Oxide CMC Components Manufactured via PIP Processing Based on Polysiloxanes

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- Introduction and Motivation
- Manufacture of OXIPOL
  - Resin transfer moulding (RTM)
  - Wet filament winding
  - Warm pressing
- Properties of OXIPOL
- Summary and outlook
Why Ceramic Matrix Composites (CMC)?

- Design of fibre/matrix interface
- Composite properties defined by fibre/matrix interface
  - Pseudo-ductile fracture behaviour
  - Weak bond between fibre and matrix
  - Formation of energy absorbing mechanisms
  - Dissipation of tension in fibre/nmatrix interface
Ceramic Matrix Composites

- Increase in fracture toughness

**Ideal stress strain behavior**
Reference: DiCarlo and Dutta (1995)

**Fracture mechanisms**
Reference: Zok, Evans and Mackin (1995)
Manufacture of OXIPOL Using LPI-Processing

- Oxide fibre fabric, e.g.: Al$_2$O$_3$·SiO$_2$ (Nitivy)
- Solution of phenolic resin
- Commercial polysiloxane as matrix precursor

Fibre coating
- (2h / 700°C)
- (2h / 175°C)

RTM
- Filament winding
- Warm pressing
- (9h / 265°C / 20 bar)

Intermediate machining

Joining

Pyrolysis
- Polysiloxane → SiOC
- (N$_2$ / 1100 °C / 90 h / $p_\infty$)

Oxidation of fugitive coating
- (20h / 700°C)

Finishing

3 – 4 x
# Fabrics Variation

## Manufacturer’s data

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Fibres</th>
<th>Fabrics</th>
<th>Manufacturer</th>
<th>Weave</th>
<th>Mass per unit area [g/m²]</th>
<th>Filament tensile strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitivy</td>
<td>Nitivy 72/28</td>
<td>2626P</td>
<td>Nitivy Co. LTD</td>
<td>Plain</td>
<td>280</td>
<td>1800</td>
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<tr>
<td>N610</td>
<td>Nextel 610</td>
<td>DF19</td>
<td>3M</td>
<td>8 harness satin</td>
<td>654</td>
<td>3100</td>
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<tr>
<td>N720</td>
<td>Nextel 720</td>
<td>XN625</td>
<td>3M</td>
<td>8 harness satin</td>
<td>637</td>
<td>2100</td>
</tr>
</tbody>
</table>
Coating of Fabrics with Phenolic Resin via Foulard
Properties of applied Polysiloxanes

<table>
<thead>
<tr>
<th>Polysiloxane</th>
<th>MSE 100</th>
<th>MK</th>
<th>MSE 100 + 50% MK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>Methoxymethyl polysiloxane</td>
<td>Methyl polysiloxane</td>
<td>-</td>
</tr>
<tr>
<td><strong>Density after curing</strong> [g/cm³]</td>
<td>1.14</td>
<td>0.6 (powder)</td>
<td>1.14</td>
</tr>
<tr>
<td><strong>Density after pyrolysis (SiOC)</strong> [g/cm³]</td>
<td>-</td>
<td>-</td>
<td>2,3</td>
</tr>
<tr>
<td><strong>Viscosity at 25 °C</strong> [mPas]</td>
<td>30</td>
<td>solid</td>
<td>solid</td>
</tr>
<tr>
<td><strong>Viscosity at 120 °C</strong> [mPas]</td>
<td>30</td>
<td>&gt; 2000</td>
<td>&lt; 100</td>
</tr>
<tr>
<td><strong>Curing type</strong></td>
<td>Polycondensation</td>
<td>Polycondensation</td>
<td>Polycondensation</td>
</tr>
<tr>
<td><strong>Ceramic yield at 1100 °C [%]</strong></td>
<td>15</td>
<td>82</td>
<td>80</td>
</tr>
<tr>
<td><strong>Volume shrinkage at 1100 °C [%]</strong></td>
<td>93</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td><strong>Cost</strong> [€/kg]</td>
<td>18</td>
<td>23</td>
<td>21</td>
</tr>
</tbody>
</table>
Resin Transfer Moulding (RTM) I

1 Pressure Inlet
2 Mould
3 Seal
4 Resin chamber
5 Fibre Structure
6 Vacuum pump

- 250°C Temperature limit
- 20 bar Pressure limit
- Possibility of processing precursors with cross-linking via condensation
- Ability of exact adjustment of fibre fraction
- Complete infiltration of preform volume
- Ability of processing in inert atmosphere
Open Porosity of OXIPOL versus PIP cycle

![Graph showing open porosity of OXIPOL versus PIP cycle. The graph plots open porosity (%) against material status (Preform, 1.Pyrolyse, 2.Pyrolyse, 3.Pyrolyse, 4.Pyrolyse, 5.Pyrolyse, Oxidation). The graph includes three distinct lines labeled A, B, and C, each representing different material statuses.](image-url)
RTM-mould for OXIPOL Manufacture
Lay-up of Oxide Fabrics into RTM-mould
Manufacture of Radomes via Filament Winding and PIP Processing I: Filament Winding

C-fibre pre-product

Clamping unit

Fence

Winding mandrel

fibre impregnation
Manufacture of Radomes via Filament Winding and PIP Processing II: Reinfiltiration in Resin Bath
Investigated PIP Process via Warm Pressing

- **Fibre coating**
  - Variation of oxide fabrics
  - Variation of phenolic resin

- **Polymerisation**
  - Powdery polysiloxane precursor

- **Pyrolysis**
  - Polysiloxane $\rightarrow$ SiOC

- **Reinfiltration**
  - Wet polysiloxane precursor bath

- **Pyrolysis**
  - Polysiloxane $\rightarrow$ SiOC

- **Oxidation**

The process involves the conversion of Polysiloxane into SiOC, followed by reinfiltration with a wet polysiloxane precursor bath. This is repeated three times (3x).
## Variation of the Fugitive Coating

<table>
<thead>
<tr>
<th>Type</th>
<th>A *</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic resin content JK60 [mass-%]</td>
<td>0</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Coating cycles</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Pyrolysis cycles</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

* Configuration N720-A is desized

⇒ OXIPOL variation on 15 sample plates
Tensile Tests: Strengths before Exposure

Before exposure

- Nitivy fibres
- Nextel610 fibres
- Nextel720 fibres

Tensile strength improvement with:
- Several coating with lower resin concentration
- Intermediate pyrolysis of the coated fabrics

Coating of N610 increases tensile strength:

$$\sigma_{\text{max}} \text{ 2 x 5\%JK60 int. pyr.} = 3.6 \times \sigma_{\text{max uncoated}}$$
Tensile Tests: Strengths after Exposure

After 20 h exposure at 1200 °C

- Nitivy fibres
- Nextel610 fibres
- Nextel720 fibres

Independently of coating:
- Tensile strength decreases after exposure

These coatings were not adapted for 1200°C
Oxidation Phenomena during Thermal Exposure

Matrix growing after exposure due to two reactions:

- Net weight loss
  \[ C + O_2 \rightarrow CO_x \]

- Net weight gain
  \[ Si-C + O_2 \rightarrow Si-O + CO_x \]

- Close the gap fibres/matrix
- Decrease of energy absorbing effects and tensile strength
- Need for oxidation resistant fibre coating
- For example \( LaPO_4 \)
Summary

• The manufacture of OXIPOL can be performed by different methods and opens up new application areas

• Resin transfer moulding (RTM) is well suited for resins cured via polycondensation and is very efficient for densification of CMC

• Filament winding of oxide fibres was successfully applied to manufacture complex structures

• OXIPOL manufacture based on warm pressing provides high potential for cost reduction

• Fugitive coating is not applicable at high temperature in air due to embrittlement of CMC (matrix degradation and gap closure)

→ new oxidation resistant coatings providing easy cleavage are needed, e.g. LaPO$_4$