Ceramic Composites for High Temperature Applications

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XXI Conference AIV
Italian Association of Science and Technology
May 15 – 17, 2013
Catania, Italy

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Outline

• Ceramic Matrix Composites (CMCs)

• Concepts of Weak Fiber/Matrix Interphases

• Processing and Properties

• Design Aspects

• Two Engineering Approaches
  
  Ceramic Composites for Friction Applications (Brakes)
  Hybrid Ceramic-Metal Pipes for Power Plants (700 °C, 350 bar)

• Summary
University and Wagner Festival City Bayreuth
Mass Specific Strength vs. Temperature of Structural Materials

- Polymers
- Metals
- Ceramics

Specific Strength ($Rm/\rho^*$) [km]

Temperature $T$ [°C]

Materials:
- CFRP
- Titanium
- Titanaluminide
- Superalloys
- Aluminum
- C/C, C/SiC, C/C-SiC, SiC/SiC
# Typical Properties of Different Structural Materials (at RT)

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\rho$ [g/cm$^3$]</th>
<th>Bending Strength $\sigma_b$ [MPa]</th>
<th>Tensile Strength $\sigma_z$ [MPa]</th>
<th>Fracture Toughness $K_{ic}$ [MPa$\sqrt{m}$]</th>
<th>Strain $\varepsilon$ [%]</th>
<th>Young’s Modulus $E$ [GPa]</th>
<th>Coefficient of Thermal Expansion $\alpha_{RT-1000 \degree C}$ $10^{-6} K^{-1}$</th>
<th>Thermal Conductivity $\lambda$ Wm$^{-1}$K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural Ceramic</td>
<td>2.25-6.00</td>
<td>30-1400</td>
<td>-</td>
<td>1-10.5</td>
<td>&lt;0.1</td>
<td>40-450</td>
<td>0-10.9</td>
<td>1-155</td>
</tr>
<tr>
<td>Glass</td>
<td>2.2-2.5</td>
<td>70</td>
<td>70-100</td>
<td>&lt;1</td>
<td>-</td>
<td>40-95</td>
<td>3-10</td>
<td>1-3</td>
</tr>
<tr>
<td>Steel</td>
<td>7.8</td>
<td>360-700</td>
<td>360-700</td>
<td>150-210</td>
<td>10-20</td>
<td>210</td>
<td>&gt;10</td>
<td>&gt;30</td>
</tr>
<tr>
<td>HT-Steel</td>
<td>7.8</td>
<td>500-1000</td>
<td>500-1000</td>
<td>50-150</td>
<td>10-30</td>
<td>210</td>
<td>&gt;6</td>
<td>&gt;30</td>
</tr>
<tr>
<td>Cast Iron</td>
<td>7.3</td>
<td>300-600</td>
<td>150-400</td>
<td>6-20</td>
<td>2-25</td>
<td>70-130</td>
<td>5-18</td>
<td>15-60</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2.8</td>
<td>150-300</td>
<td>350</td>
<td>45</td>
<td>5-20</td>
<td>70</td>
<td>20-26</td>
<td>70-130</td>
</tr>
<tr>
<td>Plastics</td>
<td>0.9-2.2</td>
<td>10-150</td>
<td>10-300</td>
<td>0.3-4</td>
<td>2-1200</td>
<td>1-5</td>
<td>20-180</td>
<td>0.14-0.25</td>
</tr>
<tr>
<td>Wood</td>
<td>0.2-1.2</td>
<td>50-150</td>
<td>70-130</td>
<td>0.5-1</td>
<td>&lt;1</td>
<td>10</td>
<td>4</td>
<td>0.1-0.2</td>
</tr>
</tbody>
</table>
Structural ceramics with high damage tolerance

- Quasi-ductility (crack deflection, fiber-pullout)
- Microcrack pattern, low fiber/matrix bondings
- Fracture does not result in failure
- High mass-specific properties (density 2 – 2.5 g/cm³)
Different Concepts of Fiber/Matrix Interfaces

Sharp, non-reactive interface
Between fiber and matrix and fiber surface roughness
Debonding effects depend on the frictional term $\mu \cdot \sigma_\perp$ ($\mu = \text{CoF}, \ \sigma_\perp = \text{clamping stress normal to the interface}$)

Fiber coating
In situ reaction of fiber and matrix during CMC fabrication
a) Interphase-fiber debond
b) Diffuse debond cracking (e.g. PyC, hBN)

Porous interphase
Debonding and shear properties derive from a succession of weak bridges between particles in a porous layer

Multilayer interphase
Heterogeneous multilayer structures with a dual function:
Diffuse crack deflection and barrier to solid state or gaseous reaction (e.g. pulsed CVD-C/SiC)

M. H. Lewis
Multilayered Interphases by Pressure-Pulsed CVI Technique

Deposit of multilayered PyC, BN or SiC layer (20 to 50 nm thick)  
PyC-B₄C-PyC-SiC multilayered self-healing matrix

R. Naslain, High Temperature Ceramic Materials and Composites, 2010
Typical Manufacturing Processes for Non-Oxide Ceramic Matrix Composites

Fiber Preforming

Adjustment of the F/M Interphase

CVI-Process
- Isothermal
- Temp. Gradient
- Press. Gradient
- Pulsing
- Rapid-CVI

PIP-Process

LSI-Process

Hybrid-Process
- CVI + LSI
- PIP + LSI
- CVI + PIP

Machining
- Grinding, milling, drilling

Joining
- In situ-joining
- Form/force-locking

Coating/Finishing
- TBC/EBC
Microstructures of Different CMC-Materials

LSI-C/C-SiC (DLR)

PIP-C/SiC (EADS)

CVI-SiC/SiC (MT Aerospace)

NPC-OFC (EADS)
Melt-Infiltration of Silicon into C/C-Preforms (Three Step LSI-Process)

- Fiber
- Additives (opt.)
- Resin

Conditioning

Compounding/Mixing

Warm Pressing and Curing

- CFRP
- Pyrolysis
- C/C

First Machining (opt.)

Joining (opt.)

In-process coating (opt.)

Siliconizing

C/SiC

Final Machining

F. Gern, Research Report DLR, 95-26
Reaction Mechanisms Between Silicon and Carbon

- **Solid-liquid reaction between carbon and molten silicon (LSI-process)**
  \[ \text{Si}_\text{(l)} + \text{C}_\text{(s)} \rightarrow \text{SiC}_\text{(s)} \]

- **Solid-gas reaction between carbon and gaseous silicon**
  \[ \text{Si}_\text{(g)} + \text{C}_\text{(s)} \rightarrow \text{SiC}_\text{(s)} \]

- **Direct solid-solid reaction at the contact surfaces between C and Si**
  \[ \text{Si}_\text{(s)} + \text{C}_\text{(s)} \rightarrow \text{SiC}_\text{(s)} \]

- **Reaction of carbon with SiO**
  \[ 2 \text{Si}_\text{(s,l)} + \text{CO}_\text{(g)} \rightarrow \text{SiO}_\text{(g)} + \text{SiC}_\text{(s)} \]
  \[ \text{SiO}_\text{(g)} + 2 \text{C}_\text{(s)} \rightarrow \text{SiC}_\text{(s)} + \text{CO}_\text{(g)} \]

- **Gas-gas reaction between SiO and CO**
  \[ 3 \text{SiO}_\text{(g)} + \text{CO}_\text{(g)} \rightarrow \text{SiC}_\text{(s)} + 2 \text{SiO}_2\text{(s)} \]

Prime reaction for the MI-process is the solid-liquid reaction

First wetting of the carbon surfaces by Si-vapour results in an initial SiC layer

Highly exothermal reaction \( \Delta H = -68 \text{ kJ/mol} \)
C/SiC Composites with Different Interphases (No Fiber Coating)

SEM micrograph of a 2D fabric-reinforced composite (cross section)

Composition:
- 25.1% SiC (by weight)
- 72.5% C
- 2.4% Si

Three different interphases:
- Fiber/Matrix: C_F-SiC (strong)
- Fiber/Matrix: C_F-C (weak)
- Matrix/Matrix: SiC-Si (strong)

Strong bondings in the C_F-SiC interphase
Weak bondings in the C_F-C interphase

SiC
C/C-Segment
Residual silicon embedded in SiC
C-fiber
Amorphous C-matrix
Characteristic Properties of C/SiC Composites

Increasing mechanical properties with higher service temperatures

- Low safety factors

High anisotropic properties and big differences in CTE to metals

- Design of strain-compatible joinings
Carbon/Carbon Composites for Aircraft and Racing Cars

- Low density of about 2 g/cm³
- High mass-specific energy absorption
- High thermal shock resistance

- Friction coefficient highly dependent on temperature and humidity

⇒ Not useable for road vehicles
Status and Characteristics of Carbon/Ceramic Brake Disks

Increasingly used in luxury sedans and sports cars (> 150 000 rotors/year)

More than 250 patents cover all aspects of the material composition, processing and design

- Low density (below 2.5 g/cm³)
- High thermal shock resistance
- High energy absorption
- Extreme thermal stability (up to 1350 °C)
- High corrosion stability
- High friction stability, low wear rates (lifetime brake)

- High costs

Courtesy of Audi AG
## Comparison of Brake Materials (Typical RT-Properties)

<table>
<thead>
<tr>
<th>Property</th>
<th>Short-Fiber C/SiC (Sigrasis SGL)</th>
<th>GG-20</th>
<th>Al-MMC (SiC-Particles)</th>
<th>C/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/dm³</td>
<td>2.3 – 2.45</td>
<td>7.25</td>
<td>2.7</td>
</tr>
<tr>
<td>Mass-Specific Heat Capacity</td>
<td>J/kg K</td>
<td>800</td>
<td>500</td>
<td>820 - 886</td>
</tr>
<tr>
<td>Volume-Specific Heat Capacity</td>
<td>J/dm³ K</td>
<td>1800</td>
<td>3600</td>
<td>2350</td>
</tr>
<tr>
<td>CTE (in-plane)</td>
<td>10⁻⁶ 1/K</td>
<td>1 (RT)</td>
<td>9 (RT)</td>
<td>14 - 21</td>
</tr>
<tr>
<td>Thermal Conductivity (transverse)</td>
<td>W/m K</td>
<td>40</td>
<td>54</td>
<td>160 - 185</td>
</tr>
<tr>
<td>Tensile Strength (in-plane)</td>
<td>MPa</td>
<td>20 - 40</td>
<td>150 - 250</td>
<td>310 - 370</td>
</tr>
<tr>
<td>Young’s Modulus (in-plane)</td>
<td>GPa</td>
<td>30</td>
<td>90 - 110</td>
<td>86 - 125</td>
</tr>
<tr>
<td>Bending Strength</td>
<td>MPa</td>
<td>50 - 80</td>
<td>150 - 250</td>
<td></td>
</tr>
<tr>
<td>Strain (in-plane)</td>
<td>%</td>
<td>0.3</td>
<td>0.3 - 0.8</td>
<td>0.4 - 1.2</td>
</tr>
<tr>
<td>Thermal Shock Resistance</td>
<td>W/m</td>
<td>&gt; 27000</td>
<td>&lt; 14000</td>
<td></td>
</tr>
<tr>
<td>Maximum Temperature</td>
<td>°C</td>
<td>1350</td>
<td>700</td>
<td>400</td>
</tr>
</tbody>
</table>

Cost Reduction Potentials (Brake Disks)

Prognosis:
Cost reduction potential due to volume effects and due to the implementation of new technologies

Effective trend:
No cost reduction because of the high diversity of geometries and shapes

Carbon fibers are still expensive

Modular Design (Separate Manufacture of Friction Layer and Load-Bearing Body)

- Friction ring: High COF, low wear
- Core material: High strength, high thermal conductivity and heat capacity

Assembly in the carbon/carbon stage

C/SiC brake disk

Process-integrated joining (reaction-bonding)
Goal: Ceramic Materials in Stationary Gas Turbines and Aeroengines

- Until now there are no CMCs in use in the core engine of serial gas turbines
- Low densities and high mass specific properties are not the only selection criteria
- High reliability, long life-time and low costs are of top priority
Hot Gas Stability of Ceramic Materials

Hot gas test: 1450 °C, v = 100 m/s, p_{H2O} = 0.27 bar, p = 1 atm

H. Klemm, Fraunhofer IKTS
Motivation – State-of-the-Art of Coal Power Plants

- Increase of efficiency of coal power plants by increase of temperature and pressure of the steam

<table>
<thead>
<tr>
<th>CO₂ emission [g/kWh]</th>
<th>worldwide</th>
<th>EU</th>
<th>state of the art</th>
<th>700 °C power plant</th>
<th>CO₂ separation and storage (CCS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>η = 28 – 30 %</td>
<td>1.100 – 1.400</td>
<td>8/0 – 1.0/0</td>
<td>730 – 930</td>
<td>700 °C power plant (up to 720 °C and 350 bar)</td>
<td>80 – 100</td>
</tr>
<tr>
<td>η = 37 – 38 %</td>
<td></td>
<td></td>
<td>660 – 800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>η = 50 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to BINE Informationsdienst, 2010

- Current steel pipes show high tertiary creep at 700 °C
  ⇒ New concept: hybrid ceramic metal pipes with a CMC jacket
Concept: Hybrid Ceramic-Metal Pipes

Separation of Functions

- **Metal pipe**
  Assures gas tightness and sufficient corrosion resistance against steam oxidation

- **Interphase**
  Compensates the mismatch of the CTE between metallic pipe and ceramic reinforcement

- **Ceramic fiber reinforcement**
  Overtakes partially the mechanical and thermal loads and prevents the metal pipe from creep

⇒ High mismatch of the coefficient of thermal expansion (steel – CMC)

⇒ Steel limits the manufacture temperature of the CMC pipe to 700 °C due to the required on-site manufacture
Fiber Selection

- **Requirements:**
  - High strength, low creep rates, high thermal stability
  - High corrosion stability
  - Availability as rovings or fabrics at reasonable costs
  - Compatible with different ceramic matrices

- **Possible Fibers:**
  - Quartz glass fibers (Quartzel, Saint Gobain)
  - Mullite fibers (Nextel™ 720, 3M)
  - Alumina fibers (Nextel™ 610, 3M)
  - SiC-based fibers (Nicalon, Tyranno) too expensive

⇒ Alumina fibers have been chosen because of their high strength and creep resistance

Filament tensile tests (ASTM D3379, gauge length 28 mm) with as-received fibers and heat-treated fibers (550 °C, 980 °C)
Matrix Selection

- **Requirements**
  - Viscous at room temperature (meltable or soluble)
  - Low toxicity, low content of solvent agents
  - Processing temperature for sintering or pyrolysis not more than 750 °C (limited due to the thermal stability of the metal pipe)
  - Corrosion stability

- **Manufacturing process:** Liquid polymer infiltration
  - Silazanes, silanes: high toxicity, highly sensitive to humidity
  - Siloxanes: processable in air, good compatibility to alumina fiber

⇒ Siloxanes (Silres H62, Wacker) have been chosen because of their low viscosity and catalyst-free polymerization

Feasibility Tests

• Test conditions
  – 600 °C, 350 bar
  – RT-measurement of the deformation of the outer diameter of the CMC jacket

• Hybrid ceramic metal pipe
  – Bainitic steel T24 pipe: wall thickness: 2 mm, outer diameter: 37 mm, length 350 mm
  – CMC: 3 mm wall thickness, alumina fiber (hoop wound) and siloxane (13 vol.% BN in cured state), no gap between steel and CMC jacket
  – Pyrolysis: 700 °C, nitrogen and air
Feasibility Test Results

- Increase of lifetime by more than factor 7
- Local damage of the CMC jacket after 3655 h
- Reduction of creep in the steel pipe
- Non-catastrophic damage behavior due to local creep failure of the steel pipe

Test conditions: 600 °C, 350 bar
- ceramic-metal pipe 1 (air pyrolysis)
- ceramic-metal pipe 2 (N₂ pyrolysis)
- reference (metal pipe only)
### Historical Development Steps and Summary

<table>
<thead>
<tr>
<th>Year</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970</td>
<td>CMC materials promised to solve all high-temperature problems, but trial and error approaches were mostly not successful</td>
</tr>
<tr>
<td>1980</td>
<td>Robust and up-scalable processing routes were established</td>
</tr>
<tr>
<td>1990</td>
<td>„Legitimation“ of CMCs as accepted structural materials for complex space applications (target design applications)</td>
</tr>
<tr>
<td>2000</td>
<td>Production experiences gained with small series and spin-offs from military and aerospace applications</td>
</tr>
<tr>
<td>2010 ff</td>
<td>New fibers, low cost manufacturing routes, life prediction models and novel hybrid ceramic/metal designs are current trends of development and prerequisites for the breakthrough of this class of ceramic materials</td>
</tr>
</tbody>
</table>
Many thanks for your kind attention as well as to my staff of the Department Ceramic Materials Engineering at the University of Bayreuth.