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London Steel Symposium
Swansea University
Tata Steel

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Industrial Supervisor: Dr Chris Owen

25th Feb 2020
TATA Steel’s Building and Services application; High Frequency Induction Welded Hot-Finished Low Carbon Steel Conveyance Tubes
TATA Steel’s Building and Services application; High Frequency Induction Welded Hot-Finished Low Carbon Steel Conveyance Tubes
High Frequency Induction Welding
Forming Rolls

HFI Welding
The Heat Affected Zone (HAZ)

- Bulk Microstructure ≠ Weld Microstructure
- Structurally weaker along the Weld Line
- More susceptible to Intergranular Corrosion
- Inability to Bend effectively
- Increased Risk of Splitting
- Lower Strength and Toughness Characteristics
How do you fix this HAZ?
Normalisation at \( \sim 900^\circ c \)

30 minute Soak Time
✓ Realign and apply homogeneity to the crystal structure

✓ Relieve the internal stresses applied during tube forming

✓ Increased Toughness and Pressure Integrity
Ah, but we have a problem...
Steel Tubes sent through natural gas furnaces at 950°C

Surface Oxidation
The Pit
Surface Condition

- Hot – Finished HFI Welded
  - Seamless Tubes: 1
  - Cold Formed HFI Welded: 2

[Image of steel tubes]
Design a coating which inhibits scale growth during reheating
Three Key Questions
1. What oxide are we dealing with?

2. How exactly does it grow?

3. Can you prevent its formation?
Oxide Characterisation
~60µm Scale Thickness for SR2 Furnace
625 X SE1 EHT = 20.00 kV I Probe = 750 pA WD = 10.0 mm
Width = 182.9 µm Swansea University College of Eng 17 Apr 2019
Haematite $\text{Fe}_2\text{O}_3$ 1%
Magnetite $\text{Fe}_3\text{O}_4$ 4%
Wustite $\text{FeO}$ 95%

Steel
FFC ‘Cubic Lattice’ Structure
Inverse Spinel Structure
Qualitative methods in oxide phase determination
1. Outline the boundary of oxide phases – not what is present

2. Indicates a phase change has occurred between the oxide layers
Raman Spectroscopy
Laser Source $*h v_0$

Rayleigh Scattering $*h v_0$

Raman Scattering $*h v_0 + \Delta v$
<table>
<thead>
<tr>
<th>Raman Configuration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>531nm</td>
</tr>
<tr>
<td>Power Output</td>
<td>0.013mW</td>
</tr>
<tr>
<td>Exposure time</td>
<td>1s</td>
</tr>
<tr>
<td>Scale Origin</td>
<td>Walking Beam</td>
</tr>
</tbody>
</table>
531nm laser source at the Inner Layer of Scale

Raman Spectral Acquisition of the Inner Wustite Layer
Indicative of Wüstite

“Mechanical properties and phases determination of low carbon steel oxide scales formed at 1200 °C in air”
Zambrano et al 2015.
531nm laser source at the Outer Layer of Scale

Raman Spectral Acquisition of the Interstitial Magnetite Layer
“Mechanical properties and phases determination of low carbon steel oxide scales formed at 1200 °C in air” Zambrano et al 2015.
1. What oxide are we dealing with?

2. How exactly does it grow?

3. Can you prevent its formation?
Oxide Kinetics
Simultaneous Thermal Analysis
TGA + DSC
3mm² Cubic Samples
10% O₂ flow
Thermal Cycle – Set Ramp Rates
Thermogravimetric Analysis
Incremental increase of 50°C

Isothermal Soak at set Temperature for 2 hours

Fixed cooling rate
Steel Grade ‘A,B,C’ Weight % vs Time (min) Thermogravimetric Analysis

Weight % vs Time (min) for Steel Grades A, B, and C at 400°C.
Steel Grade ‘A,B,C’ Weight % vs Time (min) Thermogravimetric Analysis
Steel Grade ‘A,B,C’ Weight % vs Time (min) Thermogravimetric Analysis

- Weight %
- Time (min)
- 550°C
- 500°C
- 450°C
- 400°C
Steel Grade ‘A,B,C’ Weight % vs Time (min) Thermogravimetric Analysis

Weight % vs Time (min)

- 600°C
- 550°C
- 500°C
- 450°C
- 400°C
Hi James,

Looks like we know how our steel grade oxidises!

Is this how we’ll know if a coating has been successful?

Many Thanks,

Chris
No Chris,

I’m sorry. The VOC of the coating will affect the weight percentage.

Not to worry - I have another method which should give us a reduction rate…

Many Thanks,

James
Cross – Sectional Analysis – Advanced Light Microscopy

Quantifying oxide growth through 2D observations.
Atmospheric Furnace

Vary the % of each element in the atmosphere

- Exhaust analysis Probe
- Thermocouple
- Testo 3000
- Gas Mixture Outlet
- Compressed Air
- CO₂
- Testo 3000
- Thermocouple
- Gas Mixture Outlet
- Compressed Air
Flowing at 30 L/min

<table>
<thead>
<tr>
<th>Gas</th>
<th>Carbon Dioxide</th>
<th>Oxygen</th>
<th>Flow Rate L/min</th>
<th>T Stack °C</th>
<th>NO ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>7.5</td>
<td>8</td>
<td>0.98</td>
<td>690</td>
<td>125</td>
</tr>
</tbody>
</table>
Benchmark Thermal Cycle
Thermal Cycle of flow of gas at 21% O₂ 30lpm

- Furnace Opened
- Isothermal Range
- Cool Down
- Furnace Closed

Temperature vs. Time

0 500 1000 1500 2000 2500

Time (s)
<table>
<thead>
<tr>
<th>Sample A</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade</td>
<td>E1</td>
</tr>
<tr>
<td>Max Temp</td>
<td>951°C</td>
</tr>
<tr>
<td>O₂ %</td>
<td>21%</td>
</tr>
<tr>
<td>Flow</td>
<td>30 L/min</td>
</tr>
</tbody>
</table>
Automatic Layer Detection Software

**Sample A**

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**Oxide Layer Thickness**

- Min Layer Thickness: 201.7µm
- Max Layer Thickness: 221.7µm
- Average Oxide Thickness: 214.5 µm ± 6.1µm
Why is this measurement so useful?
Observe the effect on oxide growth due to:

- Reduction in Magnetite Layer
- Variation in Oxide Porosity

Coatings

Atmospheric Conditions
Reduction in oxide thickness due to conditional changes during reheating

Steel Grade: E1
Steel Grade: E41
Steel Grade: E24

240.1 µm Oxide generated
189.7 µm Oxide generated
167.3 µm Oxide generated

8% O2 + 7.5% CO2

198.3 µm Oxide generated with no A1 Coating
38%
127.7 µm Oxide generated with A1 Coating

189.9 µm Oxide generated with no Coating
67%
71.1 µm Oxide generated with Coating X1

204.2 µm Oxide generated with no Coating
71%
59.4 µm Oxide generated with Coating X2

1800s 950 DegC 30 L/Min
1800s 950 DegC 0 L/Min
Programmed Thermal Cycle for Oxidation Kinetic Investigation

- 750°C
- 650°C
- 600°C
- 550°C
- 500°C
- 450°C
- 350°C
- 200°C

Temperature °C vs. Time (s)
1. Accelerated E24 oxidation past 550°C in line with STA Observation

2. Coating properties identical for E1,E41 – adjustment required for E24
1. What oxide are we dealing with?

2. How exactly does it grow?

3. Can you prevent its formation?
Protective Coatings
Active Coating

Oxygen scavenging reaction
Under high temperatures

Passive Coating

Blocks the $O_2$ diffusing to the steel surface by forming an impermeable barrier
Charcoal Solution

Coal Powder + Polyethylene Glycol

Using up Oxygen
Artificially creating a reducing atmosphere
Which would have been used to form scale

\[ C + O_2 = CO_2 \]

However...

\[ 2C + O_2 = 2CO \]  
Insufficient O2 = Carbon Monoxide

\[ S + O_2 = SO_2 \]  
Sulphur Present = Sulphur Dioxide
Passive Coating
Silicates
The Mullite Solution
Aluminium Silicate

Al powder

Al transforms to Liquid Al at 700°C

Al liquid begins to oxidise forming $\text{Al}_2\text{O}_3$

Combines with silica to form Mullite (barrier)

$2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$

Steel
Mullite
Orthorhombic
Crystal Structure
Initial mullite (25µm) Trail against oxide kinetics

Coated/Uncoated E1 Heat Treated Coated/Uncoated
Mullite

What’s the problem?
New Oxide Layer grown after spallation
<table>
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<th>Parameters</th>
<th>Sample</th>
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<tbody>
<tr>
<td>Maximum Temperature</td>
<td>950°C</td>
</tr>
<tr>
<td>Steel Grade</td>
<td>E1</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Coating</td>
<td>Mullite (25 Micron)</td>
</tr>
<tr>
<td>Oxide location</td>
<td>Central</td>
</tr>
</tbody>
</table>
Porosity Issues in pure mullite solutions

Large areas of continuous non – uniform unsintered mullite particles.

Sintered 2SiO2 • 3Al2O3 is causing an unwanted ‘necking’ effect

Reduced necking allows a highly porous structure from which oxygen can permeate to the steel surface

Solution: Form a composite with another (high temperature stable) material to fill/trap the pores
Zirconia Oxide
Mullite Layer

- Zirconia particles are trapped by the porous regions of the mullite during sintering
- Forming a more compact and impermeable layer for O2 prevention
ZrO$_2$ won’t sinter until over 1400°C

- Stable and unreactive
- Not as brittle as Al particle and can be made to a smaller particle size to fill the mullite pores
E1 Uncoated in a Standard Thermal Cycle

Pure Mullite

Zr Mullite Composite

37% Reduction

63% Reduction
Future Work – Descalability of the coatings and their adhesion to scale traits
Improving Surface quality by coating spallation

Reducing the oxide and ripping it away from the steel surface
Conclusions

• Characterisation of the scale generated by the mill using SEM, EDS and Raman Spectroscopy

• Kinetics of the steel grade oxidation performed using STA and further experimentation developed to quantify the reduction in oxide growth

• Initial trialling of mullite solutions aiming to produce a passive barrier layer and reductions of up to 63% observed.
Thank you for listening

Q&A

James Grant