Oxidation behavior of possible construction materials for heat exchanging components in oxyfuel plants in the temperature range 550-650 °C

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Oxyfuel concept

CO₂-H₂O rich gas
### Gas compositions

<table>
<thead>
<tr>
<th>Vol.%</th>
<th>Air firing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>1.7</td>
</tr>
<tr>
<td>Ar</td>
<td>0.8</td>
</tr>
<tr>
<td>$N_2$</td>
<td>71.6</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>9.5</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>16.1</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>0.17</td>
</tr>
</tbody>
</table>

## Oxyfuel concept: gas compositions

<table>
<thead>
<tr>
<th>Vol.%</th>
<th>Air firing</th>
<th>Oxyfuel firing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>1.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Ar</td>
<td>0.8</td>
<td>2.2</td>
</tr>
<tr>
<td>N₂</td>
<td>71.6</td>
<td>4.6</td>
</tr>
<tr>
<td>H₂O</td>
<td>9.5</td>
<td>31.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>16.1</td>
<td>59.0</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.17</td>
<td>0.46</td>
</tr>
</tbody>
</table>

→ High CO₂, H₂O and SO₂ contents in Oxyfuel gas

Materials tested during the oxidation studies

<table>
<thead>
<tr>
<th>Ferritic/martensitic steels:</th>
<th>Austenitic steels:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 13CrMo4 4 1% Cr</td>
<td>- Super 304 18% Cr</td>
</tr>
<tr>
<td>- P92 9% Cr</td>
<td>- TP347H FG 18% Cr</td>
</tr>
<tr>
<td>- VM12 12% Cr</td>
<td>- 310N 24% Cr</td>
</tr>
</tbody>
</table>

(500 - 625 C)                  (600 - 700 C)

<table>
<thead>
<tr>
<th>Nickel base alloy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Inconel 617 22% Cr</td>
</tr>
</tbody>
</table>

(650 - 700 C)
<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>CO₂</th>
<th>H₂O</th>
<th>O₂</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar/CO₂</td>
<td>50</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Ar/CO₂/O₂</td>
<td>49</td>
<td>50</td>
<td>-</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Ar/H₂O</td>
<td>50</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>CO₂/H₂O</td>
<td>-</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ar/CO₂/H₂O/O₂</td>
<td>12</td>
<td>60</td>
<td>25</td>
<td>3</td>
<td>0.5</td>
</tr>
</tbody>
</table>
In this talk

- Oxyfuel gas without SO\textsubscript{2}
- Oxyfuel gas with SO\textsubscript{2}
  - Without deposits
  - With deposits

Oxidation parameters:

250 and 1000 h, 550 / 650 °C

Exposures with deposits: 250 h only

### Oxyfuel gas (without SO\textsubscript{2}); Vol. %

- Ar: 12
- CO\textsubscript{2}: 60
- H\textsubscript{2}O: 25
- O\textsubscript{2}: 3

### Oxyfuel gas (with SO\textsubscript{2}); Vol. %

- Ar: 11.5
- CO\textsubscript{2}: 60
- H\textsubscript{2}O: 25
- O\textsubscript{2}: 3
- SO\textsubscript{2}: 0.5
Exposures with deposits

Oxyfuel gas (with SO₂); Vol. %

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>11.5</td>
</tr>
<tr>
<td>CO₂</td>
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</tr>
<tr>
<td>H₂O</td>
<td>25</td>
</tr>
<tr>
<td>O₂</td>
<td>3</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Oxidation parameters: 250 h, 550 / 650 °C

Deposits:

Main:

„L8“

Additional:

„L5P5“
„L0“
„Burner“

Without deposit

With deposit

Oxidation parameters: 250 h, 550 / 650 °C
Schwarze Pumpe pilot oxyfuel plant – Sketch of installation
Exposures with deposits

Oxidation tests:

All materials + deposit: “Level 8” (L8)

Steel P92 + different deposits (L8, L5, L0, Burner)
Temperature: 550 °C

(9-12%Cr steels)

P92, VM12
Metallographic cross-section of steel P92 after 1000h oxidation at 550 C in SO₂ free oxyfuel gas

Fe₂O₃
Fe₃O₄
Fe₃O₄ + (Fe, Cr)₃O₄
Internal oxidation
Ni-coating
Steel

25 µm
Metallographic cross-section of steel P92 after 1000h oxidation at 550 C in different gases

Oxyfuel gas (without SO₂)

- Slightly thicker oxide in SO₂ containing gas
- Presence of SO₂ suppresses internal oxidation zone

Oxyfuel gas (with SO₂)
Metallographic cross-section (SEM/EDX) of martensitic 9%Cr steel P92 after 1000h oxidation at 550 C in **Oxyfuel gas with SO₂** (Ar-60%CO₂-25%H₂O-3%O₂-0.5%SO₂)
Quantified GDOES profile (S concentration) of steel P92 after 250h oxidation at 550 C in Oxyfuel gas (with SO₂)

Measured by GDOES depth profiling
Sulphur present in inner oxide scale

mainly near:

- interface between inner and outer oxide

  Simultaneous sulphidation and oxidation during early stages of the corrosion process (transient stage)

- oxide/steel interface

  Internal sulphidation by molecular $\text{SO}_2$ transport via “rapid diffusion paths” in the oxide scale

Quantified GDOES profile (S concentration) of steel P92 after 250h oxidation at 550°C in Oxyfuel gas (with SO$_2$)

Decreasing with time

Increasing with time

Outer scale

Inner scale

Steel

Sputtering time [s]
Metallographic cross-section (SEM/EDX) of martensitic 12%Cr steel VM12 after 1000h oxidation at 550 C in Oxyfuel gas with SO$_2$ (Ar-60%CO$_2$-25%H$_2$O-3%O$_2$-0.5%SO$_2$)

Inner scale

Sulphides

Steel
After longer exposure times:

Internal sulphidation becomes more important;

Process increasing with time
Metallographic cross-sections (SEM/EDX) of steel P92 after 250h oxidation at 550 C in Oxyfuel gas with SO₂ (without and with deposit “L8”)
Temperature: 650 °C

(9-12%Cr steels)

P92, VM12
Metallographic cross-section of steel P92 after 1000h oxidation at 650 C in different gases

Oxyfuel gas (without SO$_2$)

Oxyfuel gas (with SO$_2$)

Similar results as at 550 C
Metallographic cross-section (SEM/EDX) of martensitic 9%Cr steel P92 after 1000 h oxidation at 550°C in Oxyfuel gas (with SO₂).

Sulphides
Metallographic cross-sections (SEM/EDX) of steel **P92** after 250h oxidation at 650°C in Oxyfuel gas with SO₂ (without and with deposit “L8”).

**Without deposit**

**With deposit**
Metallographic cross-sections (SEM/EDX) of steel P92 after 250h oxidation at 650 C in Oxyfuel gas (with SO₂) with deposit “L8”

- Sulphur partially tight up in the upper layer of deposits?
Temperature: 650 °C

(High alloyed materials)

- Super 304  (austenitic, 18%Cr)
- 310        (austenitic, 24%Cr)
Metallographic cross-section of austenitic steel 310N after 1000h oxidation at 650 C in different gases

- Presence of SO$_2$ hampers formation of volatile Cr species?
Metallographic cross-section of different austenitic steels after **1000h** oxidation at 650 C in Oxyfuel gas (with SO₂)

**Super 304 (18%Cr)**

- **Ni-coating**
- **Fe-rich oxide**
- **Cr-rich oxide**

**310N (24%Cr)**

- **Ni-coating**
- **Cr₂O₃**

![S element map](image)
Conclusions:

- Slightly enhanced oxidation rates of martensitic 9-12%Cr steels in Oxyfuel gas with 0.5 % \( \text{SO}_2 \) compared to similar \( \text{SO}_2 \) free gas were observed.

- Internal oxidation is “suppressed”, possibly by formation of sulphide ahead of the internal oxidation front.

- After relatively short times of 250h very small differences between oxide scales morphology with / without deposits are observed (difference near scale / alloy interface especially at 650 C) for 9-12%Cr steels. Longer exposure times are planned.

- In case of high alloyed, “real” chromia formers (such as 310), \( \text{SO}_2 \) suppresses formation of volatile Cr species; related to preferred adsorption of \( \text{SO}_2 \) ?
Acknowledgements:

This combined research project is supported by the German Federal Ministry of Economics and Technology as well as our industrial Partners Alstom, Babcock Borsig Steinmüller, Clyde Bergemann, EnBW, E.ON, EVN and Vattenfall.
Back-up
Formation of volatile Cr-Species in O₂/H₂O-containing gas mixtures

Volatile Cr-species

\[
\frac{1}{2} \text{Cr}_2\text{O}_3 + \frac{3}{4} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CrO}_2(\text{OH})_2
\]

Equilibrium constant

\[
K = \frac{p[\text{CrO}_2(\text{OH})_2]}{p(\text{O}_2)^{\frac{3}{4}} \ast p(\text{H}_2\text{O})}
\]

\[
p[\text{CrO}_2(\text{OH})_2] = K \ast p(\text{O}_2)^{\frac{3}{4}} \ast p(\text{H}_2\text{O})
\]

Formation of volatile CrO₂(OH)₂ promoted at combination of high \( p(H_2O) \) AND high \( p(O_2) \)
Oxidation behaviour of INCONEL 617 in CO₂/H₂O/O₂-rich gases during exposure at 700 C
Quantified GDOES profile (S concentration) of steel P92 after different oxidation times oxidation at 550 C in Ar-30%H₂O-0.5%SO₂
TEM element distribution of P92 after oxidation in $\text{Ar-30}\%\text{H}_2\text{O}-0.5\%\text{SO}_2$ at 550 C for 24h (1st Mechanism)

Iron-rich sulphides
TEM element distribution of P92 after oxidation in Ar-30%H₂O-0.5%SO₂ at 550 C for 24h

(2nd Mechanism)
Relative rates of adsorption

\[ \text{SO}_2 > \text{H}_2\text{O} > \text{O}_2 > \text{CO}_2 \]
Oxidation of martensitic 9% Cr steel P92 in different atmospheres after 1000h exposure at 550 °C
Effect of oxygen addition in Ar-50% CO₂ on behaviour of martensitic steel VM 12 at 550°C after 1000h

→ Oxygen addition to the CO₂ promotes protective chromia base scale formation on martensitic 9 - 12%Cr steels