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

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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

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Tungsten</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSD-OG-102045280100</td>
<td></td>
<td>MOA-B6144601XX42</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Osram</td>
<td>Osram</td>
</tr>
<tr>
<td>Diameter</td>
<td>150 µm</td>
<td>200 µm</td>
</tr>
<tr>
<td>Density</td>
<td>19.250 g/cm³</td>
<td>10.220 g/cm³</td>
</tr>
<tr>
<td>Yield strength</td>
<td>1855±18 MPa</td>
<td>1207±5 MPa</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>2780±27 MPa</td>
<td>1647±1 MPa</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>(400) GPa</td>
<td>287±2 GPa</td>
</tr>
<tr>
<td>Fracture strain</td>
<td>1.85±0.05 %</td>
<td>1.9±0.1 %</td>
</tr>
<tr>
<td>Reduction in area</td>
<td>38.5±0.7 %</td>
<td>70.2±0.2 %</td>
</tr>
<tr>
<td>K content</td>
<td>70-80 ppm</td>
<td>150-200 ppm</td>
</tr>
</tbody>
</table>

*) 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

Graph showing tensile testing results for Mo- and W-fibers with diameters of 150μm and 200μm, respectively.

Images b) and c) show SEM micrographs of Mo- and W-fibers.
Manufacture of Mo- and W-fiber ceramic matrix composites

Polymer Infiltration und Pyrolyse (PIP)

SiCFK

Infiltration der Faserpreform mit Polysilazan und Vernetzung
T = 260°C, p = 20 bar, N₂

SiC/SiCN

Pyrolyse des SiCFK
Polysilazan-Matrix → SiCN-Matrix
T = 1300°C, N₂

Polymer Infiltration

SiCFK

Infiltration der Faserpreform mit Phenolharz und Vernetzung
T = 150°C, p = 20 bar, N₂

SiC/C

Pyrolyse des SiCFK
Phenoplast-Matrix → C-Matrix
T = 1450°C, N₂

Silicierung

SiC/SiC

Infiltration des SiC/C mit Silicium
C-Matrix → SiC-Matrix
T > Schmelzpunkt von Si, Vakuum

Liquid Silicon Infiltration (LSI)

Polymer Infiltration

SiCFK

Infiltration der Faserpreform mit Phenolharz und Vernetzung
T = 150°C, p = 20 bar, N₂

SiC/C

Pyrolyse des SiCFK
Phenoplast-Matrix → C-Matrix
T = 1450°C, N₂

Silicierung

SiC/SiC

Infiltration des SiC/C mit Silicium
C-Matrix → SiC-Matrix
T > Schmelzpunkt von Si, Vakuum

Composites mit 33% Faservolumengehalt

Porosität (%) 0 10 20 30 40 50 60 70 80

PIP-Zyklus
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
### Properties of Mo/SiCN and W/SiCN composites

<table>
<thead>
<tr>
<th>Composite type</th>
<th>W/SiCN</th>
<th>Mo/SiCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber volume content</td>
<td>%</td>
<td>25 (33*)</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>MPa</td>
<td>206±27</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>GPa</td>
<td>172±19</td>
</tr>
<tr>
<td>Tensile fracture strain</td>
<td>%</td>
<td>0.126±0.018</td>
</tr>
<tr>
<td>Bending strength</td>
<td>MPa</td>
<td>427±105</td>
</tr>
<tr>
<td>Bending modulus</td>
<td>GPa</td>
<td>193±89</td>
</tr>
<tr>
<td>Bending fracture strain</td>
<td>%</td>
<td>0.24±0.08</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>7.72</td>
</tr>
<tr>
<td>Porosity</td>
<td>Vol.-%</td>
<td>6.86</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>g/cm³</td>
<td>6.38 (7.74)</td>
</tr>
</tbody>
</table>

*calculated by assuming 2.30 g/cm³ for density of SiCN
Tensile and bending testing of Mo/SiCN and W/SiCN
Fracture surface of Mo/SiCN (le.) and W/SiCN (ri.)

[Image of fracture surface of Mo/SiCN and W/SiCN]
Fracture surface of Mo/SiCN (le.) and W/SiCN (ri.)
Fracture surface of Mo/SiCN (le.) and W/SiCN (ri.)
Microstructure of Mo/SiCN

- Mo fiber
- Matrix
- C, Si, N, O elemental mapping
Crystallization of Mo/SiCN (XRD)

Detected phases

@1500°C
- Mo
- Mo$_2$C
- Mo$_5$Si$_3$
- Mo$_3$Si

@1300°C
- Mo
- Mo$_2$C
- Mo$_5$Si$_3$
Microstructure of W/SiCN
Crystallization of W/SiCN (XRD)

Detected phases

@1500°C
- W
- WC
- W₂C
- A-Si₃N₄
- Mo₃Si

@1300°C
- W
- WC
Preference of Reactions of Mo

![Diagram showing various reactions of Mo with Gibbs free energy as a function of temperature.]

- $9\text{Mo} + 3\text{SiN}_4 = 3\text{Mo}_3\text{Si} + 2\text{N}_2(g)$
- $13\text{Mo} + 3\text{SiC} + \text{SiN}_4 = 3\text{MoC} + 2\text{Mo}_5\text{Si}_3 + 2\text{N}_2(g)$
- $5\text{Mo} + \text{SiC} = \text{Mo}_2\text{C} + \text{Mo}_3\text{Si}$
- $4\text{Mo} + \text{SiC} = \text{Mo}_2\text{C} + \text{Mo}_3\text{Si}$
- $10\text{Mo} + 3\text{SiC} + \text{SiN}_4 = 3\text{C} + 2\text{Mo}_5\text{Si}_3 + 2\text{N}_2(g)$
- $5\text{Mo} + 3\text{SiC} = 3\text{C} + \text{Mo}_5\text{Si}_3$
- $8\text{Mo} + 3\text{SiC} = 3\text{MoC} + \text{Mo}_5\text{Si}_3$
- $11\text{Mo} + 3\text{SiC} = 3\text{Mo}_2\text{C} + \text{Mo}_5\text{Si}_3$
- $3\text{Mo} + 3\text{SiC} + 2\text{N}_2(g) = 3\text{MoC} + \text{SiN}_4$
- $6\text{Mo} + 3\text{SiC} + 2\text{N}_2(g) = 3\text{Mo}_2\text{C} + \text{SiN}_4$
- $16\text{Mo} + 3\text{SiC} + \text{SiN}_4 = 3\text{Mo}_2\text{C} + 2\text{Mo}_5\text{Si}_3 + 2\text{N}_2(g)$
Preference of Reactions of W

Reaction Gibbs free energy

16W + 3SiC + Si3N4 = 3W2C + 2W5Si3 + 2N2(g)

13W + 3SiC + Si3N4 = 3WC + 2W5Si3 + 2N2(g)

5W + Si3N4 = W5Si3 + 2N2(g)

11W + 3SiC = 3W2C + W5Si3

8W + 3SiC = 3WC + W5Si3

6W + 3SiC + 2N2(g) = 3W2C + Si3N4

3W + 3SiC + 2N2(g) = 3WC + Si3N4

ΔG (kJ)

T (°C)
Viable reactions of Mo and W with PSZ10 and SiCN

- **Mo + PSZ10** $\rightarrow 1300^\circ C$ $\rightarrow$ **Mo + Mo$_5$Si$_3$ + Mo$_2$C + SiCN + NH$_3$↑ + CH$_4$↑
- **Mo + SiCN** $\rightarrow 1500^\circ C$ $\rightarrow$ **Mo$_5$Si$_3$ + Mo$_3$Si + Mo$_2$C + N$_2$↑
  
  \[
  4\text{Mo} + \text{Mo}_5\text{Si}_3 \leftrightarrow 3\text{Mo}_3\text{Si} \\
  5\text{Mo} + \text{Si}_3\text{N}_4 \leftrightarrow \text{Mo}_5\text{Si}_3 + 2\text{N}_2↑ 
  \]
  (mass loss! TG ok)
- **Mo + SiCN** $\rightarrow 1700^\circ C$ $\rightarrow$ **Mo$_5$Si$_3$ + MoN + β-SiC + N$_2$↑
- **W + PSZ10** $\rightarrow 1300^\circ C$ $\rightarrow$ **W + WC + SiCN + NH$_3$↑ + CH$_4$↑
- **W + SiCN** $\rightarrow 1500^\circ C$ $\rightarrow$ **W + W$_2$C + WC + Si$_3$N$_4$
  
  \[
  \text{W} + \text{WC} \leftrightarrow \text{W}_2\text{C} \\
  3\text{W} + 3\text{SiC} + 2\text{N}_2 \leftrightarrow 3\text{WC} + \text{Si}_3\text{N}_4 
  \]
  (mass gain! TG ok)
- **W + SiCN** $\rightarrow 1700^\circ C$ $\rightarrow$ **W$_2$C + WC + WN$_2$ + β-SiC + N$_2$↑
First mechanical models of Mo/SiCN- and W/SiCN

- 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
Damage-tolerant and brittle fracture behaviour of CMCs
(Concept of He and Hutchinson)
Tensile testing of various UD-fiber reinforced SiCN II

\[ E_{rel} = \frac{E_f - E_M}{E_f + E_M} \]

- \( E_M \approx 111 \text{ GPa} \)
- \( E_f \) = Young’s modulus of fiber
- \( E_{rel} \) = relative Young’s modulus of fiber and matrix

**Graph:**
- \( E_{rel} \) values for various samples:
  - SA3/SiCN [380 GPa; 0.55] [\( E_f; E_{rel} \)]
  - XN90/SiCN [860 GPa; 0.77]
  - T800H/SiCN [294 GPa; 0.45]
  - W/SiCN [400 GPa; 0.57]
  - ZMI/SiCN [195 GPa; 0.27]
  - Mo/SiCN [287 GPa; 0.44]
Tensile testing of various UD-fiber reinforced SiCN I
[FVC: fiber volume content; FSU: fiber strength utilisation]

\[ \text{FSU} = \frac{\sigma_{\text{comp}}}{\sigma_{\text{fiber}} \cdot \text{FVC}} \]

- SA3/SiCN [45%; 44.2%] [FVC; FSU]
  - [42%; 20%] XN90/SiCN
  - [46%; 8.9%] T800H/SiCN
  - W/SiCN [33%; 29.7%]
  - ZMI/SiCN [48%; 12.6%]
  - Mo/SiCN [30%; 31.6%]
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 surficial 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