Biomass Exacerbated Cyclic Oxidation of Steels in Steam

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Introduction

- Alloys undergo oxidation at high temperature.
  - Multilayered oxides of different compositions form.
  - Modification of the underlying alloy results.
- Rate of oxidation is exacerbated under steam conditions.
- On cooling stresses develop in the oxide layer resulting in loss of the oxide (spallation).
- On reheating oxides continue to reform.
- Load following biomass plants will lead to greater thermal cycling.
Introduction

- Spallation leads to:
  - Damage of components down stream,
  - Blockage of tubes,
  - Tube ruptures,
- Unscheduled / more frequent maintenance shutdowns.
Questions

1. How will the cyclic nature of biomass power plants affect the oxidation behaviour of the heat exchanger tubing?

2. When does spallation become a big enough problem that maintenance is required?
Aims and Objectives

- To investigate the cyclic steam oxidation and spallation behaviour of an austenitic stainless steel currently used as heat exchanger tubing.

- To simulate the effect of the oxidation processes on the degradation of the alloy.
Materials

- Austenitic stainless steel TP347H FG.
  - Grain size = 20 μm
- Composition (wt.%):

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Ni</th>
<th>Cr</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.4</td>
<td>1.48</td>
<td>0.001</td>
<td>0.026</td>
<td>11.34</td>
<td>18.21</td>
<td>0.88</td>
<td>bal</td>
</tr>
</tbody>
</table>

- Commonly used as superheater and reheater tubing in fossil fired power plants.
Sample Preparation

- Samples are sectioned from standard pipe as installed in plant.

- $L_1 = 10 \text{ mm}$; $L_2 = 14 \text{ mm}$; $L_3 = 18 \text{ mm}$; $L_4 = 4.5 \text{ mm}$

- Inner surface is of interest – steam side of power plant.
Experimental Work

- Exposure to steam at 923 K for 50, 100, 300, 500, 750 and 1000 hours.
- Atmospheric pressure.
Spallation

Before spallation. At temperature.
During spallation. On cooling.
After spallation. Room temperature.
Routes to Spallation*

- Two things are necessary to initiate spallation:
  - Decohesion along the spallation interface (delamination)
  - Cracks through the oxide layer to the interface.

Routes to Spallation*

- Route I: Wedging.

\[
\Delta T_W = \sqrt{\frac{\gamma_F}{\xi E_{ox} (\alpha_m - \alpha_{ox})^2 (1 - \nu_{ox})}}
\]

\[
\gamma_F = W^* (\Delta T)^2 (\Delta \alpha)^2 E_{ox} (1 - \nu_{ox})
\]

- Route II: Buckling.

\[
\Delta T_b = \frac{1.22}{(\alpha_m - \alpha_{ox}) (1 - \nu_{ox})^2} \left( \frac{\xi}{R} \right)^2
\]

Eox = Young’s modulus, \( \alpha_m \) and \( \alpha_{ox} \) = thermal expansion coefficients of metal and oxide, \( \nu_{ox} \) = Poisson’s ratio.

\( \Delta T \) = oxidation temperature - event temperature, \( R \) = radius of delamination site, \( W^* \) = strain energy, \( \gamma_F \) = fracture energy, \( \xi \) = oxide thickness.

Spallation Map

- Unstable buckling or wedging
- Wedging
- Stable buckling
- Adherent oxide

ΔT (K)

Spalled haematite thickness, \( \xi_h \) (μm)
Imaging Spall Particles

100 hours, 923 K

500 hours, 923 K
Spalled Oxide Thickness, $\xi$

- Total spalled oxide
- Spalled haematite

Oxidation time (hours) vs. Spalled thickness, $\xi$ ($\mu$m)

Scale: 5 $\mu$m
R and ΔT Measurements

- Synchronised IR and video camera.
- Able to detect delamination and spallation sites.
- Provide localised ΔT and R values.
The Measurements

- Initial local delamination:
  - Detectable with IR camera
  - $T_D = $ temperature at which delamination occurs.

- Complete local spallation:
  - Detectable with video and IR camera
  - $T_{SP} = $ temperature at which spallation occurs.
IR Camera Results

- Images shown are the same sample on cooling after 100 hours in steam at 923 K.
  - Before delamination. \( \Delta T = 398.6 \)
  - At time of delamination. \( \Delta T_D = 405.5 \)
  - At time of spallation. \( \Delta T_{SP} = 508.9 \)
Spallation Map

- Unstable buckling or wedging
- Wedging
- Adherent oxide

\[ \gamma_F = 8.7 \text{ J.m}^{-2} \]

- Stable buckling
- Spalled haematite thickness (\(\mu\)m)
- Delamination
- Spallation
Conclusions

- A unique combination of infrared and video camera techniques has been used to obtain critical data to input into the spallation model.
- Delamination and formation of buckles at oxide interfaces occurs – illustrated by IR camera.
- Spalled oxide thickness measurements have been obtained using high resolution scanning electron microscopy.
- An approach using fracture energy of the oxide has been shown to predict the onset of spallation.
Future Work

- Planned publication for this section of the work.

- Ongoing analysis of the degradation occurring in the alloy due to oxidation processes.

- The effect of thermal cycling.
  - Including accelerated degradation techniques.
Acknowledgements.

BF2RA, EPSRC, Technical support provided by the UoB EM centre, Sumitomo Metal Industries Ltd for alloy, Dr Chris Cooper, Mr Tim Perry.