How do you make Special Steel plates?
- Mill facilities include Electric Arc Furnace melting technology as well as Special Ladle Vacuum Refining.
- Larger than standard processing and heat treatment capabilities.
- Project follow-up teams, technical support, dedicated R&D

Some steps in steelmaking
- Metal cutting with oxygen torch
- Beginning of hot-rolling operations at 1200°C
- A 200T ladle during casting operations
Steels for Special Structural Applications

- Racks for offshore industry
- Cryogenic tank

Stainless Steels

- Shipbuilding
- Gas-cleaning
- Chemical & Petrochemical Industries

Specialty Steels

- Wear resistance
- Mining, Public works...
- Cutting, Automotive market
- Molds
- ... civil and military protection
Areas and Devices subjected to severe abrasion and wear

A Shovels (excavators) ⇒ Buckets
B Trucks ⇒ Cargo Body
C Primary Crusher ⇒ Wear parts
D Storage Silo ⇒ Outlet Hopper, Chutes
E Rotating Drum ⇒ Drilled Screen

In the Rock and Mineral processing industry the most common wear resistant products are Conventional Water Quenched Steels

- 400 HB
- 450 HB
- 500 HB

Hardness (Water Quenching) ➔ Wear Resistance
It is necessary to specify more than just the hardness, the wear resistance is:

- Hardness
- Homogeneous hardness
- Toughness
- Microstructure (fine & homogeneous)
- Heat resistance
- Corrosion resistance

Abrasion Parameters?

In the Oil Sands processing industry, the main abrasion parameters which have to be considered are:

- IMPACT (High energy)
- SLIDING (High pressure)
- Presence of CORROSION (sulfur + atmospheric conditions)

Required for wear resistant steels?

- Hardness
- Homogeneous hardness
- Toughness (crack resistance)
- Moderate corrosion resistance
Wear Resistant Steels

**CONVENTIONAL WAY** (WQ, Steel)
- Conventional Analysis (C, Mn, B)
- Water Quench
- Hardness

**ALTERNATIVE CONCEPT**
- Adjustable Analysis (C, Mn, B) + (Cr, Mo, Ni, Ti)
- Controlled Cooling Rate
- Wear resistance
- High workability
- Heat resistance
- Corrosion resistance

**PASSIVE Steel**

**REACTIVE Steel**

(\textsuperscript{V} \textvisiblespace) Varies according to thickness

---

**Alternative Solution**

**TRIP Steel**
- Hardness (Oil Quenching)
- Reactive surface (retained \( \gamma \))
- Trip effect (retained \( \gamma \))
- Micro carbides (Cr, Mo, Ti)

**WEAR RESISTANCE**

---

**Reactive surface**

- TRIP steel 500HB
- Wear resistance
- Hardness
- Hardening effect
- Micro Carbides (Cr, Mo, Ti)

- WQ 500 HB *
- Wear resistance
- Hardness

\textsuperscript{*} WQ = Water Quench

---

---
**Reactive surface**

Optimal combination of Composition & Heat Treatment
(Surface hardening on a TRIP steel 500 HB sample exposed to an abrasive service)

- Superficial work hardening: +78HV
- Affected thickness: 300µm

**Microstructure**

**WATER QUENCHED**
- Martensite
- Lamellar structure (brittle)
- No Micro Carbides

**TRIP steel**
- Martensite - Bainite
- Retained Austenite
- Fine structure
- Micro Carbides (Cr, Mo, Ti)

**Consistent Hardness**

- Homogeneous Hardness
  - Homogenous performance
  - Wear rate
  - Machinability

- THK (mm)
- TVH
- WQ 400 HB
Heat Resistance

High resistance to softening during processing

Heating 500°C + Air cooling (holding time: 1 hour)

WQ = Water Quench

Oxy-cutting (Softening effect)

Hardness profile of the Heat Affected Zone

Transition curve of TRIP steel 500 HB

Transition curve of WQ 500 HB steel
Lab Tests with wet COAL

Test description: "stirring machine" which creates conditions of sliding abrasion mixed with impact (close to field conditions)

Test description: a specimen of the steel is rotated (600 rpm) in the abrasive grit. The abrasive wear is quantified by the weight loss of the sample after a given number of rotation sequences.

Abrasive grit: can be adapted to an application, by selecting the particle size, 4-9mm for typical coal provided by a coal mine.

Results are expressed in wear index: \[ \frac{W(t) - W_0}{W_0} \times 10^6 \]

\( W(t) \): weight loss at time t
\( W_0 \): initial sample weight

A higher wear index corresponds to a higher wear rate.

Behavior in wet coal (coal +20wgt % water)

TRIP steels show a good wear resistance in the wet coal media used for lab testing.

Behavior in wet coal (coal +20 wgt % water)

Wear life in wet coal (lab tests)

- TRIP steel (510HB)
- TRIP steel (400HB)
- WQ 500 HB
- WQ 450 HB
- Reference WQ 400 HB

Wear life in wet coal (lab tests)

- TRIP steel (510HB)
- TRIP steel (400HB)
- WQ 500 HB
- WQ 450 HB
- Reference WQ 400 HB
**WQ Concept**

- **Traditional route**
  - Basic Composition (C,Mn,B)
  - Water Quench
  - Martensitic structure (hardness only)
  - Wear resistance
  - Workability (gives good results for common applications)

- **TRIP Concept**
  - **Alternative Concept**
    - Specific Composition
    - Controlled Cooling
      - Micro carbides (Cr,Mo,Ti)
      - Trip effect
      - Perfect Balance
      - High wear life
      - Improved workability (answer for specific applications)

**Mining - typical applications of TRIP steels**

- Shovels
- Buckets
- Wear plates
- Crushers
- TRIP (field test on separator)

**Slurry pipes / hydrotransport**

- Materials for abrasion and corrosion combined
  - The wear mechanism is much more linked to corrosion than abrasion: it is the "rust" particles that are eroded away.
  - Strong, easily processible: stainless steels have a good behaviour

<table>
<thead>
<tr>
<th>steel type</th>
<th>typical abrasion life span</th>
<th>typical minimum temperature</th>
<th>behaviour in low pH, sulfur compounds, salts…</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;X60&quot;</td>
<td>1</td>
<td>depends on steel</td>
<td>will rust</td>
</tr>
<tr>
<td>TRIP</td>
<td>2-3</td>
<td>-20°C</td>
<td>will rust</td>
</tr>
<tr>
<td>duplex 2306</td>
<td>5-15</td>
<td>-40°C</td>
<td>fair</td>
</tr>
</tbody>
</table>

**Schematic of wear + corrosion test results**

- Under field testing
- Suggested next step
What are Duplex Stainless Steels?

- A family of stainless steels whose:
  - structures are approximately 50/50 austenite and ferrite
  - physical properties are a combination of the ferritic and the austenitic grades

Chemistry of Duplex SS

<table>
<thead>
<tr>
<th>Name</th>
<th>UNS No.</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>2304</td>
<td>S32304</td>
<td>.03</td>
<td>23</td>
<td>4</td>
<td>0.5</td>
<td>.12</td>
<td></td>
</tr>
<tr>
<td>2205</td>
<td>S31803</td>
<td>.3</td>
<td>21.8</td>
<td>5</td>
<td>2.8</td>
<td>.12</td>
<td></td>
</tr>
<tr>
<td>2205</td>
<td>S32205</td>
<td>.03</td>
<td>22.5</td>
<td>5</td>
<td>3.2</td>
<td>.16</td>
<td></td>
</tr>
<tr>
<td>2507</td>
<td>S32750</td>
<td>.03</td>
<td>25</td>
<td>7</td>
<td>4.0</td>
<td>.28</td>
<td>.5</td>
</tr>
<tr>
<td>255</td>
<td>S32550</td>
<td>.03</td>
<td>25.5</td>
<td>5.5</td>
<td>3.4</td>
<td>.20</td>
<td>2.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHASE</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>% VOLUME</th>
</tr>
</thead>
<tbody>
<tr>
<td>FERRITE</td>
<td>0.015</td>
<td>0.03</td>
<td>24.5</td>
<td>4.5</td>
<td>3.8</td>
<td>50 %</td>
</tr>
<tr>
<td>AUSTENITE</td>
<td>0.025</td>
<td>0.30</td>
<td>20.5</td>
<td>7.5</td>
<td>2.6</td>
<td>50 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2304</td>
<td>0.02</td>
<td>0.17</td>
<td>22.5</td>
<td>6</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>
General Corrosion
• Similar to relative austenitic alloys.
  (2304 is similar to 304 & 316)
• General corrosion resistance can vary greatly with changes in concentration, pH, temperature and impurities. It is important to discuss these variables for any application!

Duplex vs. Austenitic
• Duplex Grades
  • 304L
  • 2304
  • 316L
  • 317L
  • 317LMN
  • 2205
  • 255 / 2507
• Austenitic Grades
  • 316L
  • 317L
  • 904L
• 6Mo Grades
  (increased resistance)

Localized Corrosion
• Pitting / Crevice
• \( \text{PREN} = \text{Cr} + 3.3\text{Mo} + 16\text{N} \)

<table>
<thead>
<tr>
<th>Grade</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>19</td>
</tr>
<tr>
<td>316L</td>
<td>24</td>
</tr>
<tr>
<td>2304</td>
<td>25</td>
</tr>
<tr>
<td>317L</td>
<td>30</td>
</tr>
<tr>
<td>317LMN</td>
<td>33</td>
</tr>
<tr>
<td>2205(532205)</td>
<td>35</td>
</tr>
<tr>
<td>904L</td>
<td>35</td>
</tr>
<tr>
<td>255</td>
<td>42</td>
</tr>
<tr>
<td>2507</td>
<td>43</td>
</tr>
<tr>
<td>6Mo Grades</td>
<td>45</td>
</tr>
</tbody>
</table>
Chloride Stress Corrosion Cracking

- The greatest advantage for duplex stainless steels is their improved resistance to CSCC when compared to the austenitic grades.

- Only the 25% Nickel grades have similar CSCC resistance.

Mechanical Properties

- Duplex Stainless Steels have roughly twice the yield strength of their counterpart austenitic grades.

- This allows equipment designers to use thinner gauge material for vessel construction!
### Room Temperature Strength

<table>
<thead>
<tr>
<th>Grade</th>
<th>Min Tensile (KSI)</th>
<th>Min Yield (KSI)</th>
<th>%Elong.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2304</td>
<td>87</td>
<td>58</td>
<td>25</td>
</tr>
<tr>
<td>2205</td>
<td>95</td>
<td>65</td>
<td>25</td>
</tr>
<tr>
<td>2507</td>
<td>116</td>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>255</td>
<td>110</td>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>304</td>
<td>70</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>316L</td>
<td>70</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>317LMN</td>
<td>80</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>6Mo</td>
<td>94</td>
<td>43</td>
<td>35</td>
</tr>
</tbody>
</table>

### ASME (allowable stress in KSI)

<table>
<thead>
<tr>
<th>Grade</th>
<th>@100F</th>
<th>200F</th>
<th>300F</th>
<th>400F</th>
<th>500F</th>
<th>600F</th>
</tr>
</thead>
<tbody>
<tr>
<td>2304</td>
<td>24.9</td>
<td>24.0</td>
<td>22.5</td>
<td>21.7</td>
<td>21.3</td>
<td>21.0</td>
</tr>
<tr>
<td>2205</td>
<td>25.7</td>
<td>25.7</td>
<td>24.8</td>
<td>23.9</td>
<td>23.3</td>
<td>23.1</td>
</tr>
<tr>
<td>2507</td>
<td>33.1</td>
<td>33.0</td>
<td>31.2</td>
<td>30.1</td>
<td>29.6</td>
<td>29.4</td>
</tr>
<tr>
<td>255</td>
<td>31.4</td>
<td>31.3</td>
<td>29.5</td>
<td>28.6</td>
<td>28.2</td>
<td>--</td>
</tr>
<tr>
<td>316L/316L</td>
<td>20.0</td>
<td>17.3</td>
<td>15.6</td>
<td>14.3</td>
<td>13.3</td>
<td>12.6</td>
</tr>
<tr>
<td>316L</td>
<td>16.7</td>
<td>14.2</td>
<td>12.7</td>
<td>11.7</td>
<td>10.9</td>
<td>10.4</td>
</tr>
<tr>
<td>317LMN</td>
<td>20.5</td>
<td>18.9</td>
<td>16.7</td>
<td>15.6</td>
<td>15.1</td>
<td>--</td>
</tr>
<tr>
<td>6Mo</td>
<td>24.9</td>
<td>23.2</td>
<td>21.3</td>
<td>19.8</td>
<td>18.3</td>
<td>17.3</td>
</tr>
</tbody>
</table>

### Hardness

- High hardness provides better wear resistance in abrasive environments.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Max. Hardness (BHN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>215</td>
</tr>
<tr>
<td>316L</td>
<td>217</td>
</tr>
<tr>
<td>317L</td>
<td>217</td>
</tr>
<tr>
<td>317LMN</td>
<td>223</td>
</tr>
<tr>
<td>904L</td>
<td>220</td>
</tr>
<tr>
<td>6Mo</td>
<td>240</td>
</tr>
<tr>
<td>2304</td>
<td>290</td>
</tr>
<tr>
<td>2205</td>
<td>293</td>
</tr>
<tr>
<td>255</td>
<td>302</td>
</tr>
<tr>
<td>2507</td>
<td>310</td>
</tr>
</tbody>
</table>
### Erosion-Corrosion by Solid Particles

<table>
<thead>
<tr>
<th>Materials</th>
<th>Heat Treatment</th>
<th>Testing Conditions (linear velocity: 1.5 m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water 30% H2O (2.4 g/l NaCl)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetic Acid 0.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WL, mg (8h)</td>
</tr>
<tr>
<td>2011</td>
<td>Annealed</td>
<td>4</td>
</tr>
<tr>
<td>304</td>
<td>Annealed</td>
<td>0</td>
</tr>
<tr>
<td>304L</td>
<td>Annealed</td>
<td>0</td>
</tr>
<tr>
<td>2205</td>
<td>Annealed</td>
<td>0</td>
</tr>
<tr>
<td>2304 DUPLEX</td>
<td>Improved Abrasion Corrosion Resistance</td>
<td></td>
</tr>
</tbody>
</table>
- Duplex 2304 has improved corrosion resistance properties when considering aqueous solutions containing chloride ions and/or abrasive particles (SiO2, sand...)

### Effect of Erosion by Solid Particles

200 ppm Cl-, 20°C. Solid particles: 300 microns, 100 g/l
Thermal Expansion (°F x 10^-4)

<table>
<thead>
<tr>
<th>Grade</th>
<th>@212°F</th>
<th>392°F</th>
<th>572°F</th>
<th>754°F</th>
<th>932°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C- Steel</td>
<td>6.70</td>
<td>7.22</td>
<td>--</td>
<td>7.78</td>
<td>--</td>
</tr>
<tr>
<td>2304</td>
<td>7.22</td>
<td>7.50</td>
<td>7.78</td>
<td>8.06</td>
<td>8.33</td>
</tr>
<tr>
<td>2205</td>
<td>7.22</td>
<td>7.50</td>
<td>7.78</td>
<td>8.06</td>
<td>8.33</td>
</tr>
<tr>
<td>2507</td>
<td>7.22</td>
<td>7.50</td>
<td>7.78</td>
<td>8.06</td>
<td>8.33</td>
</tr>
<tr>
<td>255</td>
<td>6.72</td>
<td>7.00</td>
<td>7.22</td>
<td>7.39</td>
<td>7.56</td>
</tr>
<tr>
<td>304L</td>
<td>9.10</td>
<td>9.40</td>
<td>9.60</td>
<td>9.80</td>
<td>10.00</td>
</tr>
</tbody>
</table>

Heat Transfer

- Provides a 5% advantage compared to austenitic grades.
- This advantage is increased when design strength is used to decrease wall thickness!

FATIGUE - CORROSION RESISTANCE

Fatigue and fatigue corrosion resistance of stainless steels are enhanced by the use of duplex grades (higher mechanical properties, chromium content and duplex microstructure).
Fracture Toughness

- Due to the high ferrite content the Duplex SS have a ductile – brittle transition temperature of -50°F.
- This restricts the minimum operating temperature to -50°F.
- In certain circumstances the Duplex SS may be used down to -100°F.

TYPICAL PRECIPITATIONS

- s phase
- Cr₂N nitride
- c phase
- g₂ phase
- M₂₃C₆ carbide
- R Phase
- p phase
- e phase (Cu)
- a' phase
- G phase...

Possible precipitations in super duplex stainless steels
2304 ~8 hours for significant sigma vs. 2205 ~1 hour

Fabrication

Fabrication with the 2304 will be different but no more difficult than with the austenitic grades.
Welding

- Welding procedures must be developed to achieve acceptable corrosion resistance and mechanical properties/toughness in the weld zone.
- Welding of Duplex SS is not difficult. It is just different!
- 2304 is welder friendly!

WHAT ABOUT WELDED STRUCTURES?

WE NEED

- CORROSION RESISTANCE
- TOUGHNESS AT LOW TEMPERATURE

CONTROL OF FERRITE
Not required for 2304 when using fully austenitic 309L filler metal

CONTROL OF OXYGEN CONTENT
SMAW with appropriate flux basicity

CONTROL OF HYDROGEN CONTENT
Degasing of welding consummables...
No hydrogen in shielding gas

CONTROL OF NITROGEN LEVEL
Not required for 2304 when using 309L filler metal

CONTROL OF THERMAL CYCLE
Thermal stability minimizes potential for sigma phase from slow cooling

Weld Procedure Pre-qualification

- A data base program to pre-evaluate weld procedures for Duplex SS is available.

- The program can be used to predict structural, corrosion resistance and mechanical characteristics of the weld zone (HAZ and weld deposit).
### Standard Specifications

<table>
<thead>
<tr>
<th>Grade</th>
<th>ASTM</th>
<th>ASME</th>
<th>(See VIII Div I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2304(S32304)</td>
<td>A240</td>
<td>SA240</td>
<td>yes</td>
</tr>
<tr>
<td>2205(S31803)</td>
<td>A240</td>
<td>SA240</td>
<td>yes</td>
</tr>
<tr>
<td>2205(S32205)</td>
<td>A240</td>
<td>--</td>
<td>no</td>
</tr>
<tr>
<td>255 (S32550)</td>
<td>A240</td>
<td>SA240</td>
<td>yes (tube/pipe)</td>
</tr>
<tr>
<td>2507(S32750)</td>
<td>A240</td>
<td>SA789/790</td>
<td>only</td>
</tr>
</tbody>
</table>

### Cost Comparison

Cost ratio based on 304L=1.0 (pattern mill plate)

- Duplex
  - Austenitic
  - 304L=1.00
- 2304=1.05
- 316L=1.45
- 2205=1.45
- 317L=1.90
- 317LMN=2.40
- 255=2.15
- 2507=2.20
- 904L=3.20
- 6Mo=3.40-4.30
- C-family=10.80-11.60

### 2205 - 2304 DUPLEX COST SAVINGS

If you save weight (wall thickness reductions):

- You reduce the amount of material needed for the project
- You reduce labor costs (welding of thinner plates)
- You reduce transportation costs
- You reduce erection costs
- You reduce structural costs (concrete...)

**THINK ABOUT TOTAL COSTS**
What 2304 Means!

- An excellent engineering material!
- A very cost effective material!

- Comparable to 304/316 in corrosion resistance – with improved CSCC.
- Twice the yield strength of 304/316.
- Advantageous physical properties.
- Covered by standard specifications.
- Advantages with both material cost and engineered fabrication cost.

The use of 2304 to replace 304L and 316L in many designs can offer cost savings and provide improved performance.
Other equipment / materials to help minimize maintenance costs

- special C-Mn steels, specifically melted and mill-guaranteed, for HIC resistance in H2S-containing environments
  - minimizing Hydrogen Induced Cracking phenomena
- special Cr-Mo materials for resistance to disbonding of clad overlays in hydrogen-containing atmospheres
  - Vanadium alloyed 2.25Cr-1Mo steels with enhanced resistance
- special 5Cr-0.5Mo steel plate material for sulfur containing process fluids
  - parts of upgraders / refineries - also heaters, boilers (API RP 571)
- special creep resistant 9%Cr steels for ultra-hot steam piping (up to 600°C)
  - e.g. for power plants, but also boilers etc… with sulfur content
- special 2205 duplex stainless steel grades for low temperature conditions
  - high strength, inherent corrosion resistance, and advanced metallurgy for base material and weld toughness guarantees down to -60°C