Module Design for MIEC Membranes in OXYCOAL-AC

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Institute for Materials Applications in Mechanical Engineering
Module design in OXYCOAL-AC

Agenda

1. Introduction
2. Materials
3. Joining Techniques
4. Membrane Concepts
5. Conclusion
Oxyfuel-Combustion

Simple Oxyfuel-Process

AF = Air Fractorization

Oxycoal-AC-Process

OTM = Oxygen Transport Membran

BMWI-Project at Aachen University

6 Mechanical Engineering Institutes

Industrial participants: EON, RWE, MAN-Turbo, Hitachi, Linde, WPS
Pressure driven OTM-Reactors

Air (20 bar) → N₂ → CO₂ → N₂ (+ O₂) → CO₂ (+ O₂) → Exhaust gas CO₂

O₂ (0.8 - 0.3 bar) → N₂ (+ O₂) → O₂ (850°C, 20 bar) → Exhaust gas 850°C, 1 bar

Air 850°C, 20 bar → OTM tube → Inner metal tube
Extraction by vacuum pump

\[ J_{O_2}^\prime = C(T) \frac{1}{Sm} \ln \frac{p_{O_2\text{air}}}{p_{O_2\text{flue}}} \]

\{ lower \( pO_2 \)-ratio means:
- lower permeation rate
- larger membrane area\}

Comparison of Oxygen Flux (850°C, 20 bar air) for 1mm \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x} \)

\begin{array}{c|c|c}
\text{p}_{O_2}\text{-ratio} & \text{Vacuum 800 mbar:} & 5 & 1 \text{ ml/cm}^2\text{min} \\
\text{Exhaust gas:} & 25 & 2 \text{ ml/cm}^2\text{min} \\
\end{array}

Measured by S. Engels RWTH 2009
Outer influences:
- High temperature (850°C)
- Air pressure up to 20bar (Feed)
- Corrosive atmosphere (Permeate)
- Vacuum (Permeate)

Requirements:
- Gas tight joining (Feed ↔ Permeate)
- Long term stable joining
- High mechanical strength of materials
- High chemical resistance
- High creep stability
Characteristic strength $\sigma_0 = 130$ MPa (sample size) $\rightarrow \sim 50$ MPa (component size)

Weibull modulus $m = 6.7$

Temperature effect $\overline{\sigma}_z (850^\circ \text{C}) / \overline{\sigma}_z (\text{RT}) \sim 0.6$

Size effect

$$\frac{\sigma_1}{\sigma_2} = \left( \frac{V_2}{V_1} \right)^{\frac{1}{m_e}}$$
**Materials Characterisation**

**Creep**

- Time (h): 0 10 20 30 40 50 60 70
- S [μm]: 0 200 400 600 800 1000
- k₁=0.95 [μm/h]
- k₂=8.1 [μm/h]
- k₃=52.8 [μm/h]

**Coefficient of thermal expansion**

- Temperature [°C]: 0 200 400 600 800 1000
- α [10⁻⁶/K]: 0.0 0.4 0.8 1.2
- λ [W/mK]: 0.0 0.4 0.8 1.2

**Head capacity and thermal conductivity**

- F=1%
- F=43.5%
- F=1%

**Table**

<table>
<thead>
<tr>
<th>Material</th>
<th>ρ</th>
<th>ρₜₜ</th>
<th>σₕₜₜ</th>
<th>m</th>
<th>σ₄PB</th>
<th>E</th>
<th>α</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSCF</td>
<td>5.70</td>
<td>5.80</td>
<td>130</td>
<td>6.7</td>
<td>62</td>
<td>60-90</td>
<td>18.2</td>
<td>1.8</td>
</tr>
<tr>
<td>SCMF (porous)</td>
<td>3.84</td>
<td>5.12</td>
<td>53</td>
<td>6.1</td>
<td>33</td>
<td>30-70</td>
<td>15.8</td>
<td>2.2</td>
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**Failure propability**

- ln(ln(1/1-F)) = 2.5 43.25 4.52 2.75 4.25 3.75 3.5

**Corrosion in exhaust gas**

- Exhaust gas BSCF
- Exhaust gas SCMF

**Microstructure**

- Image of microstructure
## Materials Characterisation

### Creep

![Creep Diagram](image)

- Initial measurement: 11.08 mm
- Initial measurement: 10.76 mm
- $k_1 = 0.95 \, \mu m/h$
- $k_3 = 52.8 \, \mu m/h$

### Coefficient of thermal expansion

![Coefficient of thermal expansion Diagram](image)

- $\alpha_{tech} = [10^{-6}/K]$

### Head capacity and thermal conductivity

![Head capacity and thermal conductivity Diagram](image)

- $\lambda = [W/mK]$

### Table: Materials Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$</th>
<th>$\rho_{th}$</th>
<th>$\sigma_{O-Ring}$</th>
<th>$m$</th>
<th>$\sigma_{4PB}$</th>
<th>$E$</th>
<th>$\alpha$</th>
<th>$\lambda$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>[g/cm³]</td>
<td>[g/cm³]</td>
<td>[MPa]</td>
<td>[-]</td>
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<td>[GPa]</td>
<td>[10^{-6} K^{-1}]</td>
<td>[W/mK]</td>
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### Failure probability

![Failure probability Diagram](image)

- $F = 43.5\%$
- $F = 1\%$

### Corrosion in exhaust gas

![Corrosion in exhaust gas Diagram](image)

- Exhaust gas BSCF
- Exhaust gas SCMF

### Microstructure

![Microstructure Image](image)
Joining alternatives

**Force Closure**
- gas tight (sealing elements)
- resoluble
- temperature sensitive
- high joining stresses

Only at low temperature

**Solid Closure**
- gas tight
- not resoluble
- high temperature range
- adjustable joining stresses

Possible joining for OTM-applications

**Form Closure**
- not gas tight
- resoluble
- temperature sensitive
- low joining stresses

*Only at low temperature Possible joining for OTM-applications*
Reactive Air Brazing (RAB) Ceramic/Metal-Joints

Method:
- Air atmosphere
- Joining temperature <1000°C
- Pressureless

Advantage:
- No degradation of Perovskite by O₂-removal
- Excellent wettability
- Similar CTE
- Low Joining stresses

Braze diffuses into porous substrates

No long term experience
Geometrical brazing optimization

Brazed seam on inner side

Brazed seam on outer side

Burst testing:
Inner side brazed seam → < 10bar
Outer side brazed seam → >35bar
→ reduction of joining stresses!
Alternatives for membrane elements

Tubes

Honeycombs

Foils

Joining Problems for honeycombs

Patent of Norsk Hydro

Source: HITK

Solid Oxid Fuel Cell, Research-Center-Jülich
Module design in OXYCOAL-AC

One side closed tubes allow:
- cold joining $T < 200 \, ^\circ C$ (O-Rings, Glue)
- warm joining $T < 600 \, ^\circ C$ (Brazing)

Low temperature at metal-components
- metal alternatives
- large module units possible
- low heat lost

Parameters:
- 800 - 900°C
- 5 - 20 bar air (Feed site)
- 400 mbar (Permeate site)
Module design for larger applications

Inner Isolation

Membrane Tubes

Degraded Air

Air in

Degraded Air

Base Plate Geometrie

Diameter : 600 mm
Tubes per plate: 500
Total Tubes: 1000
Tubes Length: 500 mm
Membrane Area: ~ 23.5 m²

Oxygen capability: 1.4 tons per day
Modulare Assembly

Pipework concept allows duplicating for larger units

- Upper Pressure Tank
- Base Plate
- Exhaust Oxygen
- lower Pressure Tank
- Flange
- Security Devices Valves (switch off defect modules)
- insulated Manifolds

Oxygen capability: 2.8 tons per day
Planar design, Air Products

The Heart of ITM Oxygen Technology
Planar Membrane Wafer Stack

- Thin membrane
- Porous membrane support
- Dense, slotted backbone
- Spacer between wafers
- Product Withdrawal Tube
- Pure Oxygen

Compressed air
800-900°C
200-300 psig

Oxygen capability per module
0.5 tons per day

Presented at Gasification Technology 2005 and 2008
Conclusions

**Concept Principles**
4-end concept with overflowing exhaust gas
   best efficiency but CO₂-problem for BSCF-ceramic
3-end concept with extraction O₂ by vacuum pump
   applicable for vacuum > 0.3 bar, needs compressed air on feed site

**Structures**
Tubes seems to be best choice: high packing density, easy to join,
optimum diameter for 3-end: Ø = 10 mm

**Joining**
Handling of high thermal expansion
RAB manageable, up to now no long term experience
Glass seals applicable up to 600 °C
Best choice for 3-end: cooled joints using special glues

**Modul design**
Modular concept necessary for removement of failed ceramic tubes
The authors gratefully acknowledge financial support by BMWi and MIWFT as well as the companies RWE Power AG, E.On AG, Hitachi Power Europe, Linde AG, MAN Turbo and WS-Wärme-Prozesstechnik.
Back-Up
### Size effect on fractural strength

\[
\frac{\sigma_1}{\sigma_2} = \left( \frac{V_2}{V_1} \right)^{\frac{1}{m_v}}
\]

Depends on scattering strength values \((m=10)\)

Strength depends on surface finishing

<table>
<thead>
<tr>
<th>(V_{\text{effx}}/V_{\text{eff1}})</th>
<th>1 ((15,62 \text{ mm}^3))</th>
<th>0,00034</th>
<th>0,026</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma)</td>
<td>87 MPa</td>
<td>193 MPa</td>
<td>125 MPa</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>(V_{\text{effx}}/V_{\text{eff1}})</th>
<th>&gt;1</th>
<th>5,91</th>
<th>295,58</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma)</td>
<td>&lt; 87 MPa</td>
<td>73 MPa</td>
<td>50 MPa</td>
</tr>
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![Diagram of testing methods](image)