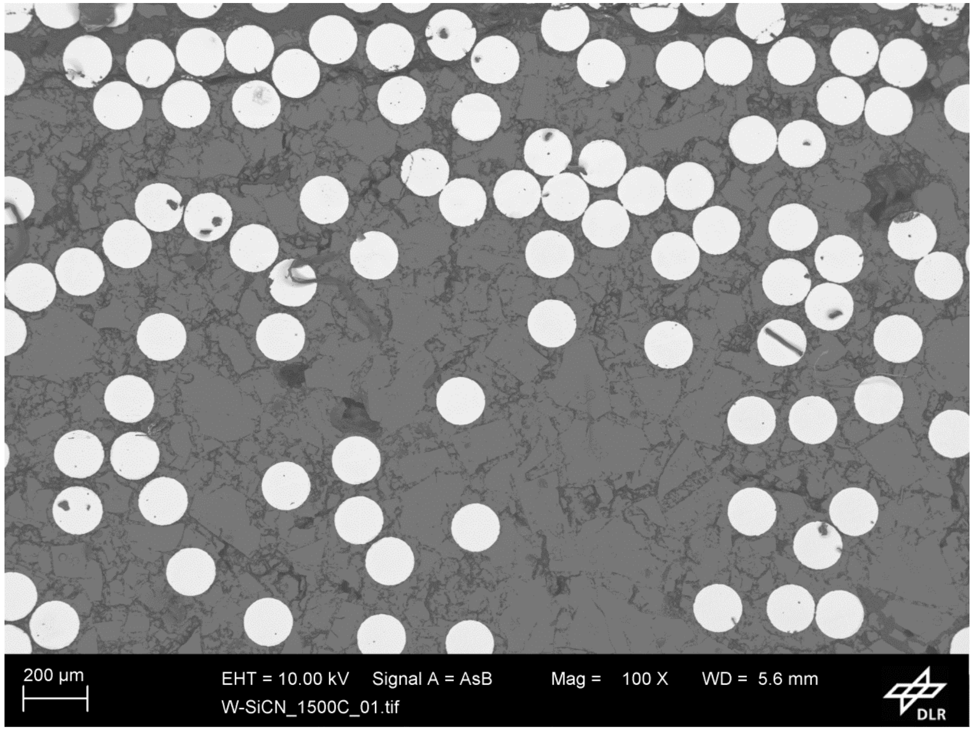
Microstructure of Mo/SiCN (le.) and W/SiCN (ri.) after pyrolysis at 1300°C



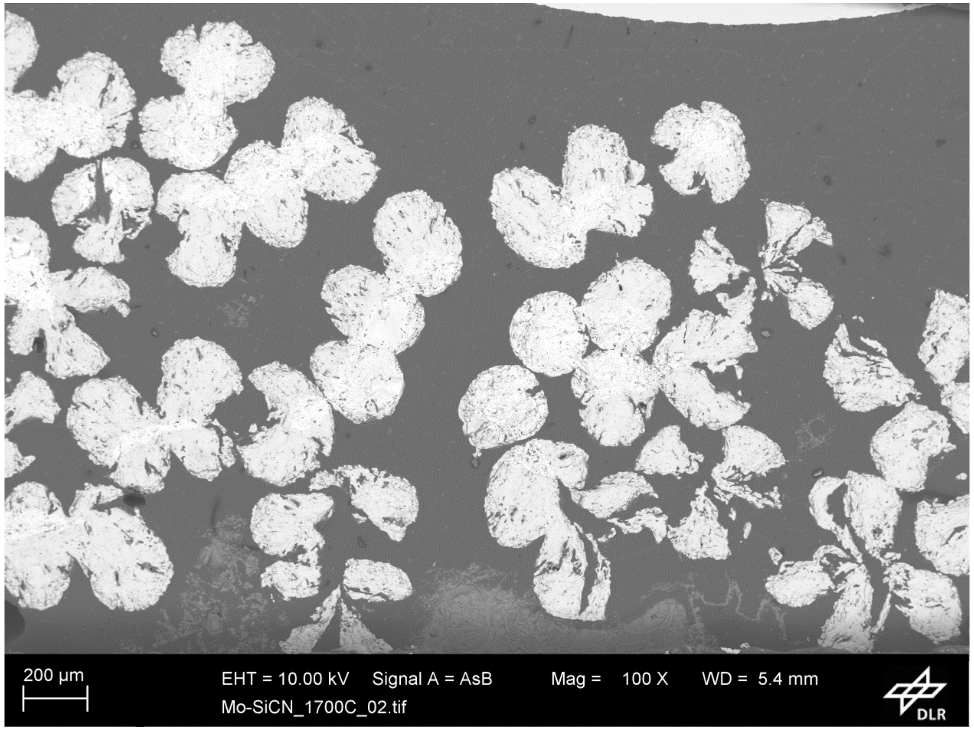


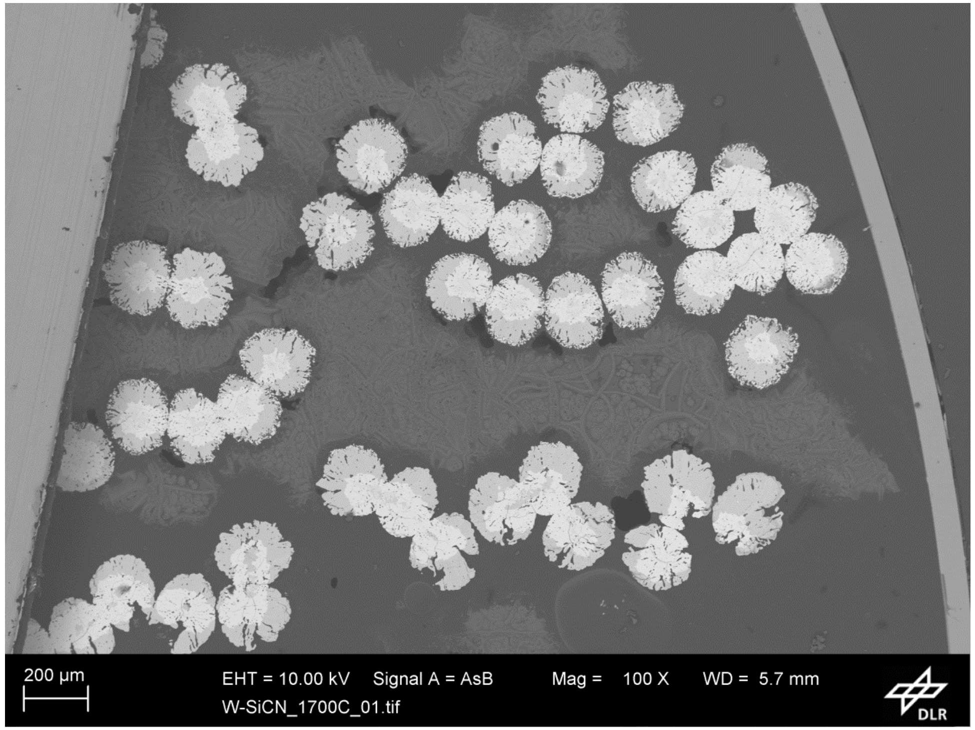
Microstructure of Mo/SiCN (le.) and W/SiCN (ri.) after annealing at 1500°C



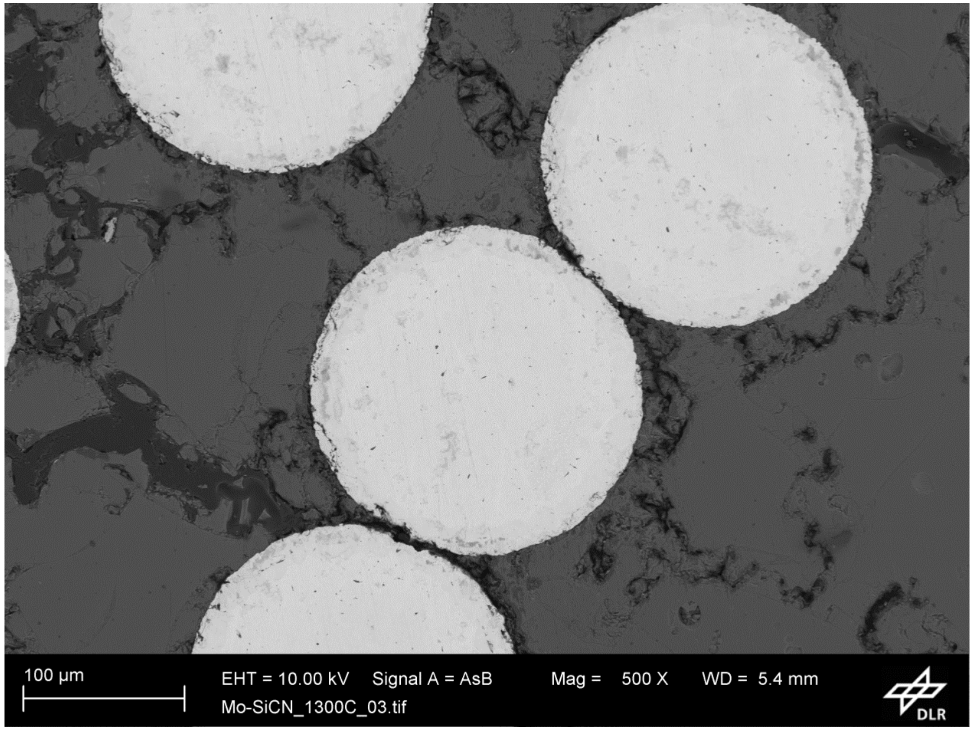


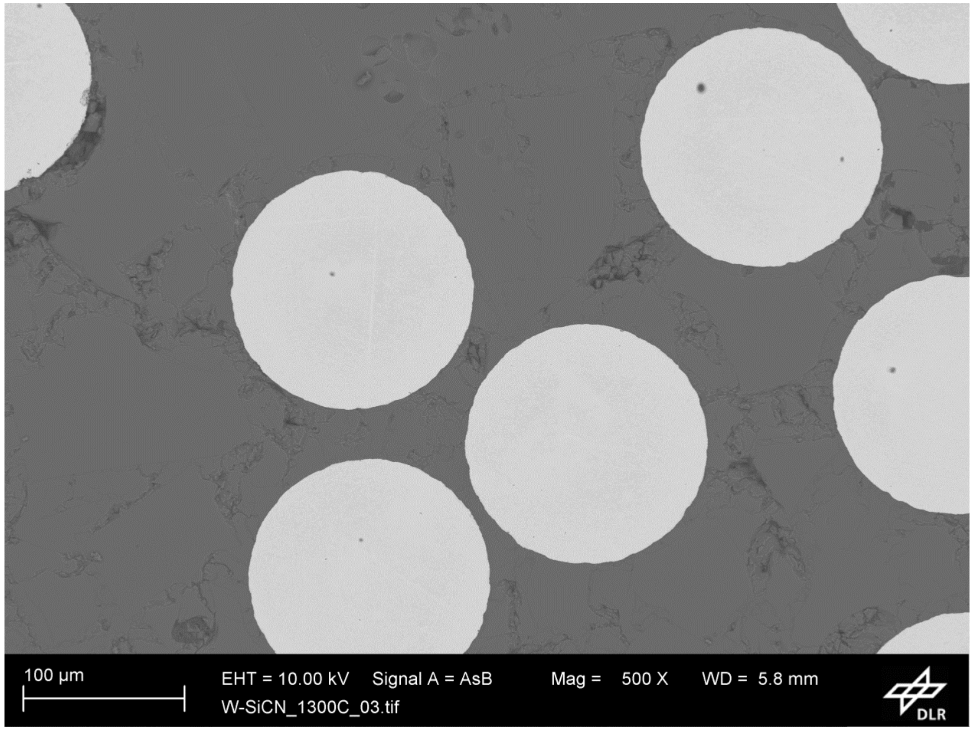
Microstructure of Mo/SiCN (le.) and W/SiCN (ri.) after annealing at 1700°C



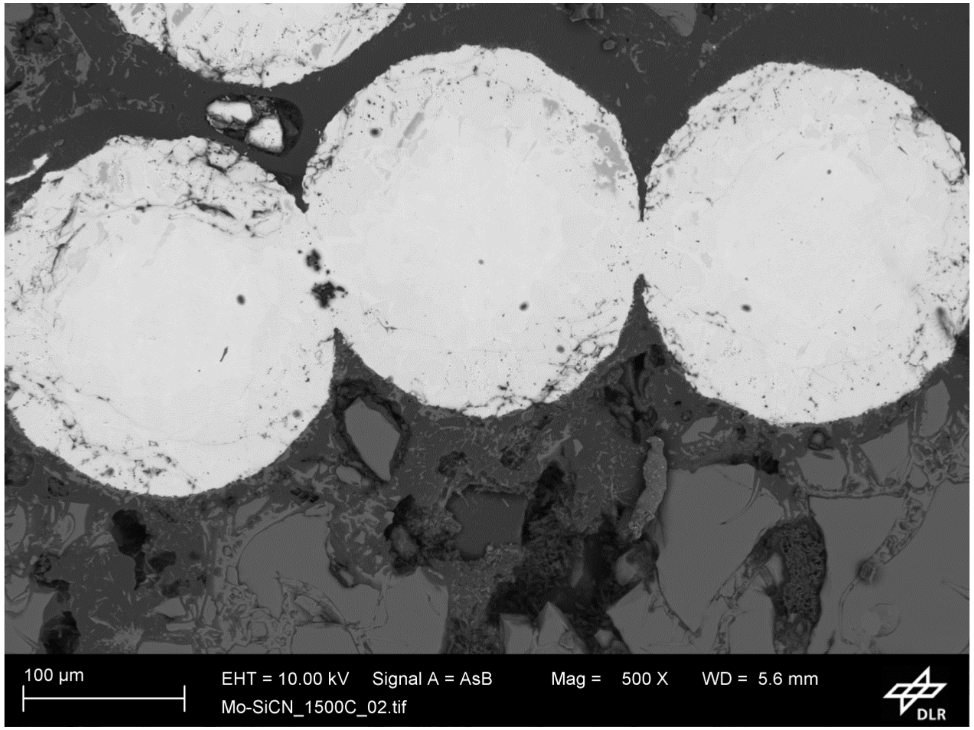


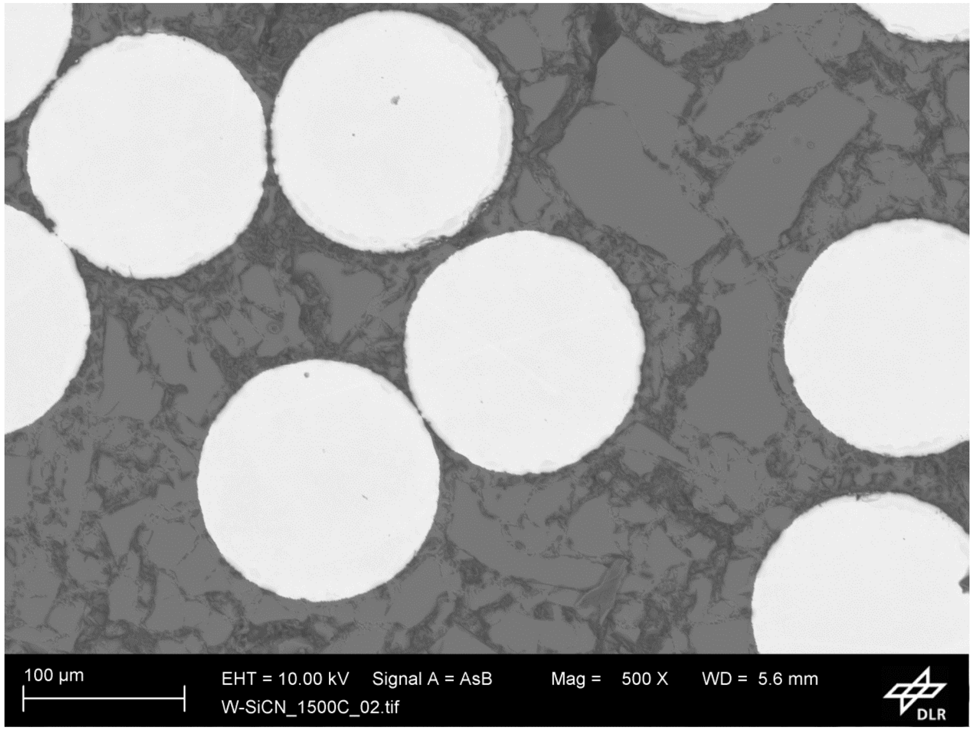
Microstructure of Mo/SiCN (le.) and W/SiCN (ri.) after pyrolysis at 1300°C



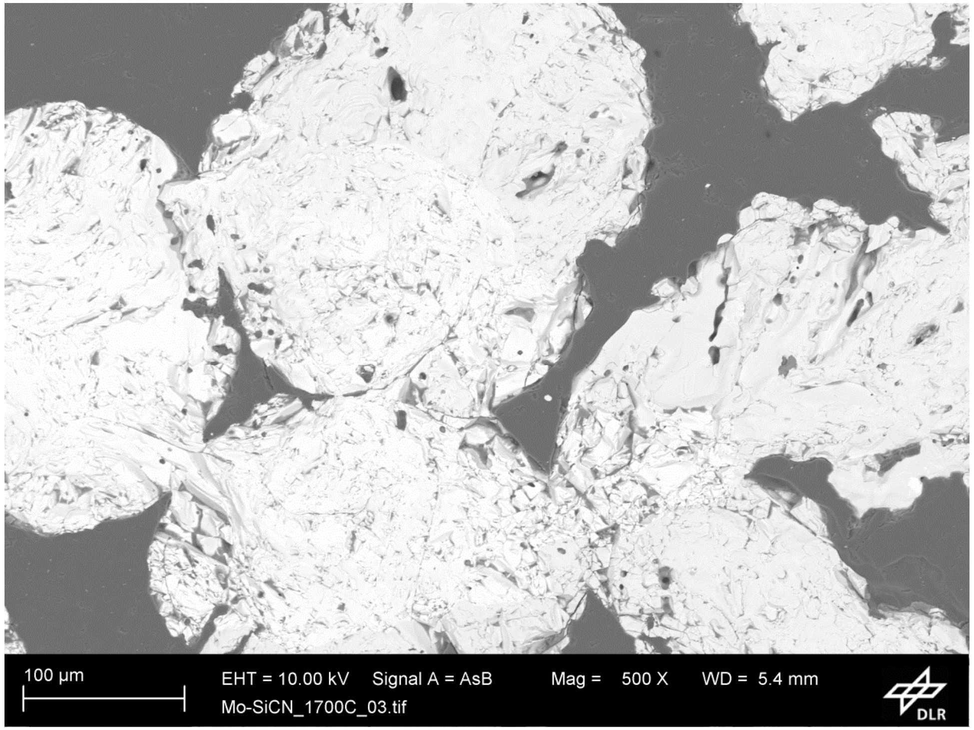


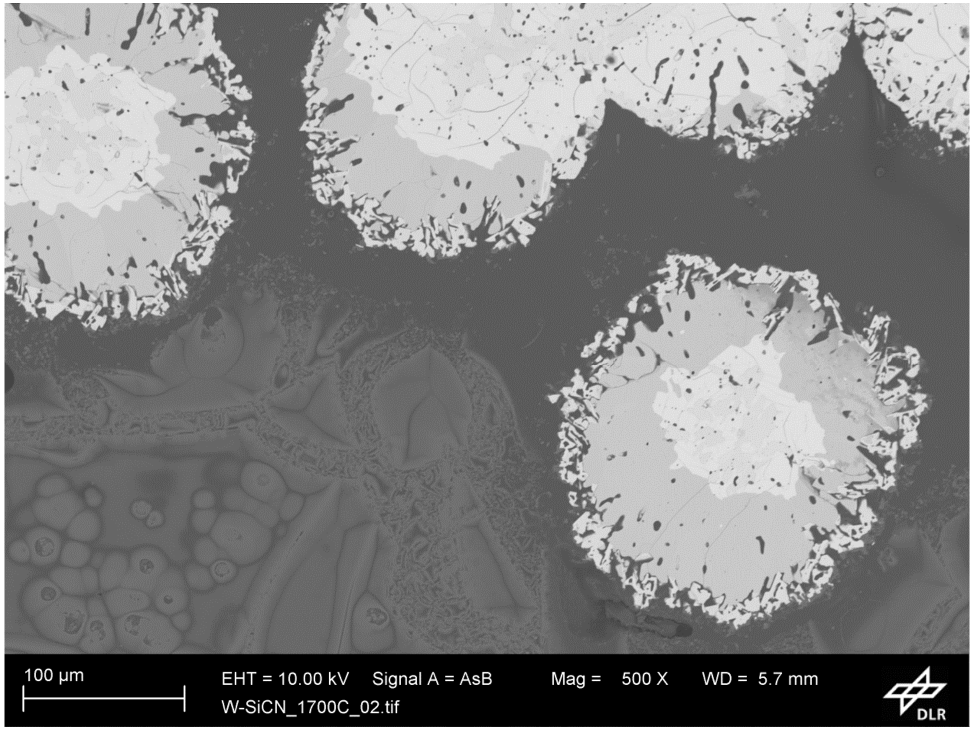
Microstructure of Mo/SiCN (le.) and W/SiCN (ri.) after annealing at 1500°C



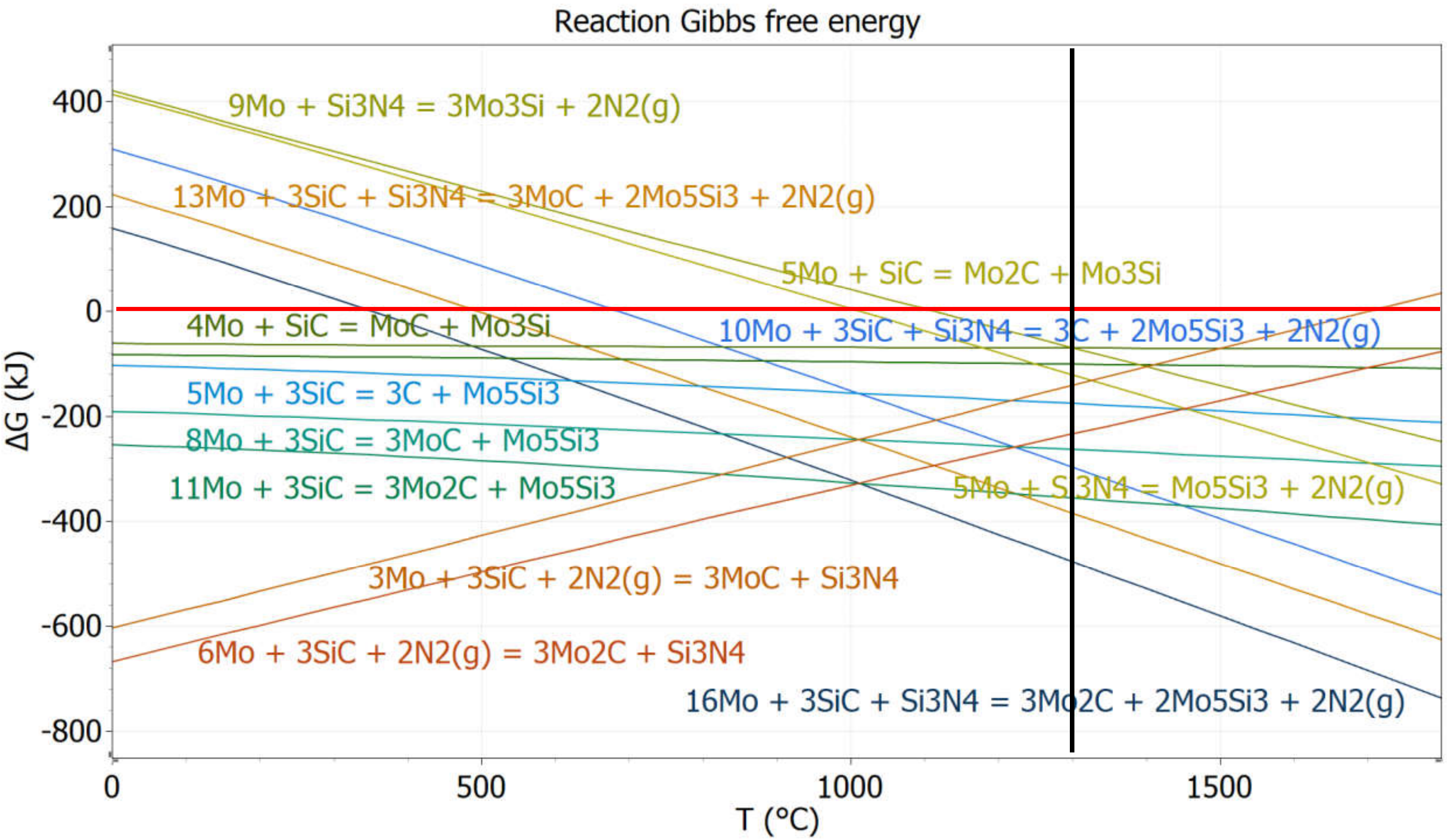


Microstructure of Mo/SiCN (le.) and W/SiCN (ri.) after annealing at 1700°C





Preference of Reactions of Mo



Thermodynamic calculations

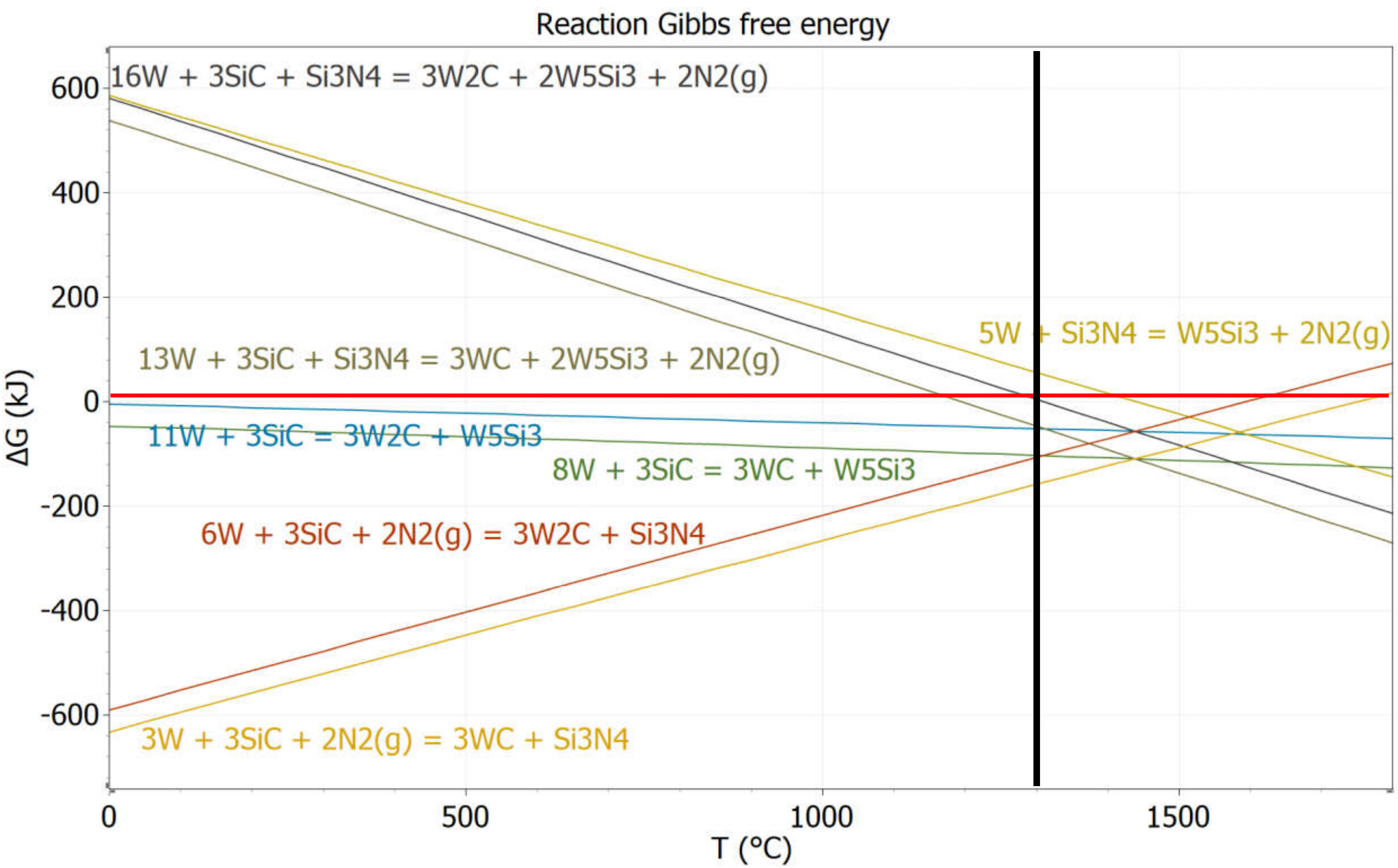
- performed by minimizing Gibbs free energy applying:
- HSC Chemistry 9.0 code, Outokumpu Oy (Finland)

- All reactions beyond the red line are feasible, the lowest line shows the most likely at a given temperature

- @1300°C: formation of
- Mo_2C
- Mo_5Si_3

- @1500°C: formation of
- Mo_2C
- Mo_5Si_3

Preference of Reactions of W



Thermodynamic calculations

- performed by minimizing Gibbs free energy applying:
- HSC Chemistry 9.0 code, Outokumpu Oy (Finland)

- All reactions beyond the red line are feasible, the lowest line shows the most likely at a given temperature

- @1300°C: formation of
- WC
- α-Si_3N_4 (obviously kinetically not favoured)

- @1500°C: formation of
- WC
- W_2C
- α-Si_3N_4

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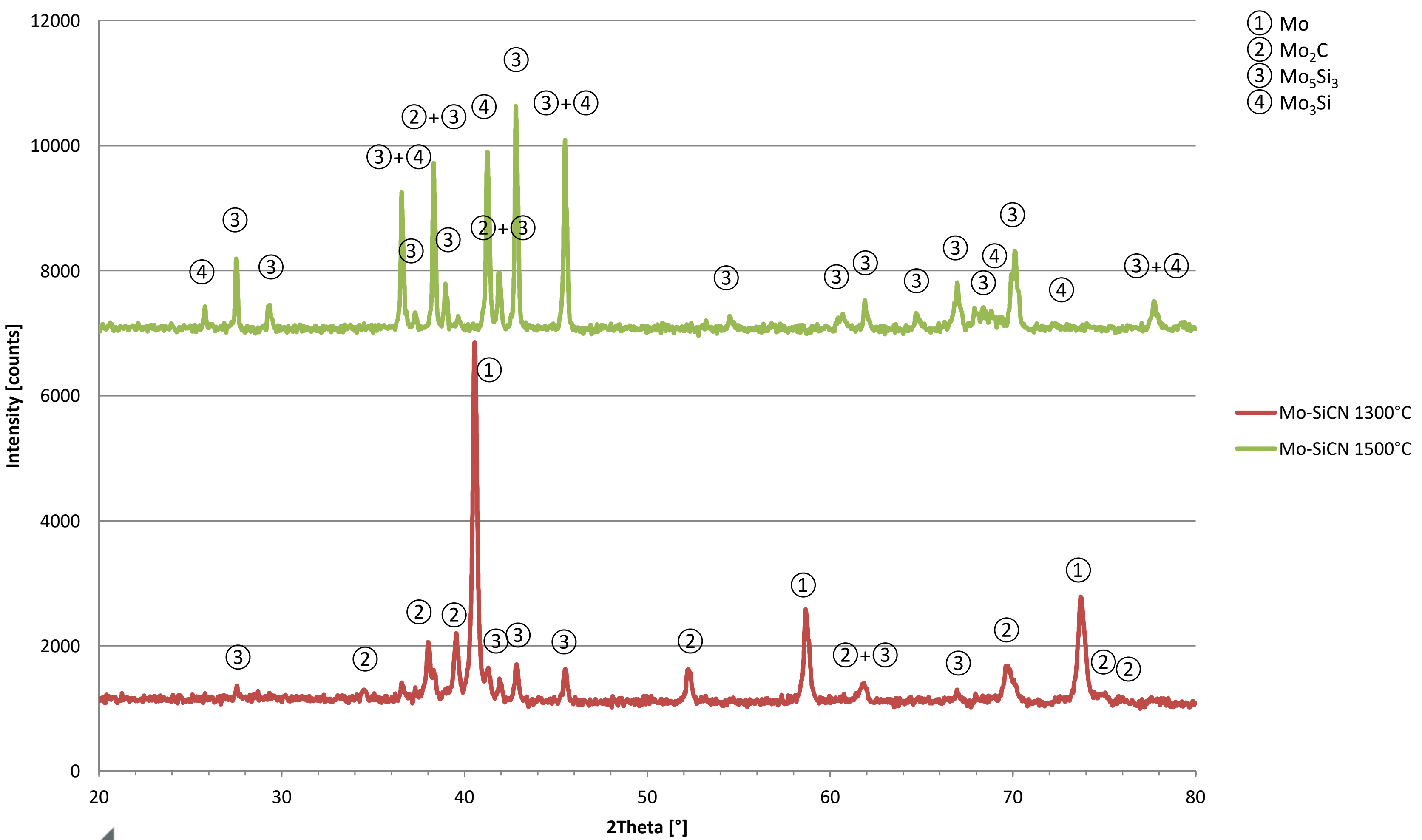
Crystallization of Mo/SiCN (XRD of bulk material)

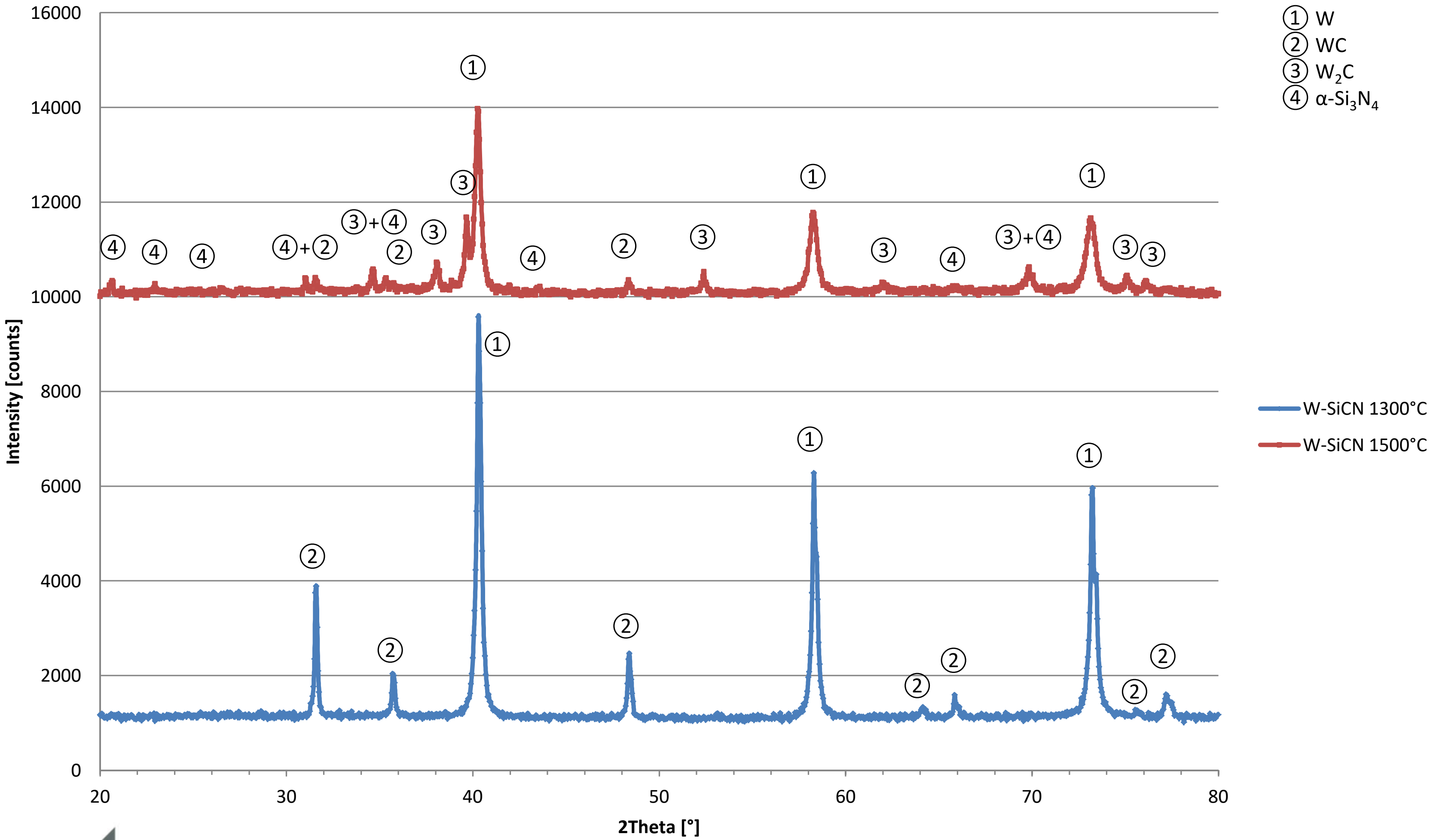


Detected phases

@1500°C
- Mo_2C
- Mo_5Si_3
- Mo_3Si
- (amorphous SiCN matrix)

@1300°C
- Mo
- Mo_2C
- Mo_5Si_3
- (amorphous SiCN matrix)

Crystallization of W/SiCN (XRD of bulk material)

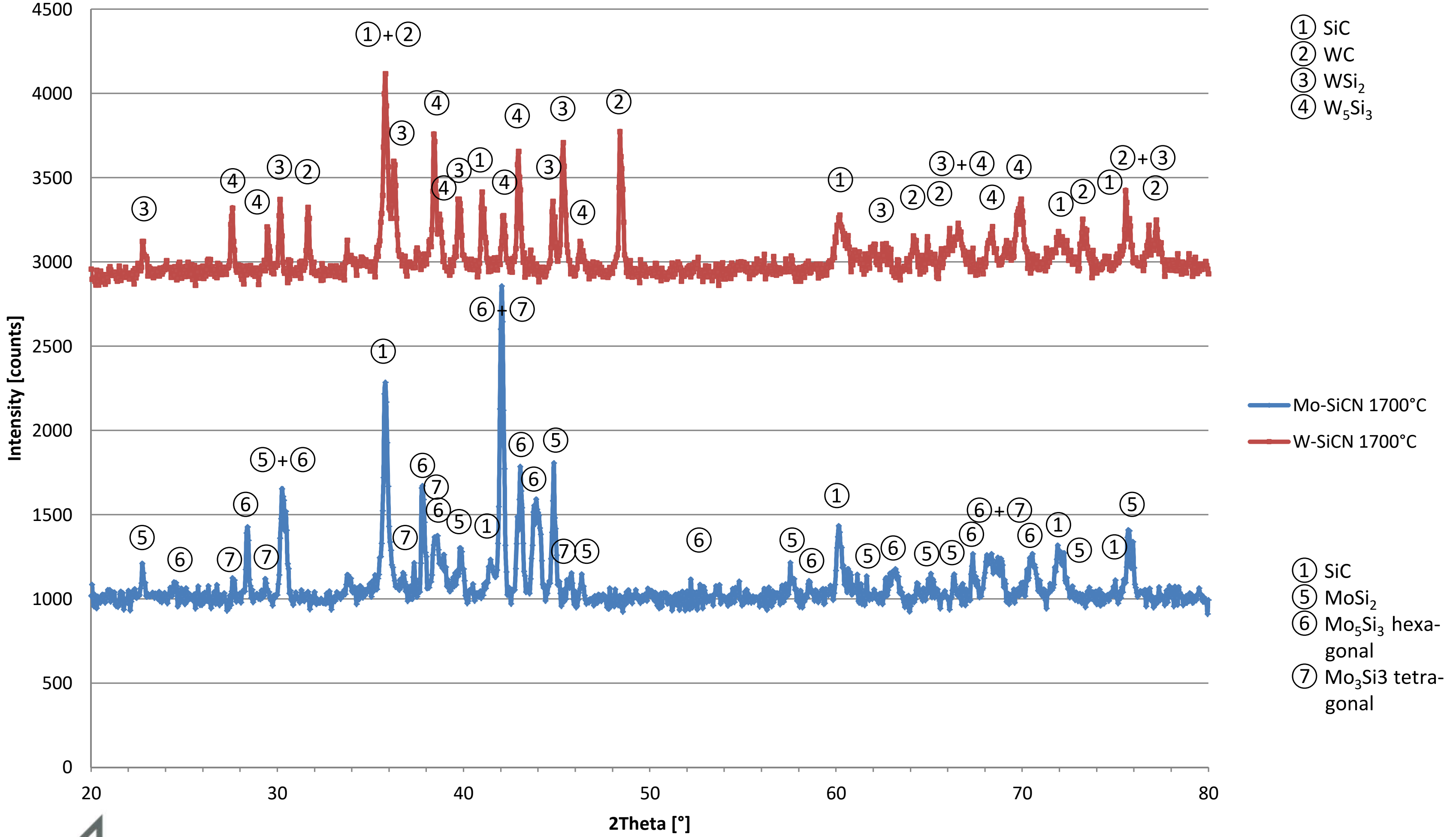


Detected phases

@1500°C
- W
- WC
- W_2C
- α-Si_3N_4
- (amorphous SiCN matrix)

@1300°C
- W
- WC
- (amorphous SiCN matrix)

Crystallization of Mo/SiCN and W/SiCN @ 1700°C



Detected phases

W/SiCN

- SiC
- WC
- WSi_2
- W_5Si_3

Mo/SiCN

- SiC
- $MoSi_2$
- Mo_5Si_3

Viable reactions of Mo and W with PSZ10 and SiCN

- **Mo + PSZ10 →1300°C→ Mo + Mo_5Si_3 + Mo_2C + SiCN + NH_3↑ + CH_4↑**
- **Mo + SiCN →1500°C→ Mo_5Si_3 + Mo_3Si + Mo_2C + N_2↑**
  4Mo + Mo_5Si_3 ↔ $3Mo_3Si$
  5Mo + Si_3N_4 ↔ Mo_5Si_3 + $2N_2$↑ **(mass loss! confirmed by TG analysis)**
- **Mo + SiCN →1700°C→ $MoSi_2$ + Mo_5Si_3 + β-SiC + N_2↑**

- **W + PSZ10 →1300°C→ W + WC + SiCN + NH_3↑ + CH_4↑**
- **W + SiCN →1500°C→ W + W_2C + WC + Si_3N_4**
  W + WC ↔ W_2C
  3W + 3SiC + $2N_2$ ↔ 3WC + Si_3N_4 **(mass gain! confirmed by TG analysis)**
- **W + SiCN →1700°C→ WSi_2 + W_5Si_3 + WC + β-SiC + N_2↑**

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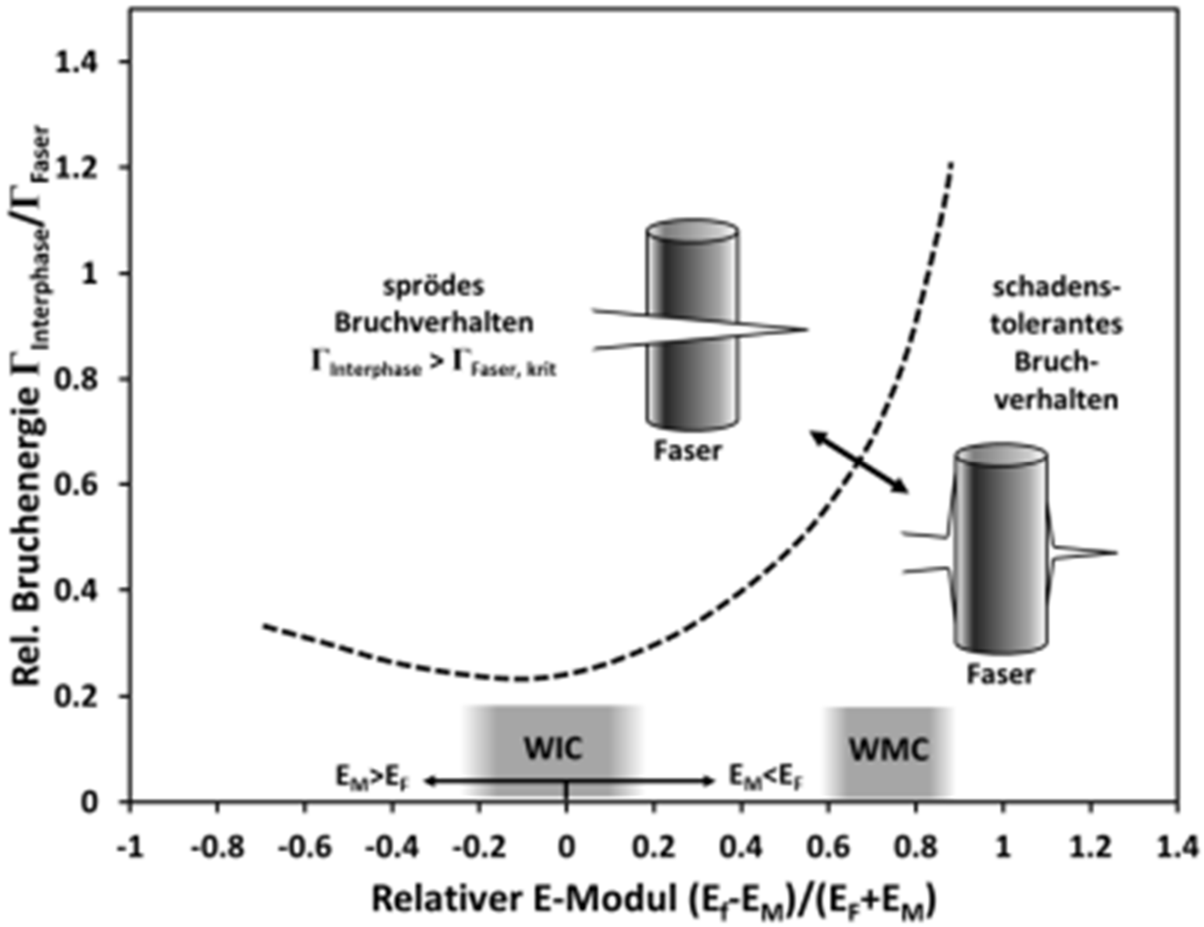
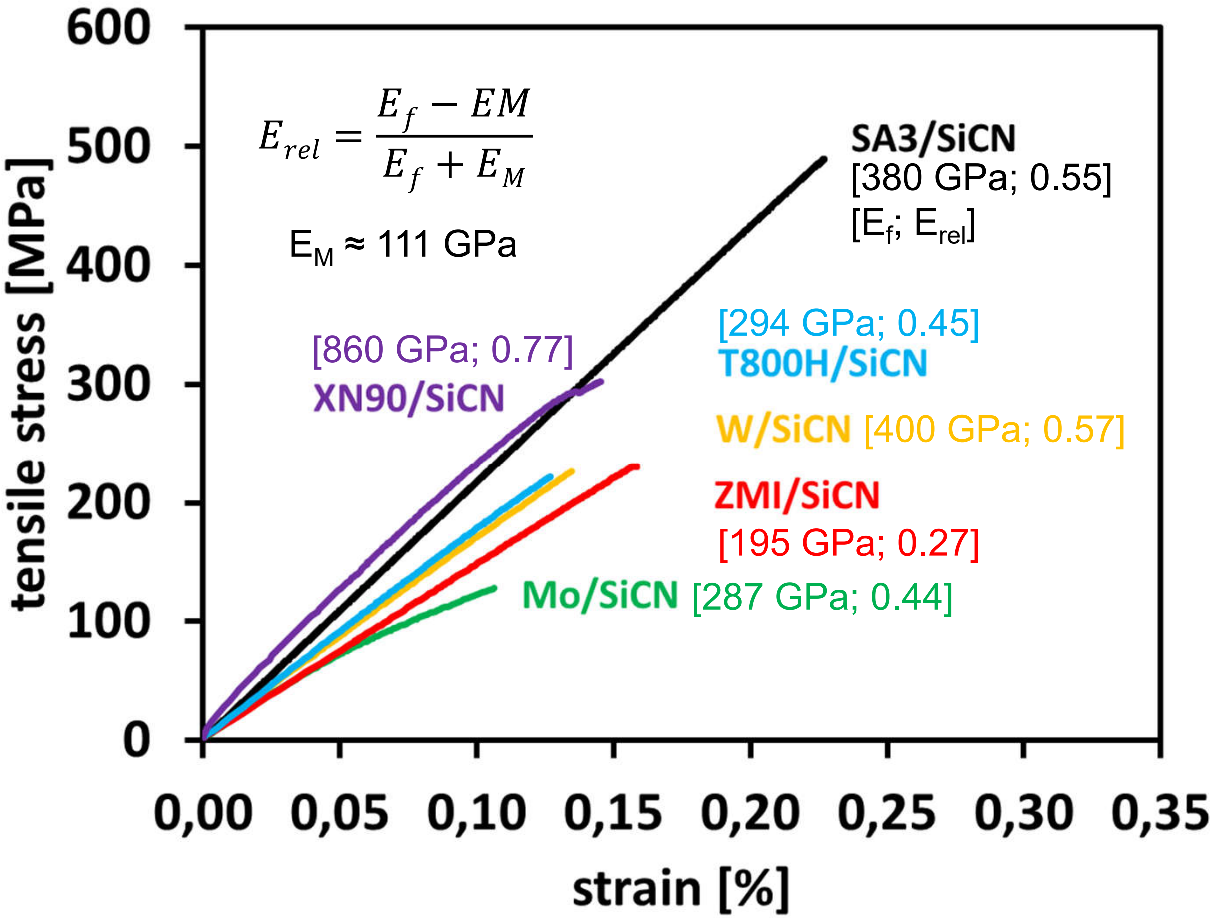
Damage-tolerant and brittle fracture behaviour of CMCs
(Concept of He and Hutchinson)

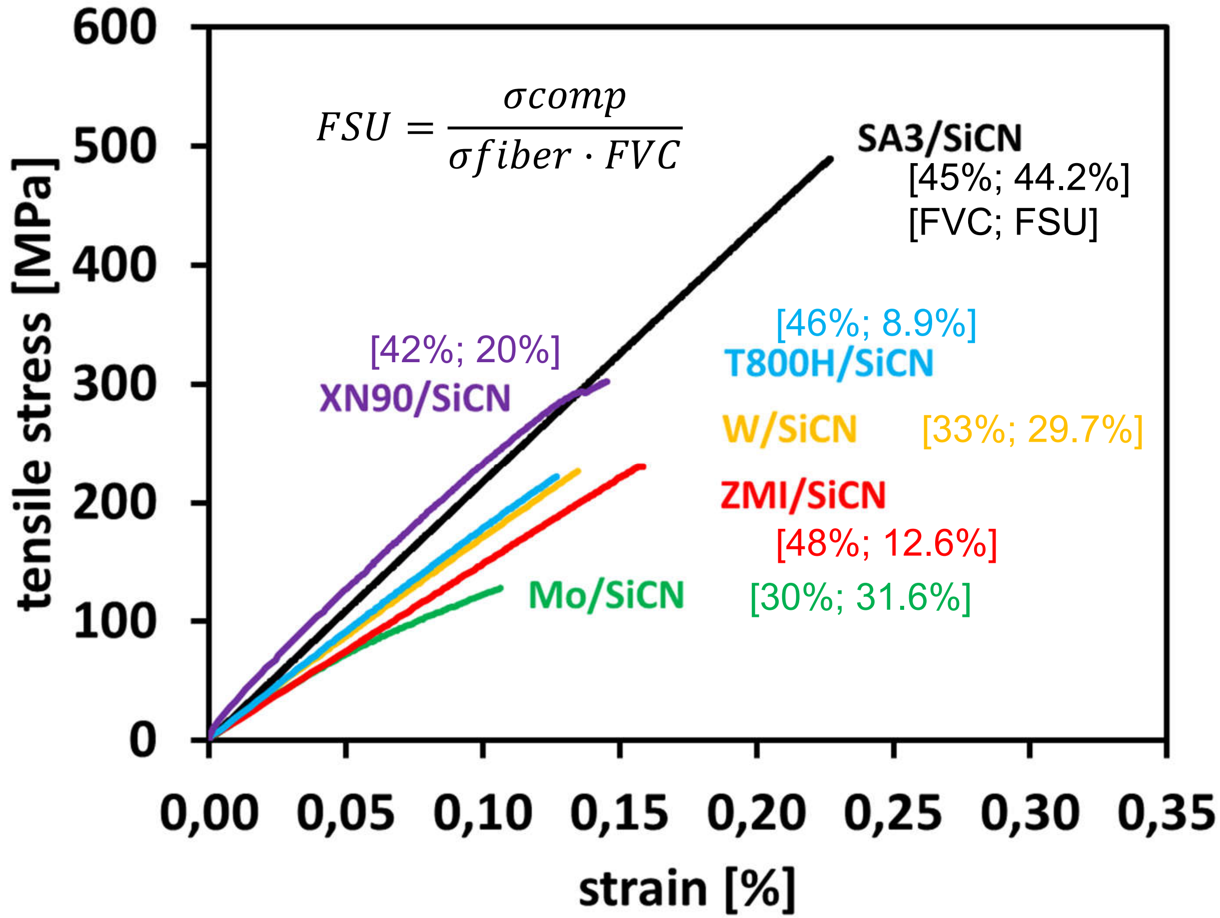
- Application of the model of He and Hutchinson to the new composites Mo/SiCN and W/SiCN
- Comparison to other fiber reinforced SiCN composites based on C- and SiC-fibers
- First estimations and explanations on fracture behaviour as well as damage tolerance of such composites can be predicted



Tensile testing of various UD-fiber reinforced SiCN I
[E_f: Young's modulus of fiber; E_{rel}: relative Young's modulus of fiber and matrix]



Tensile testing of various UD-fiber reinforced SiCN II [FVC: fiber volume content; FSU: fiber strength utilisation]



Summary and outlook I

- Mo- and W-fiber reinforced CMCs can be easily manufactured via polymer infiltration and pyrolysis at 1300 °C (PIP)
- Mo/SiCN and W/SiCN composites are light-weight in comparison to Mo/Mo and W/W composites
- Mo/SiCN and W/SiCN show increased fracture strain compared to CMCs
- Mo/SiCN and W/SiCN can be considered as WMCs and thus need no weak interphase
- Microstructural and phase analyses have shown that Mo- and W-fibers are still present and thermally resistant in the SiCN matrix even at 1300 °C
- Thermodynamical calculations strongly recommend an additional fiber coating from C-attack!

Summary and outlook II

- Microstructural and phase analyses have shown that Mo- and W-fibers suffer from surfacial attack, mainly by C-based materials

- Applying a coating as reaction barrier (e.g. Y_2O_3) should provide further improvement in mechanical properties

- New applications are feasible due to:
    - increased fracture strain
    - good tensile and fracture strain
    - high stiffness
    - high thermal conductivity
    - low thermal expansion
    - high thermal shock resistance
    - anisotropic behaviour of composite according to tailor-made design

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    - German Ministry of Defense as well as
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    - many colleagues DLR internal as well as
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- **Any questions?**