Development of Corrosion Resistant Steel for Cargo Oil Tanks

6 September 2007

Sumitomo Metal Industries, Ltd.
1. Corrosion Problems of Cargo Oil Tank
2. Research Results by “The Shipbuilding Research Association of Japan”
3. Corrosion Mechanism, Simulated Test Method and Corrosion Resistance of Developed Steel
   - Deck Plate
   - Bottom Plate
4. Mechanical Properties of Developed Steel
5. Onboard Test Results of Developed Steel (Upper deck)
6. Summary
Corrosion Problems of Cargo Oil Tank

- General corrosion
  - Maximum corrosion rate > 0.1 mm/y
  - Cost of repair coating, recoating

- Pitting corrosion
  - Cost of inspection and repair
  - Pits initiate at defects of paint film

Deck plate
- Vapor space
- Crude oil
- Drain water

Bottom plate
1. Corrosion Problems of Cargo Oil Tank

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4. Mechanical Properties of Developed Steel

5. Onboard Test Results of Developed Steel (Upper deck)

6. Summary
The Shipbuilding Research Association of Japan Panel #242 (SR242 committee)

Field examination of VLCCs were carried out by SR242
Corrosion at Deck Plate

- **Corrosion rate**: > 0.1mm/y (Maximum)

- **Corrosion environments**:
  - Inert gas ($O_2$, $CO_2$, $SO_2$)
  - $H_2S$ (from crude oil)
  - Cyclic wet & dry condition

- **Corrosion products**: rusty (FeOOH), elemental S [layered structure]

Deck Plate

- Vapor space
- Crude oil

Research by SR242

Sumitomo Metals
Examples of Analysis Results of Gas Composition in Vapor Space of Cargo Oil Tanks

<table>
<thead>
<tr>
<th>COT No.</th>
<th>3S</th>
<th>4C</th>
<th>4S</th>
<th>5C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Oil type</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>Cargo loading ratio</td>
<td>93%</td>
<td>89%</td>
<td>92%</td>
<td>31%</td>
</tr>
<tr>
<td>H₂S [vol. ppm]</td>
<td>2790</td>
<td>1330</td>
<td>498</td>
<td>817</td>
</tr>
<tr>
<td>H₂O [vol.%]</td>
<td>4.9</td>
<td>3.9</td>
<td>5.3</td>
<td>2.5</td>
</tr>
<tr>
<td>O₂</td>
<td>1.7</td>
<td>2.5</td>
<td>1.8</td>
<td>3.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.7</td>
<td>4.0</td>
<td>2.2</td>
<td>10.9</td>
</tr>
<tr>
<td>SOₓ [vol. ppm]</td>
<td>1.3</td>
<td>3.9</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>N₂</td>
<td>32.9</td>
<td>45.0</td>
<td>25.7</td>
<td>62.0</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>54.9</td>
<td>42.4</td>
<td>62.2</td>
<td>15.0</td>
</tr>
<tr>
<td>CO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

High concentration of H₂S exists in vapor space

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Appearance of Upper Deck Plate

flaky corrosion products
Loss in Thickness of Upper Deck Plate with Age

Average Loss (mm) vs. Age at inspection (year)

Maximum corrosion rate is over 0.1 mm/y

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Pitting Corrosion at Bottom Plate

- **Pitting rate**: 4mm/y maximum
- **Corrosion environments**:
  - Inert gas (O\(_2\), CO\(_2\), SO\(_2\))
  - H\(_2\)S (from crude oil)
  - Drain water (Cl\(^-\))
  - Crude oil, elemental S
- **Corrosion products**:
  - Rust, FeS, elemental S

---

Crude oil

Drain water
### Examples of Chemical Analysis Results of Water Sampled from the Bottom of Cargo Oil Tanks

<table>
<thead>
<tr>
<th>tank</th>
<th>Na</th>
<th>Cl</th>
<th>SO$_4^{2-}$</th>
<th>S$_2$O$_3^{2-}$</th>
<th>T-Fe</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>13600</td>
<td>42500</td>
<td>14</td>
<td>&lt;0.1</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>B</td>
<td>40000</td>
<td>48000</td>
<td>1470</td>
<td>&lt;0.1</td>
<td>42</td>
<td>7.15</td>
</tr>
<tr>
<td>C</td>
<td>40000</td>
<td>54000</td>
<td>1350</td>
<td>&lt;0.1</td>
<td>2.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Chloride is detected in high concentration.

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Appearance of Specimen Exposed at the Bottom of Cargo Oil Tank

exposed for 2.5 years

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4. Mechanical Properties of Developed Steel

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6. Summary
Corrosion Mechanism at Upper Deck Plate

< dawn : ∼25°C (wet) >

< daytime : ∼50°C (dry) >

Corrosion in low pH water

pH = 2 ~ 4

\[
\begin{align*}
H_2O + SO_2 & \rightarrow H_2SO_3 \xrightarrow{O_2} H_2SO_4 \\
H_2O + CO_2 & \rightarrow H_2CO_3
\end{align*}
\]

Elemental S

\[2H_2S + O_2 \rightarrow 2S + H_2O\]

FeOOH

corrosion product contains a lot of elemental S (60% max.)
Simulated Corrosion Test (Upper Deck Plate)

< Test conditions >
Temperature
50°C (20 h) ⇔ 25°C (4h)
[cyclic wet & dry condition]

Gas*
[A] 13% CO₂ - 5% O₂ - 0.01% SO₂
-bal. N₂ (simulated inert gas)
[B] simulated inert gas + 0.2% H₂S

* Gas A and B are blew alternately every 2 weeks
Cross Sectional Analysis of Corrosion Product Formed on Steel after Simulated Corrosion Test

Layered structure was reproduced in laboratory

Distribution of elements

Epoxy resin
Corrosion product
Steel

layerd elemental S
mixture of rust and elemental S
rust (FeOOH)
Corrosion product after simulated test was similar to cargo oil tank.

Laboratory corrosion test simulates corrosion at upper deck of cargo oil tank.
Corrosion Resistance - Deck Plate -

Average corrosion loss (mm)

Test duration (days)

Conventional Steel

Normalized corrosion rate

Developed Steel

84 days

Normalized corrosion rate

Conventional steel

Developed steel

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Corrosion resistance in low pH water by alloying elements

- Steel + alloying elements
- Low pH (2~4)
- Dew water

Graph showing:
- Ratio of corrosion rate
- Conventional steel
- Developed steel

Bar graph:
- H₂SO₄ (pH=0.5), 24h
- Ranges from 0 to 1.2 on the y-axis

Mechanism for Improvement of Corrosion Resistance [upper deck]
1. Corrosion Problems of Cargo Oil Tank

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Pitting Corrosion Mechanism at Bottom Plate

Drain water (Cl⁻) (Neutral pH)

Oil coating

Defect

Pit (Anode) Cathode

Elemental S

H₂S

Inert gas

Bottom plate

Anode: Fe → Fe²⁺ + 2e
Cathode: O₂ + 2H₂O + 4e → 4OH⁻
S + 2H₂O + 2e → H₂S + 2OH⁻ (accelerate pitting corrosion rate)

Pits initiate at the defects of oil coating film and grow rapidly by creating corrosion electric cell.
Simulated Corrosion Test –Bottom Plate–

< Test conditions >

Temperature
40°C

Gas
13%CO₂-5%O₂-0.01%SO₂
-0.2%H₂S-bal.N₂

Appearance of specimen after corrosion test

We reproduced pitting corrosion by laboratory test.
Corrosion product after simulated test was similar to cargo oil tank.

Laboratory corrosion test simulates corrosion at bottom of cargo oil tank.
Corrosion Resistance - Bottom Plate -

Maximum pit depth (mm) vs. Test duration (days)

Conventional Steel

Developed Steel

Normalized pitting rate

Conventional steel
Developed steel

56 days

1/2

1/3

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Mechanism for Improvement of Corrosion Resistance [bottom]

Sulfide film suppresses growth of pitting corrosion

Drain
Oil coating
H₂S
Rust
Steel + alloying elements

Cross section

Sulfide film

SE
FeS
Rust
Steel

Distribution of elements

Cu
S
Fe
O

concentration
high
low

200 μm

Sulfide film suppresses growth of pitting corrosion
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6. Summary
Mechanical Properties of Developed Steel

Plate thickness : 16.5 mm

<table>
<thead>
<tr>
<th>Tensile Tests</th>
<th>Charpy Impact Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>YP (N/mm²)</td>
<td>TS (N/mm²)</td>
</tr>
<tr>
<td>EL (%)</td>
<td>Test Temp. (°C)</td>
</tr>
<tr>
<td>Absorbed Energy (J)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grade</th>
<th>Spec.</th>
<th>Charpy Impact Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>D32</td>
<td>≥ 315</td>
<td>440/570 ≥ 22 -20 ≥ 31</td>
</tr>
</tbody>
</table>

Mechanical properties satisfied the specification.
Toughness of Welded Joint

- Plate thickness: 16.5 mm

<table>
<thead>
<tr>
<th>Method</th>
<th>3 electrodes, FCB (Single side 1 pass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat input</td>
<td>108 kJ/cm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Notched Position</th>
<th>Absorbed Energy at 0°C (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W.M.</td>
<td>174</td>
</tr>
<tr>
<td>F.L.</td>
<td>132</td>
</tr>
<tr>
<td>F.L. + 1mm</td>
<td>172</td>
</tr>
<tr>
<td>F.L. + 3mm</td>
<td>224</td>
</tr>
<tr>
<td>F.L. + 5mm</td>
<td>250</td>
</tr>
</tbody>
</table>

- Toughness of welded joint is good.

- Edge preparation

- Sumitomo Metals
Corrosion resistance of weld metal is equivalent to that of base metal.
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### Certification of Classification

**LR, NK, ABS, DNV**

**Trial Applications to Cargo Oil Tanks**

<table>
<thead>
<tr>
<th>Shipyard</th>
<th>Type</th>
<th>Exposure test</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Deck</td>
<td>Bottom</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>AFRA-MAX</td>
<td>plates</td>
<td>plates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>test coupons</td>
<td>test coupons</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>AFRA-MAX</td>
<td>test coupons</td>
<td>-</td>
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</tr>
<tr>
<td>B</td>
<td>AFRA-MAX</td>
<td>test coupons</td>
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<tr>
<td>C</td>
<td>VLCC</td>
<td>test coupons</td>
<td>plates</td>
<td></td>
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<tr>
<td>D</td>
<td>VLCC</td>
<td>test coupons</td>
<td>plates</td>
<td></td>
</tr>
</tbody>
</table>

Developed steel has been applied to cargo oil tanks for trial.
Onboard Test Results of Developed Steel (Upper Deck Plate)

Test coupons were exposed in vapor space of 3 tanks for 1 year.

Developed steel has good corrosion resistant in actual environments at upper deck.
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6. Summary
1. We established simulated corrosion test method.
2. We developed corrosion resistant steel plate for cargo oil tank which can be used at both upper deck and bottom.
3. Performance of developed steel:
   - corrosion rate $< 1/2$ [at deck plate]
   - pitting rate $< 1/3$ [at bottom plate]
4. Mechanical properties of developed steel satisfy the specification.
5. Corrosion resistance of weld metal is good.
6. Developed steel has good corrosion resistance in upper deck of actual cargo oil tanks.
END OF PRESENTATION

THANK YOU FOR KIND ATTENTION

September 2007
Sumitomo Metal Industries, Ltd.
Structure of Corrosion Product on Pit

Sulfide film that is hard to dissolve improves corrosion resistance

Conventional steel

Developed steel

2FeS + 3/2O₂ + H₂O → 2FeOOH + 2S

FeOOH

FeS

Sulfide

Steel

Steel
Corrosion resistance of welded joints was good
No galvanic corrosion on these welded joints
Corrosion resistance of developed steel in sea water

Corrosion resistance of developed steel is equivalent to conventional steel in sea water.
Test coupons on deck and bottom

**Deck**

- Grinded (\(\bigvee\bigvee\bigvee\) )
- Epoxy painted
- Silicon coated

**Bottom**

- Grinded (\(\bigvee\bigvee\bigvee\) )
- Epoxy painted
- Silicon coated

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Effect of oil coating on corrosion at bottom (simulated test)

Corrosion of specimen with oil coating is accelerated

Generation of corrosion electric cell in this environment
Effect of H$_2$S on corrosion at bottom (simulated test)

H$_2$S accelerate corrosion in this environment.

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