Corrosion Resistance of Titanium and Its Alloys in the Chlor Alkali Industry

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Anodic side

2Cl⁻ → Cl₂ + 2e⁻

Cathodic side

2H₂O + 2e⁻ → H₂ + 2OH⁻

H₂

Cl₂ (Moist)

Semi Permeable Membrane

Concentrated Caustic

Lean Caustic Feed

Depleted Brine

Concentrated Brine (NaCl)

Titanium Alloy

Na⁺
Electrolyser Stacks

Electrolyser Stack

Compressive forces

Direction of Current flow

Electrolyser stacks in Parallel
Electrolyser Stacks

Electrolyser Stack

Compressive forces

Direction of Current flow

Electrolyser stacks in Parallel
Electrolyser Stacks

Electrolyser Stack

Compressive forces

Direction of Current flow

Electrolyser stacks in Parallel
Electrolyser Stacks

Electrolyser Stack

Direction of Current flow

Single cell leakage

Electrolyser stacks in Parallel

Compressive forces
Electrolyser Stacks

Electrolyser stack compressive forces

Direction of Current flow

Single cell leakage

Electrolyser stacks in Parallel
Electrolyser Stacks

Electrolyser Stack

Direction of Current flow

Compressive forces

Single cell leakage

Electrolyser stacks in Parallel
Electrolyser Stacks

Electrolyser Stack

Direction of Current flow

Compressive forces

Single cell leakage

Electrolyser stacks in Parallel

PRODUCTION LOSS

Electrolyser Stacks in Parallel
Normal Operating Conditions

• Anolyte Brine pH ~ 4
• Cell Temperature = 88°C
• Voltage across each cell = 3.0V
• Brine concentration ~ 280gpl = 4.486 gm equ. / litre solution
Voltage drop across the Titanium half cell

\[
E_{\text{Theo cl2/pt}} + \eta_a + IR_a = -0.0422 + 0.2208 + 0.20 = 0.412
\]

\[
IR_a = IL\sigma/A = 0.2
\]

\[
E_{\text{Theo cl2/pt}} = 0.05915 \times \log(1/4.786) = -0.04022
\]
E 1. The phase stability diagram of the Ti–H$_2$O system at 25 and 100°C with a titanium ion activity of 0.]
Corrosion Characteristics of Titanium Alloys

- Excellent corrosion resistance.
- Protection afforded by a passive and tenacious oxide film; highly resistant to aggressive chloride ions.

- Group I  CP Ti
- Group II  Low alloy content with Pd/Ru
- Group III  $\alpha$ and Near $\alpha$ Alloys
- Group IV  $\alpha$-$\beta$ Alloys
- Group V  $\beta$ Alloys
Titanium Alloys in Failure Mode

- During operation, titanium alloys are susceptible to failure in an electrolyser cell.

- Failure is in the form of:
  - Pit formation
    - Pin hole gas leakages
    - Cell leakages
  - Catastrophic failure.
Failure Modes: Pit formation

Pit coalescence after CPT: Larger leakages, cells leak of brine

Pin Holes: Cl2 leakage
Objectives

- Determine the best Titanium alloy for Chlorine service.

- Identify failure modes.

- Explore titanium alloy treatment methods.

- To minimize corrosion, recommendations are made in start up and shut down procedures.
Critical Pitting Temperature

Comparison of the two best alloys

CP-Ti: CPT=83°C

Ti-6Al-4V ELI/Ru: CPT=96°C
## Alloy selection

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ti-6Al-4V ELI</th>
<th>Ti-6Al-4V ELI/Ru</th>
<th>Ti 5111</th>
<th>CP-Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl (pH = 4)</td>
<td>98.2</td>
<td>94.1</td>
<td>94.7</td>
<td>83.1</td>
</tr>
<tr>
<td>HCl (pH = 4) + 500 ppm NaCl</td>
<td>99.8</td>
<td>94.1</td>
<td>86.1</td>
<td>87.0</td>
</tr>
<tr>
<td>HCl (pH = 2)</td>
<td>88.2</td>
<td>88.6</td>
<td>95.1</td>
<td>93.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution</th>
<th>No. of peaks</th>
<th>Mean (pA)</th>
<th>S.D. (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti 5111</td>
<td>pH = 4</td>
<td>33</td>
<td>236</td>
<td>355</td>
</tr>
<tr>
<td>CP-Ti</td>
<td>pH = 4</td>
<td>53</td>
<td>103</td>
<td>246</td>
</tr>
<tr>
<td>Ti-6Al-4V ELI</td>
<td>pH = 4</td>
<td>123</td>
<td>193</td>
<td>172</td>
</tr>
<tr>
<td>Ti-6Al-4V ELI/Ru</td>
<td>pH = 4</td>
<td>75</td>
<td>153</td>
<td>147</td>
</tr>
<tr>
<td>Ti 5111</td>
<td>pH = 4 + NaCl</td>
<td>39</td>
<td>596</td>
<td>736</td>
</tr>
<tr>
<td>CP-Ti</td>
<td>pH = 4 + NaCl</td>
<td>57</td>
<td>263</td>
<td>367</td>
</tr>
<tr>
<td>Ti-6Al-4V ELI</td>
<td>pH = 4 + NaCl</td>
<td>119</td>
<td>52</td>
<td>68</td>
</tr>
<tr>
<td>Ti-6Al-4V ELI/Ru</td>
<td>pH = 4 + NaCl</td>
<td>64</td>
<td>614</td>
<td>964</td>
</tr>
<tr>
<td>Ti 5111</td>
<td>pH = 2</td>
<td>61</td>
<td>685</td>
<td>845</td>
</tr>
<tr>
<td>CP-Ti</td>
<td>pH = 2</td>
<td>57</td>
<td>684</td>
<td>744</td>
</tr>
<tr>
<td>Ti-6Al-4V ELI</td>
<td>pH = 2</td>
<td>21</td>
<td>486</td>
<td>409</td>
</tr>
<tr>
<td>Ti-6Al-4V ELI/Ru</td>
<td>pH = 2</td>
<td>55</td>
<td>1429</td>
<td>1540</td>
</tr>
</tbody>
</table>

*Lowest values are highlighted.*
Recommendations: Alloy Selection

Selection was based on the examination of:

- Current transients which were observed with and without presence of NaCl.
- Critical pitting temperature.
- Current transients which is an indication of the stability of the surface.
- CPT, was verified using microscopic observations.
- Selected alloy, Ti-6Al-4V ELI.
Further improvements

Examines further improvements aimed at the corrosion resistance of the alloy.

- Laser surface treatment (LSM)
- Laser gas nitration (LGN)
- Operational changes (start up, shut down)
  - To avoid stress corrosion cracking of the chosen $\alpha$-$\beta$ titanium alloys.
Potentiodynamic scan of a laser treated alloy

**Table 2. Electrochemical corrosion parameters**

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{corr}$ /mV</th>
<th>$I_{corr}$ /µA cm$^{-2}$</th>
<th>Corrosion rate /µm y$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>-0.323</td>
<td>0.371</td>
<td>12.7</td>
</tr>
<tr>
<td>Laser treated</td>
<td>0.085</td>
<td>0.168</td>
<td>5.74</td>
</tr>
</tbody>
</table>
Laser Gas Nitrided Ti6Al4V

XRD spectrum

Surface layer: TiN dendrites

Excellent interfacial bonding

Cumulative weight Loss(mg)

MDER (μm h⁻¹) = \( \frac{\Delta W}{10 \rho \Delta t} \)

\( R_c = (\text{MDER})^{-1} \)

Ti6Al4V

LGN Ti6Al4V

Titanium substrate
Surface appearance of eroded samples after 8 hrs of erosion time

MP Ti  Pit  Laser Gas Nitided Ti
Anodic side

Cathodic side

2Cl⁻ → Cl₂ + 2e⁻

H₂ + 2OH⁻ → H₂O + 2e⁻

2H₂O + 2e⁻ → H₂ + 2OH⁻

Titanium Alloy

Semi Permeable Membrane

Na⁺

Cl₂ (Moist)

Stress Corrosion Cracking
Current direction during normal operation

Cathodic side

H₂

2H₂O + 2e⁻ → H₂ + 2OH⁻

Semi Permeable Membrane

Titanium Alloy

Anodic side

Cl₂ (Moist)

2Cl⁻ → Cl₂ + 2e⁻

Stress Corrosion Cracking
Anodic side

Cl\textsubscript{2} (Moist)

Cathodic side

H\textsubscript{2}

2H\textsubscript{2}O + 2e\textsuperscript{-}

H\textsubscript{2} + 2OH\textsuperscript{-}

2Cl\textsuperscript{-} \rightarrow Cl\textsubscript{2} + 2e\textsuperscript{-}

Semi Permeable Membrane

Titanium Alloy

Stress Corrosion Cracking
Anodic side

Cathodic side

1.5 V

2Cl⁻ → Cl₂ + 2e⁻

Cl₂ (Moist)

H₂ + 2OH⁻

2H₂O + 2e⁻

H₂

Semi Permeable Membrane

Titanium Alloy

Na⁺

Stress Corrosion Cracking
Anodic side

Titanium Alloy

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \]

Cathodic side

\[ \text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^- \]

\[ \text{H}_2 \]

1.5 V

\[ \text{Cl}_2 \text{ (Moist)} \]

Semi Permeable Membrane

Stress Corrosion Cracking
**Stress Corrosion Cracking**

**Anodic side**

- $2Cl^- \rightarrow Cl_2 + 2e^-$

**Cathodic side**

- $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
- $Cl_2$ (Moist)
- $H_2$

**Semi Permeable Membrane**

**Titanium Alloy**

1.5 V
Stress Corrosion Cracking

Cathodic side

2H₂O → 2H₂ + 2OH⁻

H₂ + 2OH⁻ → Cl⁻ → Cl₂ + 2e⁻

Anodic side

2Cl⁻ → Cl₂ + 2e⁻

Polarization Current during plant trip

1.5 V

Semi Permeable Membrane

Titanium Alloy
Stress: Where does it come from

Electrolyser Stack

Direction of Current flow

Compressive forces

Weight of Caustic

Weight of Brine
Ductility of Ti-6Al-4V (an α-β-type titanium alloy) is drastically reduced when hydrogen content > 2000ppm.

Titanium alloys can absorb hydrogen when they are charged at cathodic potentials.

Hydrides form when hydrogen absorption reaches critical level (2000ppm).

Due to the preferential attack of hydrogen along the grain α boundaries, the use of α-β titanium alloys is recommended.
Recommendations to avoid SCC

After plant trip / shut down

• Immediately shut down the brine heat exchangers

• Increase brine flow rate to maximum to cool down the cells(below 80°C).

• 80°C is critical temperature for the evolution of atomic hydrogen.

• Care should be taken that the reverse potential does not go over 0.82V(evolution potential of H₂ on Ti).
Recommendations

• To prevent SCC, the reversecurrent should be controlled to strict tolerances (to avoid exceeding 0.82V over potential).

• As the transients and peaks for Ti-6Al-4V ELI increased at a higher(basic) pH, cells should be drained immediately after shut down.
  – To prevent migration of the caustic from cathodic side to the anodic side.
Recommendations (cont’d)

• Due to the preferential attack of hydrogen along the grain $\alpha$ boundaries, the use of $\alpha$-$\beta$ titanium alloys should be explored.

• The use of Pd on the $\alpha$-$\beta$ titanium alloys is recommended.

• Although, the addition of highly reactive Pd seems counter intuitive, it speeds up formation of surface oxide layer.

• Because higher concentrations of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ ions accelerate corrosion, the quality of brine in the clarifier and ion exchange column should be lowered.
Recommendations (cont’d)

- Avoid Fe Surface contamination in temperatures above 77°C.
  - Clean Ti surface by immersion in 35% HNO₃ - 5% HF solution for 2-5mins followed by a water rinse.
Thank you

Questions?