Investigating Links between Problematic Inclusions and EAC Initiation in Pipeline Steels

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Research Objectives

• SCC Initiation
  • Spatially resolve & characterize micro-galvanic activity of major inclusions types
    • potential, current and hydrogen production efficiency – with & without applied stress

• HIC Initiation
  • Spatially resolve & characterize hydrogen charging activity of major inclusion types
    • microvoid formation/growth, trapping efficiency, residual stress – with & without applied stress
Focus on X50-X65 (F+P) Steels

- EAF Steelmaking
- BOF Steelmaking
- Skelp
- Phases
- Texture
- Banding
- Centreline
- Inclusions
- Precipitates
- Standard Service
- Sour Service
- SCC HIC

X65
SCC (Pit) Initiation Studies

- X52 | EAF | Thick Slab | Sour Service
  - Links between inclusion chemistry and pitting corrosion

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
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<tbody>
<tr>
<td>C</td>
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- Microstructure Characterization
  - LOM
  - SEM-EDS
  - AES
  - ASPEX

- Accelerated Pit Initiation
  - Potentiodynamic Polarization
  - Electrolyte Screening
  - Galvanostatic Polarization

- Initiation Site Characterization
  - SEM-EDS
  - TEM-EDS of FIB-Prepared Samples
Typical Shape-Controlled Inclusion
SEM/EDS (2 μA/cm²)
TEM Foil Preparation by FIB
TEM-EDS | Site 1

[Images of various chemical element maps (Ca Ka1, S Ka1, Fe Ka1, O Ka1, Cl Ka1)]
TEM-EDS │ Site 2

Ca Ka1

S Ka1

Fe Ka1

O Ka1

Cl Ka1
Major Findings

• Short-term galvanostatic polarization effective to initiate localized dissolution in and around inclusions

• CaS in sour-service grades particularly problematic due to intrinsic dissolution behavior
  • Dissolved sulphur compounds increase the corrosivity of solution at inclusion/steel interfacial region

• Working theory: encapsulating CaS oxide during steelmaking beneficial inclusion control strategy to mitigate pit initiation
HIC Initiation Studies

Microstructure Characterization
- SEM-EDS
- AES
- Potentiodynamic polarization

Diffusible H Characterization
- H charging in As$_2$O$_3$
- H flux by Hydrosteel Probe (CMAT)

H Embrittlement
- H pre-charging in NH$_4$SCN
- Tensile testing in lab air

H Fracture Characterization
- SEM imaging of fracture surface
- TEM analysis of FIB samples

H Trap Characterization
- H charging in As$_2$O$_3$
- Thermal Desorption Spectroscopy (CMAT)
Pipeline Steel

- EAF | Sour-Service (X60) v. Standard Service (X70)

<table>
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<tr>
<th>Composition (wt.%): X60</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
<th>Ca</th>
<th>S</th>
<th>P</th>
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<tr>
<td>X60</td>
<td>0.026</td>
<td>0.14</td>
<td>1.3</td>
<td>0.066</td>
<td>0.044</td>
<td>0.01</td>
<td>0.003</td>
<td>0.0005</td>
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<table>
<thead>
<tr>
<th>Composition (wt.%): X70</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
<th>Ca</th>
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<td>X70</td>
<td>0.033</td>
<td>0.13</td>
<td>1.57</td>
<td>0.004</td>
<td>0.067</td>
<td>0.016</td>
<td>0.001</td>
<td>0.0039</td>
<td>0.008</td>
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Heterogeneities of interest: inclusions and elemental segregation
ASPEX Results – X60

Average diameter between ~1.5 & 3.5 μm
Hydrogen Permeation Results

X60 (Sour Service)

X70 (Standard Service)
Hydrogen Embrittlement

- ½ depth tensile samples pre-charged at $-10\ \text{mA/cm}^2$ at $85\%$ of $\sigma_y$ in $30\ \text{g/L NaCl} + 5\ \text{g/L NH}_4\text{SCN} + 7.07\ \text{g/L H}_3\text{BO}_3 + 8.27\ \text{g/L Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}$
Potentiodynamic Polarization – X70

- Pre-charged for 24 h in 0.6 M NaCl adjusted with NaOH to pH 10
- Polarized in 0.1 M NaCl + 0.1 M NaHCO₃ + 0.05 M Na₂CO₃ (pH 9.6)
Major Findings

• Ca-treated (sour service) X60 steel exhibits a more uniform H trapping (not shown) and H permeation (shown) response through-thickness than standard service X70 steel.

• Significance variation in H embrittlement extent after pre-charging of both steels – likely related to micro-scale heterogeneities – need to be confirmed.

• Little success thus far in linking H embrittlement susceptibility to anodic and/or cathodic kinetics in a passivating solution.
Model Inclusion Studies

• SCC (Pit) Initiation Experiments
  • Effect of electrolyte (active vs passive corrosion)
  • Effect of chemistry (simple sulphides, nitrides, carbides)
  • Potency ranking of inclusions types

• HIC (Void/Delamination) Experiments
  • Effect of chemistry (simple oxides, sulphides, nitrides, carbides)
  • Hydrogen charging
  • Potency ranking of inclusions types
‘Pit’ Initiation Studies

- Sample Mounting & Surface Preparation
- Light Optical Microscopy
- Optical Profilometry Mapping
- Scanning Kelvin Probe Mapping
- Bulk Immersion
- Visual Inspection
- Scanning Vibrating Probe Mapping
- Corrosion Product Removal
- Optical Profilometry Mapping
Bulk Immersion in NS4 Solution

0 h

Fe
Fe-MnS
Fe-Al₂O₃
Fe-TiN
Fe-TiC

48 h

Fe
Fe-MnS
Fe-Al₂O₃
Fe-TiN
Fe-TiC
De-Scaled Surfaces (After 48 h)
Galvanic Corrosion

Fe-TiC

0 minutes  20 minutes  60 minutes  120 minutes
Optical Profilometry (Fe-TiC)
Scanning Probe Measurements

Fe-Al₂O₃

Fe-TiN

Lab Air

NS4 Solution

Scanning Kelvin Probe

Scanning Vibrating Probe
Major Findings

• Fast (active state) corrosion easily visualized in 48 h bulk immersion in NS4 solution

• Corrosion of Fe-TiC model inclusion sample consistent with galvanic cell activity
  • Needs to be confirmed by scanning Kelvin probe (SKP) and scanning vibrating probe (SVP measurements)

• Corrosion Fe-MnS, Fe-Al$_2$O$_3$ and Fe-TiN consistent with pure iron, indicating little effect of inclusion on active state corrosion
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