Diffusion Coatings for Corrosion Protection of Ferritic-Martensitic Steels for Co-firing Biomass with Coal

Cofiring 8, Copenhagen

Supported by:

Federal Ministry of Economics and Technology

on the basis of a decision by the German Bundestag
High Temperature Corrosion under Complex Conditions, Deposits and Salts: Towards Greener Energy

European Federation of Corrosion Workshop

26. – 29. September 2018

DECHEMA, Frankfurt am Main
Motivation
Coal-fired power plant

Superheater

• Cofiring of biomass leads to increased amounts of chlorides and alkali species
  → Cofiring commonly limited to low temperatures and small amounts of biomass

Goal of this study:
Development of coatings extending the lifetime of superheater tubes
Motivation
Cofiring of Biomass: Corrosion mechanisms

- Formation of eutectic salt mixtures (from alloying elements and deposit)
- Dissolution of protecting oxide scales by fluxing mechanisms
- “Active oxidation” by chlorine

Phases and Eutectics below \((\text{Na},\text{K})_2\text{SO}_4\) melting \(T\) \([°C]\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{K}_3\text{Fe(SO}_4)_3)</td>
<td>618</td>
</tr>
<tr>
<td>(\text{Na}_3\text{Fe(SO}_4)_3)</td>
<td>624</td>
</tr>
<tr>
<td>(\text{Na}_2\text{SO}_4-\text{NiSO}_4)</td>
<td>671</td>
</tr>
</tbody>
</table>

Phases and Eutectics below \((\text{Na},\text{K})\text{Cl}\) melting \(T\) \([°C]\)

<table>
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<th>Compound</th>
<th>(T) [°C]</th>
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<tbody>
<tr>
<td>(\text{FeCl}_3)</td>
<td>300</td>
</tr>
<tr>
<td>(\text{KCl-K}_2\text{Cr}_2\text{O}_7)</td>
<td>368</td>
</tr>
<tr>
<td>(\text{KCl-K}_2\text{SO}_4-\text{Na}_2\text{SO}_4)</td>
<td>478</td>
</tr>
</tbody>
</table>

[T. Topoda et al. EPRI Report GS-6422, 36-1 (1988)]
**Diffusion Coatings**

**Coating Concept**

**Coal-fired plants:**
Cr↑ to avoid Na$_2$SO$_4$ - NiSO$_4$ formation

**Cl-rich environments:**
With ↑Ni and ↓Fe the resistance of the alloys in Cl-containing atmospheres increases, see also:

[F. H. Stott et al., High Temperature Technology, 6, 115 (1988)];
[P. Gawenda et al., Materials and Corrosion, 48 176 (1997)];
Diffusion Coatings
Material Selection / Experimental Procedure

- **Cost-Efficient Base Material:**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Mo</th>
<th>V</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>X20CrMoV12-1 [wt.%]</td>
<td>0.60</td>
<td>11.30</td>
<td>0.22</td>
<td>0.63</td>
<td>0.33</td>
<td>0.02</td>
<td>&lt; 0.01</td>
<td>1.01</td>
<td>0.26</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

- **(Optional) 1st Step: Interlayer**
  Ni for protection against Cl-attack

- **2nd Step: Diffusion layer**
  enrichment of base metal/interlayer with Cr as potentially protective element using the pack cementation process

- **High-Grade Reference Material:**

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<th>Alloy</th>
<th>Ni</th>
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<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>N</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMV310N [wt.%]</td>
<td>20.93</td>
<td>25.18</td>
<td>0.06</td>
<td>1.21</td>
<td>0.45</td>
<td>0.02</td>
<td>&lt; 0.01</td>
<td>0.09</td>
<td>0.28</td>
<td>0.46</td>
</tr>
</tbody>
</table>

[Tatay. Solution Processed Spin Electronics (2014)]
Diffusion Coatings

Overview of Cr-based coatings

...based on an electroplated Ni-layer
Diffusion Coatings

**X20 + Cr-Diffusion coating**

- Pack cementation: 1050°C, 2h (10 wt.% Cr, 2 wt.% MnCl₂)

- Chromium enriched subsurface zone
Pack cementation: 1050°C, 2h (10 wt.% Cr, 2 wt.% MnCl₂)

- Chromium enriched subsurface zone

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<tr>
<td>DMV310N [wt.%)</td>
<td>20.93</td>
<td>25.18</td>
<td>51.32</td>
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</tbody>
</table>
### Corrosion Test

#### Experimental Conditions for Accelerated Testing

| Gas composition  |  
|------------------|------------------|
| **O₂ [vol.%]**   | 4                |
| **CO₂ [vol.%]**  | 15               |
| **SO₂ [vol.%]**  | 0.1              |
| **H₂O [vol.%]**  | 6                |
| **HCl [ppm]**    | 500              |
| **N₂**           | balance          |

- **Temperature:** 650°C
- **Duration:** 100h, 300h
- **Slurry-coated by aggressive salt mixtures:**
  - Na₂SO₄ (50 wt.%) + K₂SO₄ (50 wt.%)
  - Na₂SO₄ (40 wt.%) + K₂SO₄ (40 wt.%) + KCl (20 wt.%)
    (melting point ≈ 600°C)

Corrosion test
650°C in different salt mixtures

DMV310N Ref.

Salt mixture 1:
Na$_2$SO$_4$ (50 wt.%) + K$_2$SO$_4$ (50 wt.%)

Salt mixture 2:
Na$_2$SO$_4$ (40 wt.%) + K$_2$SO$_4$ (40 wt.%) + KCl (20 wt.%)

Atm. [vol.%]:
<table>
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<th></th>
<th>4% O$_2$</th>
<th>15% CO$_2$</th>
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<th>500ppm HCl</th>
<th>Bal. N$_2$</th>
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Mixed oxide Fe/Cr/Ni
Fe$_3$O$_4$, NiS

Sulfidation

Mixed oxide Fe/Cr/Ni
(Na,K)$_2$SO$_4$, (Cr,Fe)$_2$O$_3$
Corrosion test
Overview of Cr-based coatings

...based on an electroplated Ni-layer
**Corrosion test**

650°C in different salt mixtures

**X20 + Cr**

Salt mixture 1:
Na$_2$SO$_4$ (50 wt.%) + K$_2$SO$_4$ (50 wt.%)

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**Images:**

- 100h: Cr$_2$O$_3$, Fe$_2$O$_3$, (Cr,Fe)$_2$O$_3$, Sulfides at interface, Cr$_x$C$_y$ left over
- 300h: Cr$_2$O$_3$, Fe$_2$O$_3$, (Cr,Fe)$_2$O$_3$, Sulfides at interface, Cr$_x$C$_y$ left over

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Corrosion test
650°C, 300h in KCl-containing salt mixture

X20 + Cr

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Salt mixture 2:
Na₂SO₄ (40 wt.%) + K₂SO₄ (40 wt.%) + KCl (20 wt.%)

- Carbide is not present any more
- Coating mainly dissolved in presence of KCl
- S at metal interface → Sulfidation of Cr
- Active oxidation of substrate after coating failure?
  (Cl attacks Fe by FeCl₂/FeCl₃)
- K/Na on the outer Cr oxide scale: Chromate formation?
Corrosion test
Overview of Cr-based coatings

X20 + Cr

X20 + Ni + Cr

...based on an electroplated Ni-layer
Corrosion test
650°C in different salt mixtures

**X20 + Ni + Cr**

| Salt mixture 1: Na$_2$SO$_4$ (50 wt.%) + K$_2$SO$_4$ (50 wt.%) |
| Salt mixture 2: Na$_2$SO$_4$ (40 wt.%) + K$_2$SO$_4$ (40 wt.%) + KCl (20 wt.%)

| Atmosphere [vol.%]: | 4% O$_2$ | 15% CO$_2$ | 0.1% SO$_2$ | 6% H$_2$O | 500ppm HCl | Bal. N$_2$
|---------------------|---------|-----------|-----------|---------|---------|---------|

**Atm. [vol.%]:**
- 4% O$_2$
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- 6% H$_2$O
- 500ppm HCl
- Bal. N$_2$

**100h**
- Cr$_2$O$_3$
- Cr$_x$C$_y$
- Ni-Diffusion Zone

**300h**
- Mixed oxides of Ni/Fe/Cr with Ni sulfides

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Corrosion test
650°C, 300h in KCl-containing salt mixture

X20 + Ni + Cr

Salt mixture 2:
Na₂SO₄ (40 wt.%), K₂SO₄ (40 wt.%), KCl (20 wt.%)

- Coating shows pitting behavior with KCl
- K/Na on the outer Cr oxide scale: Chromate formation?
- In unattacked spots much better than without Ni, but if it fails → Type II Hot Corrosion

Ni-Ni₃S₂ (635°C)
Ni-NiS (645°C)
Na₂SO₄-NiSO₄ (671°C)

[Bürgel. Hochtemperaturwerkstoffe (2006)]
Corrosion test
Statistical analysis of the attack on the substrate

Salt mixture 1:
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Salt mixture 2:
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Both coatings highly resistant

Both Coatings increase the lifetime, but are destroyed after 300h

Similar performance outside the laboratory?
Corrosion test
Pilot scale test facility: conditions of Biomass cofiring

Pulverised fuel combustion rig, 500 kW

Calentur

Concentration (normalised)

Si 100%
Fe 90%
Al 80%

Cl (wf)
0.01 wt.% 0.1 wt.%

S (wf)
1.2 wt.% 0.1 wt.%

Torr. Straw

Ca

Mg

K

Air preheater, SCR Catalyst, ESP, fabric filter

20h 25h 20h
10/90% 50/50% 100%

[https://www.ifk.uni-stuttgart.de]
Corrosion test
Samples before and after exposure

X20 Ref.

X20 + Cr

X20 + Ni + Cr

Exhaust gas

Exhaust gas

[https://www.ifk.uni-stuttgart.de]
Corrosion test
650°C, 65h, mixed straw firing conditions

X20 Ref.

Deposits
Mixed oxide Fe/Cr
S-species

O
C
Fe
K
S
Na
Cl
Cr

40 μm

50 μm
Corrosion test
650°C, 65h, mixed straw firing conditions

X20 coated

X20 + Cr

X20 + Ni + Cr

20 mm

50 μm

50 μm
Corrosion test
650°C, 65h, mixed straw firing conditions

X20 coated

Cr-oxide & carbide Deposits
Cr-enriched diffusion zone

Corrosion test
650°C, 65h, mixed straw firing conditions

X20 coated
Summary and Outlook

- **Accelerated testing shows improvement in corrosion resistance for both coatings**
  - Valuable ranking, performance approved during exposure in pilot scale test facility as well
  - However, long term testing in deposits required for promising candidates

- **KCl accelerates the attack**
  - Scale dissolution
  - Carbides preferentially attacked and dissolved by Cl-species
    - [Grabke et al. Mat. Res. 7, 1 (2004)]
  - $K_2CrO_4$-formation can occur
  - Active oxidation? ($MCl_x$-formation)
  - Shorter incubation till type II Hot Corrosion

- **Ni influences corrosion behavior**
  - Higher resistance of Ni over Fe in Cl environments
  - Ni-induced Hot Corrosion II upon failure of Cr scale

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Thank you for your attention!