Long term performance of aluminide coatings in contact with molten Solar Salt at 580º C in CSP plants

A. Agüero, P. Audigié and S. Rodríguez

Instituto Nacional de Técnica Aeroespacial
Torrejón de Ardoz (Madrid), SPAIN

RAISELIFE Dissemination Workshop
Dusseldorf, November 2019
Molten salts are excellent as heat storage fluids but they can be very corrosive
CONCENTRATING SOLAR PLANT (CSPs) WITH THERMAL STORAGE

- Receiver
- Heat exchanger and steam turbine
- Cold Tank
- Hot Tank
IN CSP PLANTS THE LCOE MUST BE REDUCED

Less expensive longer lasting materials should be used

Ni based alloys are 10 times more expensive than ferritic steels
Protective Coatings allow:

- Increase the lifetime of alloys in contact with molten Solar Salts (tubes and tanks)
- Use lower cost alloys such as ferritic steels
GOAL OF THE STUDY

Coating lower cost ferritic steels
10,000 h testing in contact with the Solar Salt at 580°C

Base materials
- P91
- VM12
- IN617

Coating
- Fe Aluminide

Environment
- Solar Salt at 580°C
## MATERIALS

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Co</th>
<th>N</th>
<th>Ni</th>
<th>Si</th>
<th>V</th>
<th>S</th>
<th>Mo</th>
<th>C</th>
<th>Mn</th>
<th>W</th>
<th>Nb</th>
<th>Cu</th>
<th>Al</th>
<th>Ti</th>
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<tbody>
<tr>
<td>P91</td>
<td>Bal.</td>
<td>8.6</td>
<td>-</td>
<td>0.04</td>
<td>0.08</td>
<td>0.4</td>
<td>0.20</td>
<td>0.006</td>
<td>0.96</td>
<td>0.10</td>
<td>0.5</td>
<td>1.80</td>
<td>0.08</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
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<tr>
<td>VM12</td>
<td>Bal.</td>
<td>11.5</td>
<td>1.60</td>
<td>0.05</td>
<td>0.25</td>
<td>0.50</td>
<td>0.25</td>
<td>0.005</td>
<td>0.30</td>
<td>0.12</td>
<td>0.30</td>
<td>1.50</td>
<td>0.08</td>
<td>0.25</td>
<td>0.02</td>
<td>-</td>
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<tr>
<td>IN617</td>
<td>1.40</td>
<td>22.5</td>
<td>12.5</td>
<td>-</td>
<td>Bal.</td>
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<td>-</td>
<td>0.01</td>
<td>8.2</td>
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<td>0.10</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
<td>1.20</td>
<td>0.40</td>
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</table>
Fe ALUMINIDE COATINGS

As deposited Al slurry

1050°C
30 min

On P91

(a) 20-24wt.% Al
FeAl
Kirkendall porosity
Al interdiffusion zone

On VM12-

(b) 20-22wt.% Al
FeA
Al interdiffusion zone
TESTING: Static, isothermal conditions at 580° C

Industrial grade “solar salt” (60 % NaNO₃ – 40 % KNO₃) was obtained from BrightSource

up to 10,000h

To weight and analyse:
- the samples are taken out of the furnace (still at test T°)
- Leave to cool under air
- Washed with hot water
ISOTHERMAL TESTING AT 580° C: SUBSTRATES
ISOTHERMAL TESTING AT 580° C:

Significant spallation was observed
ISOTHERMAL TESTING AT 580° C: VM12

1000 h

5000 h

10,000 h

On going
ISOTHERMAL TESTING AT 580° C: ferritic steels

SEM images of the sample surface

10,000 h

Extensive spallation
No Cr detected
Expected oxide on the surface: NaFeO_2
Presence of K and N: residues of KNO_3 salt
ISOTHERMAL TESTING AT 580° C: P91 (10,000 h)

- Fe$_2$O$_3$
- NaFeO$_2$
- KNO$_3$
ISOTHERMAL TESTING AT 580°C: P91

5,000 h

Thin NaFeO$_2$ scale on thick Fe, Cr oxides

No apparent penetration of Na inside the Fe, Cr oxides
ISOTHERMAL TESTING AT 580° C: 5,000 h

Columnar NaFeO$_2$

Nitriding
ISOTHERMAL TESTING AT 580° C: IN617

Cr is present in the oxide (8-20 wt. %)

Cr is only present at the interface with the substrate
ISOTHERMAL TESTING AT 580° C: IN617

NiO and some CoCr$_2$O$_4$ present – substrate peaks visible

5,000 h
ISOTHERMAL TESTING AT 580°C: IN617

Spallation takes place

View of sample surface after 10,000h
Mainly Ni, Co and Na detected on the surface of the oxide
ISOTHERMAL TESTING AT 580° C: IN617

No Cr on the oxide despite the alloy having 22.5 wt. % - substrate peaks are not visible.
ISOTHERMAL TESTING AT 580° C: IN617

Mainly Co, O and Na detected on the surface of the oxide

[Image of cross-section with Elemental mapping for Co, O, Ni, Al, Fe, Cr, Mo]
COMPARISON BETWEEN STATIC AND DYNAMIC TESTING AT 580° C: IN617

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Static</th>
<th>Dynamic</th>
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<tbody>
<tr>
<td>1,000</td>
<td>2 μm</td>
<td>5 μm</td>
</tr>
<tr>
<td>2,000</td>
<td>2 μm</td>
<td>5 μm</td>
</tr>
<tr>
<td>3,000</td>
<td>15 μm</td>
<td>15 μm</td>
</tr>
<tr>
<td>4,500</td>
<td>27 μm</td>
<td>27 μm</td>
</tr>
<tr>
<td>5,000</td>
<td>2 μm</td>
<td>5 μm</td>
</tr>
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</table>

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ISOTHERMAL TESTING AT 580°C: substrates

Salts after the test

**Uncoated P91**
Cr: 544 ppm
Fe: 145 ppm
measured by ICP after 2000 h
Cr VI confirmed by spectrophotometry

**IN617**
To be measured

**Uncoated A516**
Fe: 145 ppm

**Aluminized P91**
No metals could be measured

**Cr is dissolved by the salt forming chromates**
ENVIRONMENTAL ISSUES CAUSED BY Cr CONTAINING ALLOYS

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O}^{2-}
\]

\[
\text{Cr}_2\text{O}_3 + 5\text{O}^{2-} \rightarrow 2\text{CrO}_4^{2-}
\]

Basic fluxing mechanism (Rapp, Luthra, Stringer, Petit, etc.)

Cr VI is carcinogenic
Fe Aluminide Coatings
ISOTHERMAL TESTING AT 580° C: Fe aluminide

On P91

1000 h

4000 h

10,000 h

On VM12
ISOTHERMAL TESTING AT 580° C: Fe aluminide on VM12

4,000 h

22 wt.% Al
ISOTHERMAL TESTING AT 580° C: Fe aluminide on P91

10,000 h
ISOTHERMAL TESTING AT 580°C: Fe aluminide on P91

10,000 h

Rich in Al, Fe, Na, O

17 wt.% Al

10 μm

100 μm
CONCLUSIONS

• Ferritic steels can not be used for the heat storage system in CSPs

• Ni base materials behave better but degradation after relatively long exposures may be high

• Aluminide coated ferritic steels can last significantly longer, at lower cost than Ni base materials

• If Cr containing alloys are used, Cr VI will have to be removed from the Solar Salt at the end of its life
Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 686008.

All members of the Metallic Materials Area at INTA for technical support.