adding STAINLESS quality to life

make sure it’s STAINLESS

your future in STAINLESS
Stainless Steels for Hot Water Tanks
Hot Water Tanks

* Columbus Stainless
  - History
  - Processes

* Material Selection for hot water tanks
  Austenitic, ferritic and duplex stainless steels

* History of Duplexes
  - Around the world
  - Columbus Stainless

* Duplexes for hot water tanks
  - Laboratory testing
  - Conclusions
History of Columbus Stainless

1966  First stainless produced in Middelburg, part of Rand Mines Group
1979-1981 Expansion to 150 000 tons/year
1991  Columbus Joint Venture formed (IDC, Highveld Steel & Vanadium, Samancor)
1992-1995 Expansion to 500 000 tonnes/year
2002  Acerinox acquired 64% of Columbus Stainless
2002-2004 Investment plans implemented and achieved 720 000 tons 2004
2005  Acerinox acquired Highveld Steel & Vanadium’s 12% shareholding in Columbus Stainless
2011 → Investment to improve quality and flexibility
Hot Water Tanks

*Historically*

- **316L or 304L used**
  - Stress Corrosion Cracking
- **444 used extensively in Japan and Scandinavia**
  - Fabrication difficulties
- **441 used in South Africa**
  - Pitting if fabrication and design substandard
  - Fabrication difficulties
- **3CR12 used in South Africa**
  - Pitting if fabrication and design substandard
  - Weld HAZs tend to pit
Hot Water Tanks

* Material Selection
  - Corrosion resistance
  - Formability
  - Weldability
  - Strength
Hot Water Tanks

* Material Selection
  • Corrosion resistance
    ➢ Stress Corrosion Cracking
Stress Corrosion Cracking

Susceptibility to Chloride Stress Corrosion Cracking
Boiling 42\% \text{MgCl}_2 \text{ Test}
Hot Water Tanks

Material Selection

- Corrosion resistance
  - Stress Corrosion Cracking
    - Austenitics are prone
    - Ferritics and duplexes are resistant
Hot Water Tanks

* Material Selection
  
  • Corrosion resistance
    - Stress Corrosion Cracking
    - Pitting Resistance
**Pitting Resistance**

*PRE to Predict Pitting Resistance*

- **PREcs** = $1.1\text{Cr} + 2.2\text{Mo} + 24\text{N} - 1.5\text{Mn} + 0.25\text{Ni}$
  - 304L or 2001, 2101, 441, 434 and 436
  - 316L or 2304, 444
  - 2205 much better than 316L

- Choose suitable stainless steel based on
  - Environment (water quality, chlorides and temperature)
  - Fabrication practices
Hot Water Tanks

Material Selection

- Corrosion resistance
- Formability
  - Austenitics = 40% elongation, Rm – Rp = 320MPa
  - Duplex = 25% elongation, Rm – Rp = 250MPa
  - Ferritics = 20% elongation, Rm – Rp = 200MPa
Hot Water Tanks

Material Selection

- Corrosion resistance
- Formability
- Weldability
  - Austenitics – no limitations
    - Tough welds
  - Duplex – controlled heat input, use filler and N shielding
    - Tough welds
  - Ferritics – low heat input, thin gauges,
    - Brittle welds
Hot Water Tanks

* Material Selection
  - Corrosion resistance
  - Formability
  - Weldability
  - Strength
    - Austenitics – 250MPa
    - Duplexes – 500MPa
    - Ferritics – 250MPa
Hot Water Tanks

Material Selection Conclusion

- Duplexes are material of choice
- Best combination of properties
- Choose duplex to suit environment
History of Duplexes

* First duplex in 1929 in Sweden
  - Type 329 developed after 1945

* Patent granted in France in 1935
  - Uranus 50 and became 2404

* Second generation duplexes in 1980s
  - 2205 (PRE 35) – 50% of duplex use
  - Lean duplexes such as 2304 and 2001 (PRE<30)
    - 2304 was first and most well known lean duplex
    - 2001 Armco patent in 1988 for automotive applications
    - 2101 Outokumpu patent in 2002
  - Super duplexes (PRE>40)
Columbus Duplexes

* First produced duplex in 1980s
  - SAF 2205 under license from Sandvik

* Lean Duplexes
  - R&D started in 1990
    - 160 lab heats, hot rolled and annealed plates
    - Doctoral thesis in 1995
    - Alloy same as 2101 without 1% nickel
      - Patent
      - Production
      - Prototype trials – mining industry in South Africa
Columbus Duplexes
Columbus Duplexes

* First produced duplex in 1980s
  - SAF 2205 under license from Sandvik

* Lean Duplexes
  - R&D started in 1990
    - 160 lab heats, hot rolled and annealed plates
    - Doctoral thesis in 1995
      - Alloy same as 2101 without 1% nickel
  - Production of tried and tested grades in 2005
    - Already in all relevant specifications
    - Already have applications history
    - Successfully produced around the world
Rationale for Columbus duplex range

- 2205 as this is 50% of the duplex market
- 2304 as 316 equivalent
- 2001 as 304 equivalent
* What is 2001?

- Patented in the USA in 1988 by Armco
- Marketed as Nitronic 19D
  - Good toughness
  - Good ductility
  - Good corrosion resistance
  - Good SCC resistance
  - Strength
  - Good forming and drawing characteristics
  - Ease of welding
* What is 2001?

- Patented in the USA in 1988 by Armco
- Marketed as Nitronic 19D
- Developed for automotive industry
  - Automotive modular frame
- Major application undersea oil umbilical tubing
Hot Water Tanks

* Extensive Lab Benchmark Testing
  - Columbus Metallurgical Laboratory
  - Acerinox Europa R&D+I Laboratories
  - Mintek Research Laboratories

* Columbus Duplexes for Hot Water Tanks
  - Extensive fabrication record
  - Hot water tank application history
Material Selection for HWT

- Standard tests cannot predict fitness for purpose
  - Must replicate real life
    - Immersion testing
      - 6% FeCl₃ (ASTM G48, practice A) at 18°C
      - Reducing environment (stagnant, silt, scale)
    - Critical Pitting Temperature
      - 3.5% FeCl₃
      - 250ppm chlorides
    - Cyclic potentiodynamic polarization (CPP)
      - 3.5% NaCl at 30°C – PRE vs. PREcs
      - Potable water with 250ppm chlorides at 65°C
    - Salt Spray
      - 5% NaCl (ASTM G85) – fabrication effects
Material Selection for HWT

- Standard tests cannot predict fitness for purpose
  - Must replicate real life
    - Immersion testing
      - 6% FeCl$_3$ (ASTM G48, practice A) at 18°C
Material Selection for HWT

* 6% FeCl₃ (ASTM G48, A) at 18°C
  • To test pitting and crevice corrosion
    - University of Sheffield
    - Full results not available
Material Selection for HWT

- Standard tests cannot predict fitness for purpose
  - Must replicate real life
    - Immersion testing
      - 6% FeCl₃ (ASTM G48, practice A) at 18°C
      - Reducing environment (stagnant, silt, scale)
Material Selection for HWT

Corrosion Resistance in reducing acids

• To test stability of passive layer
  ➢ Immersion weight loss in sulfuric acid
  ➢ Stability important
    ▪ Deaerated or stagnant conditions
    ▪ Silt deposits
    ▪ Scaled tanks
Material Selection

* Sulfuric acid at room temperature

- 2001 similar to 316
- 2001 iso-corrosion curve double 2101 at 20°C
Material Selection for HWT

- Standard tests cannot predict fitness for purpose
  - Must replicate real life
    - Immersion testing
      - 6% FeCl₃ (ASTM G48, practice A) at 18°C
      - Reducing environment (stagnant, silt, scale)
    - Critical Pitting Temperature
      - 3.5% FeCl₃
      - 250ppm chlorides
Water Corrosion

2001, 2101, 444 in 250ppm chlorides

- Electrochemical pitting scans (CPT)
  - 300mV (potable water)
    - All had CPT > 80°C
  - 700mV (chlorinated seawater)
    - 444 = 38°C
    - S32001 = 34°C
    - S32101 = 44°C
Material Selection for HWT

- Standard tests cannot predict fitness for purpose
  - Must replicate real life
    - Immersion testing
      - 6% FeCl$_3$ (ASTM G48, practice A) at 18°C
      - Reducing environment (stagnant, silt, scale)
    - Critical Pitting Temperature
      - 3.5% FeCl$_3$
      - 250ppm chlorides
    - Cyclic potentiodynamic polarization (CPP)
      - 3.5% NaCl at 30°C – PRE vs. PREcs
Pitting Resistance

Pitting Potential in 3.5% NaCl at 30°C

Copyright vests in this presentation and is the property of Columbus Stainless (Pty) Ltd. This presentation is confidential and this confidentiality must be respected.
Pitting Resistance

Epit vs PRE

\[ R^2 = 0.9176 \]

\[ \text{PRE} = \text{Cr} + 3.3\text{Mo} + 16\text{N} \]
Pitting Resistance

Epit vs PRE

R² = 0.9923

PRE = 1.1Cr + 2.2Mo + 24N - 1.5Mn + 0.25Ni
* PRE to Predict Pitting Resistance

- **PRE**
  - **PRE** = Cr + 3.3Mo + 16N
    - Ignores beneficial effect of nickel
    - Ignores detrimental effect of manganese
  - **PREcs** = 1.1Cr + 2.2Mo + 24N – 1.5Mn + 0.25Ni
    - Ni increases passive layer Cr:Fe ratio
    - Mn decreases pit initiation (MnS inclusions)
      - High Mn duplexes drops PRE by 4
Pitting Resistance

\[
\text{PRE} = \text{Cr} + 3.3\text{Mo} + 16\text{N}
\]

\[
\text{PREcs} = 1.1\text{Cr} + 2.2\text{Mo} + 24\text{N} - 1.5\text{Mn} + 0.25\text{Ni}
\]
Material Selection

* PREcs

- Literature
  - Difference of 2 is considered insignificant
- Only useful as alloy ranking
  - Can not predict relative performance in specific conditions
    - 304, 441, 436, 2101 and 2001 similar
    - 2304 better than 316, same as 316 (2.5%Mo)
    - 2205 exceptionally good PRE
Material Selection for HWT

- Standard tests cannot predict fitness for purpose
  - Must replicate real life
    - Immersion testing
      - 6% FeCl₃ (ASTM G48, practice A) at 18°C
      - Reducing environment (stagnant, silt, scale)
    - Critical Pitting Temperature
      - 3.5% FeCl₃
      - 250ppm chlorides
    - Cyclic potentiodynamic polarization (CPP)
      - 3.5% NaCl at 30°C – PRE vs. PREcs
      - Potable water with 250ppm chlorides at 65°C
Water Corrosion

*S32001, S32101, 444*

- Cyclic polarisation scans
  - Maximum operating conditions for hot water tank
    - 65°C
    - 250ppm chlorides
Cyclic Polarisation Scan

250ppm Chlorides at 65°C

- Epit
- Ecrv
- Epitprot
- E crvprot

mV relative to Ecorr

S32001  S32101  S44400

Copyright vests in this presentation and is the property of Columbus Stainless (Pty) Ltd. This presentation is confidential and this confidentiality must be respected.
Water Corrosion

* Cyclic Polarisation Scans (250ppm Cl, 65°C)

- All three alloys are unlikely to pit or crevice
- 2001 and 2101 versus 444
  - Large hysteresis loop
  - Repassivation is difficult
  - All had low corrosion rates of 0.002mm/yr
Material Selection for HWT

- Standard tests cannot predict fitness for purpose
  - Must replicate real life
    - Immersion testing
      - 6% FeCl₃ (ASTM G48, practice A) at 18°C
      - Reducing environment (stagnant, silt, scale)
    - Critical Pitting Temperature
      - 3.5% FeCl₃
      - 250ppm chlorides
    - Cyclic potentiodynamic polarization (CPP)
      - 3.5% NaCl at 30°C – PRE vs. PREcs
      - Potable water with 250ppm chlorides at 65°C
    - Salt Spray
      - 5% NaCl (ASTM G85) – fabrication effects
Water Corrosion

*Salt Spray S32001, S32101*

- Fabricated water tanks subjected to salt spray
  - No significant differences
  - Corrosion occurred at
    - Welds
    - Cut edges
    - Crevices
Water Corrosion

Salt Spray S32001, S32101

• Good fabrication critical
  ➢ Restore passive layer by Pickling and passivation
    • Welds and weld discolouration
    • Grinding or polishing
    • Exposed cut edges
  ➢ Ensure good design
    • Eliminate crevices
    • Eliminate stagnant areas
• Fabrication more important than steel difference
Water Corrosion

* Not just chlorides and temperature

- Corrosivity also determined by
  - pH
  - Sulphates
  - Alkalinity
  - Hardness
  - Conductivity
  - Total dissolved solids
  - Ionic strength
3CR12 Pitting Resistance

Sulphates (ppm)
- 3000
- 2500
- 2000
- 1500
- 1000
- 500

Chlorides (ppm)
- 2000
- 1500
- 1000
- 500
- 100

Nitrates (ppm)
- 1500
- 1000
- 500
- 100
- 10

Copyright vests in this presentation and is the property of Columbus Stainless (Pty) Ltd. This presentation is confidential and this confidentiality must be respected.
## Potable Water Corrosion (65°C)

<table>
<thead>
<tr>
<th>Max Cl⁻ (ppm)</th>
<th>Austenitic</th>
<th>Ferritic</th>
<th>Duplex</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CONs</strong></td>
<td><strong>SCC Strength</strong></td>
<td><strong>Fabrication Strength</strong></td>
<td></td>
</tr>
<tr>
<td><strong>PROs</strong></td>
<td><strong>Fabrication</strong></td>
<td><strong>SCC</strong></td>
<td><strong>SCC Strength</strong></td>
</tr>
<tr>
<td>50ppm</td>
<td></td>
<td>3CR12</td>
<td></td>
</tr>
<tr>
<td>150ppm</td>
<td>202</td>
<td>430, 439</td>
<td></td>
</tr>
<tr>
<td>300ppm</td>
<td>304L</td>
<td>441, 434, 436</td>
<td>2101, 2001</td>
</tr>
<tr>
<td>700ppm</td>
<td>316L</td>
<td>444</td>
<td></td>
</tr>
<tr>
<td>1 250ppm</td>
<td>316L (2.5Mo)</td>
<td></td>
<td>2304</td>
</tr>
<tr>
<td>5 000ppm</td>
<td></td>
<td></td>
<td>2205</td>
</tr>
</tbody>
</table>
Stainless Steels for Hot Water Tanks

* Duplex is the Obvious Choice
  - Strength, SCC resistance, fabricability
  - Which type
    - Operating conditions?
      - 2001 vs. 2304 vs. 2205
    - How good is the fabrication?
      - Poor fabrication demands 2304 or 2205
    - Ease of forming?
      - 2001, 2304, 2205 easier, less springback and memory than 2101
        - Due to lower nitrogen content gives less work hardening

* 2001, 2304 or 2205?
Disclaimer

“The material contained in this presentation has been designed as a guide for customers of Columbus Stainless. However, the material contained herein is not intended as a substitute for any person’s procedures and should not be used or relied upon for any specific or general application without first obtaining competent advice. Furthermore, Columbus Stainless disclaims any responsibility for the suitability of the steel in question for any particular purpose or for the performance or selection of the steel, unless Columbus Stainless specifically and expressly authorises the purpose or selection. The material contained in this presentation does not purport to be a comprehensive or exhaustive statement of all relevant material applicable to special and general steel products and no representation, condition or warranty, expressed or implied, is given by Columbus Stainless as to the accuracy or completeness of this presentation and, so far as is permitted by law, Columbus Stainless, its members, staff and consultants disclaim any duty of care in relation to the preparation of this presentation and the information that it contains and shall not be liable for any direct, indirect or consequential loss, damage or injury suffered by any person howsoever caused as a result of relying on any statement or omission in this presentation and any such liability is expressly disclaimed. (Columbus Stainless shall not be liable in the event of a breakdown, malfunction or failure occurring due to faulty design, material or workmanship of the steel, whether it is based on the information contained herein or not and shall not under any circumstances be liable for any damages, either direct or indirect, particularly consequential damages, including but not limited to damages for loss of profits)”. 