Titanium Gaining Favor in Seawater Service

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The technical case for titanium application to seawater service was well established in the early 1970’s and performance of titanium over the last 40 years has validated the technical case. Widespread use of titanium for process plant application has grown significantly over the last 40 years in spite of comparative cost with competing alloys. This challenge began to reverse in the early 2000’s as global expansion of titanium production accelerated and the cost for competing alloys continued to rise.

With expanding global production (see FIGURE 1) the application base for titanium was able to expand and this expansion allowed the stocking of service centers worldwide to support existing and developing applications. Concurrent with this improved market position for titanium the global nickel and copper industries faced increasing demand, rising energy prices and most importantly declining ore grades. Producing commodities from low grade resources requires higher energy input and capital intensive plants for the processing of large tonnage and low grade run-of-mine ore.

![FIGURE 1](image)

GLOBAL TITANIUM SPONGE PRODUCTION
USGS minerals information

This business case for titanium was demonstrated in 2010 with the largest ever industrial project for titanium when the Ras Al Khair desalination plant was constructed utilizing near 6000 MT of titanium tubing. The application of titanium on this large scale was a result of the proven 40 year history of titanium in power generation and thermal desalination service together with the improved delivery for titanium products and the rising price of copper alloys.

With titanium often the economic choice for seawater application the importance of the technical case cannot be overstated and should be revisited. Many application engineers have ignored the potential for titanium based on the misconception that titanium is hard to find and if found was too expensive to consider. For that reason the technical case for titanium in seawater service is presented.
Corrosion resistance of titanium

The corrosion resistance of titanium is the result of a tenacious surface oxide composed of titanium dioxide that autogenously repairs itself when damaged in the presence of even very low levels of oxygen or water. The ceramic-like corrosion resistance of titanium can be relied upon to resist corrosion in seawater as follows (Ref 1):

General corrosion

Commercially pure titanium is immune to general corrosion in seawater and brackish water to temperatures as high as 130 °C. Low levels of alloying additions such as palladium in the case of Grades 7, 11, 16, and 17 or Ni & Mo in the case of Grade 12 will extend general corrosion resistance to temperatures in excess of 260 °C. Table 1 presents chemical composition ranges of those titanium grades applied to seawater service.

<table>
<thead>
<tr>
<th>Titanium Grade</th>
<th>O max</th>
<th>C max</th>
<th>N max</th>
<th>Fe max</th>
<th>Pd range</th>
<th>Mo range</th>
<th>Ni range</th>
<th>Al range</th>
<th>Va range</th>
<th>Ti</th>
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<tbody>
<tr>
<td>1</td>
<td>0.18</td>
<td>0.08</td>
<td>0.03</td>
<td>0.20</td>
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<td></td>
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<td>2</td>
<td>0.25</td>
<td>0.08</td>
<td>0.03</td>
<td>0.30</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Balance</td>
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<tr>
<td>3</td>
<td>0.35</td>
<td>0.08</td>
<td>0.05</td>
<td>0.30</td>
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<tr>
<td>5</td>
<td>0.20</td>
<td>0.08</td>
<td>0.05</td>
<td>0.40</td>
<td>2.5-3.5</td>
<td>2.0-3.0</td>
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<td></td>
<td></td>
<td>Balance</td>
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<tr>
<td>7</td>
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<td>0.08</td>
<td>0.03</td>
<td>0.30</td>
<td>0.12-0.25</td>
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<td></td>
<td></td>
<td></td>
<td>Balance</td>
</tr>
<tr>
<td>11</td>
<td>0.18</td>
<td>0.08</td>
<td>0.03</td>
<td>0.20</td>
<td>0.12-0.25</td>
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<td></td>
<td></td>
<td></td>
<td>Balance</td>
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<tr>
<td>12</td>
<td>0.25</td>
<td>0.08</td>
<td>0.03</td>
<td>0.30</td>
<td>0.2-0.4</td>
<td>0.6-0.9</td>
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<td></td>
<td></td>
<td>Balance</td>
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<tr>
<td>16</td>
<td>0.25</td>
<td>0.08</td>
<td>0.03</td>
<td>0.30</td>
<td>0.04-0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Balance</td>
</tr>
<tr>
<td>17</td>
<td>0.18</td>
<td>0.08</td>
<td>0.03</td>
<td>0.20</td>
<td>0.04-0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 1
Composition of Selected ASTM Titanium Grades

Crevice corrosion

Commercially pure titanium (Grades 1, 2, and 3) is immune to crevice corrosion in aerated seawater to temperatures of at least 70 °C. In deaerated seawater commercially pure titanium will resist crevice corrosion to temperatures as high as 94 °C. When higher service temperatures are required or crevices cannot be engineered out of the process equipment titanium grades containing alloy addition can be applied to provide protection from crevice corrosion. Titanium grades containing additions of palladium...
such as Grades 7, 11, 16 and 17 or titanium Grade 12 containing small additions of nickel and molybdenum are economical choice to enhance protection from crevice corrosion.

**Pitting Corrosion**

Pitting is the localized attack of the exposed metal surface in the absence of crevices. Titanium is highly resistant to pitting attack in seawater unless impressed currents higher than +5 volts are applied. Titanium is routinely used in impressed current systems as the anodic breakdown potential exceeds that of most common engineering materials.

**Hydrogen Damage**

Titanium is resistant to hydrogen damage in a wide range of applications including galvanic couples and impressed current systems. The naturally occurring oxide film on titanium protects the base metal from hydrogen absorption which would result in reduced ductility of the metal. Factors required for hydrogen damage to titanium are:

- Mechanism for generating nascent hydrogen
- Metal temperature > 80 °C
- Solution pH <3 or >12

Eliminating anyone of these conditions will result in titanium being immune to hydrogen damage. (Ref 1)

**Galvanic Corrosion**

Galvanic corrosion is not normally a concern for titanium due to the noble nature of the metal. Coupling with dissimilar metals will not result in corrosion issues as long as the entire system remains passive. If active corrosion is occurring in the system then potential for hydrogen damage to titanium is possible. Factors which influence galvanic corrosion are the cathode to anode surface area ratio, the solution chemistry and temperature as indicated in the section on hydrogen damage. Avoiding galvanic corrosion can be accomplished by coupling with a more compatible metal, electrical insulation of the connection or designing the system in 100% titanium.

**Erosion Corrosion**

The hard adherent oxide on titanium provides a high level of protection from erosion corrosion in flowing seawater even when sand particle are entrained in the process steam. Velocities as high as 30 meter/second are acceptable for titanium when no sand is present and 5 meters/sec when heavily laden with sand.

**Microbial Influenced Corrosion (MIC)**

“Microbiologically influenced corrosion has been reported for all engineering metal and alloys with the exception of predominantly titanium and high chromium -nickel alloys” (Ref 2) MIC can occur over a wide range of temperature to 100 °C; however titanium is not affected by microbial influenced corrosion in flowing or stagnant seawater service.
**Enhancing the corrosion resistance of titanium**

The addition of small amounts of certain elements will result in improved corrosion resistance of titanium in reducing environments. The common alloy additions include:

- Ti Grades 16 and 17 0.04% to 0.08% Pd
- Ti Grades 7 and 11 0.12% to 0.25% Pd
- Ti Grade 12 0.2% to 0.4% Mo and 0.6% to 0.9% Ni

These alloy “additions facilitate cathodic depolarization by providing sites of low hydrogen overvoltage, which shifts alloy potential in the noble direction where oxide film passivation is possible” (Ref 3).

Materials commonly selected for seawater heat exchanger and piping systems include alloys which are predominately copper and/or nickel and titanium. Each of the materials has benefits and limitations in seawater service which will be compared and contrasted in the following paragraphs. Additionally, the current comparative cost of these materials and factors which will likely influence future pricing for copper and nickel will be addressed.

Resistance to the various forms of corrosion in seawater for selected alloys is presented in Table 2. It is clear that only titanium is resistant to all forms of corrosion in seawater to temperature exceeding 70 °C; super duplex alloys have a maximum reported service temperature of 40 °C (Ref 4) but are susceptible to pitting of welds at much lower temperatures.

<table>
<thead>
<tr>
<th>Corrosion Mode</th>
<th>Cu Alloys</th>
<th>AL Alloys</th>
<th>316 SS</th>
<th>Adv SS</th>
<th>Ni Alloys</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform</td>
<td>R/S</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Erosion Corrosion</td>
<td>S</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Pitting</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Crevice</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>R</td>
</tr>
<tr>
<td>Stress</td>
<td>R/S</td>
<td>S</td>
<td>R/S</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>MIC</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Weld</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Galvanic</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
</tbody>
</table>

**TABLE 2**
Performance of Alloys in Seawater Service
R-resistant, S-susceptible
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A system for ranking Corrosion Resistant Alloys (CRAs) pitting resistance has been developed to predict alloy resistance to pitting corrosion in chloride solutions. The Pitting Resistance Equivalency Number (PREN) is based on the formula:

\[
\text{PREN} = W_{Cr} + 3.3(W_{Mo} + 0.5W_{W}) + 16W_{N}
\]

Where:
- \(W_{Cr}\) is the weight % chromium in the alloy
- \(W_{Mo}\) is the weight % molybdenum in the alloy
- \(W_{W}\) is the weight % tungsten in the alloy
- \(W_{N}\) is the weight % nitrogen in the alloy

Recommended PREN for seawater service is >40 (Ref 4), this requirement eliminates austenitic stainless steels, duplex and super austenitic stainless from consideration. Only super duplex with a PREN value of 42 can be considered and this alloy is limited to a maximum service temperature of 20 °C according to ISO 21457, “Petroleum, petrochemical and natural gas industries – Materials selection and corrosion control for oil and gas production systems”. Table 3 presents limitations for materials selected for seawater service per ISO 21457.

<table>
<thead>
<tr>
<th>Material</th>
<th>Typical Limitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 625</td>
<td>Maximum temperature: 30 °C</td>
</tr>
<tr>
<td></td>
<td>Maximum residual chlorine 0.7 mg/l</td>
</tr>
<tr>
<td>Alloy C276</td>
<td>Maximum temperature: 40 °C</td>
</tr>
<tr>
<td></td>
<td>Maximum residual chlorine 0.7 mg/l</td>
</tr>
<tr>
<td>25Cr duplex</td>
<td>Maximum temperature: 20 °C</td>
</tr>
<tr>
<td></td>
<td>Maximum residual chlorine 0.7 mg/l</td>
</tr>
<tr>
<td>Titanium Grades 1 &amp; 2</td>
<td>Unchlorinated seawater maximum temperature: 95 °C</td>
</tr>
<tr>
<td></td>
<td>Chlorinated seawater maximum temperature: 85 °C</td>
</tr>
<tr>
<td>CuNi 90/10</td>
<td>Maximum velocity 2.5 m/s</td>
</tr>
</tbody>
</table>

**TABLE 3**
ISO 21457
Even in the allowed temperature range there is danger of pitting due to chlorination of the system to eliminate fouling and microbial activity. (Ref 5)

Figure 2 provides a comparison of pricing for various alloys often considered for seawater service (Ref 6). The data is based on the current purchase price of 6mm thick plate 305mm x 305mm. The relative lower cost of titanium is due to continuing price increases for copper and nickel and the higher density of these products.

Historical copper and nickel price trends are presented in Figure 3 and Figure 4, respectively. Production of copper and nickel is relying on continually decreasing ore grades as high grade readily accessible resources have been mined. The trend of decreasing mine grade requires ever greater energy input to produce required tonnage of metal. With energy prices continuing to rise for many of the same reasons, the expectation is that copper and nickel prices will continue steady escalation. Figure 5 presents the trend of declining mine grade for copper produced at U.S. mines from 1862 through 2003.

The abundance of titanium in nature together with an installed global mining industry for titanium minerals and global expansion of titanium metal production has facilitated growth in the industrial titanium market. As the production base for titanium expands industry will benefit from improved deliveries and less price volatility.
Figure 3
Copper Price Trend
January 2008 to January 2013

Figure 4
Nickel Price Trend
January 2008 to January 2013
Optimizing design to reduce weight and space requirements

Titanium has twice the strength of copper-nickel alloys and is nominally ½ the density. There is significant savings to be realized when designs are optimized for titanium (Ref 7). The higher strength means thinner wall sections, the higher velocity limitations for flowing seawater allows smaller diameter pipe both of which add to space and weight savings. The cost to support a 1 kilogram load on the deck of a floating oil production system has been estimated at 12 Euros by Doble & Havn (Ref 8) so weight savings have a significant impact on project cost.

Case histories of titanium in seawater

Ras Al Khair (formerly Ras Al Zwar) Multi Stage Flash (MSF) desalination plant was built with 100% titanium tubes based on capital costs being better than the costs with historical material selection. The life of the MSF plant is expected to be more than 50 years which also impacts capital amortization and subsequent operating costs. See Figure 6 for operation cost comparisons of desalination technologies. According to Global Water Intelligence:
“The figure (6) refers to large seawater plants (100,000 m³/d) with the capital cost amortized over a life of 20 years, and assuming an interest rate of 6%. Given that the lifespan of an MSF plant may be longer than 40 years, the capital cost calculation would need to be adjusted accordingly”. (Ref 9)

When life of plant construction with titanium is considered, the operating cost of providing water for the various technologies compares favorably. This new perspective on capital cost has resulted in two new world class MSF plants in the last three years and is having an impact on material selection for certain SWRO components which are exposed to seawater.

Developing applications

- SWRO plants for LoSal Enhanced Oil Recovery (EOR). Plants destined for installation on floating oil production units where weight, reliability and temperature fluctuations are concerns. See Figure 7
- Evaporation and crystallization plants for treating water produced from hydraulically fractured gas wells
Conclusions

The industrial titanium market has expanded globally both in terms of supply and application to process plant equipment. The expanded supply base has brought improved availability, reliable delivery and more economical pricing to the market; the expanded application base has provided a robust reference list of successful applications for titanium to a variety of industrial applications. These success stories are fueling even more interest in using titanium products to combat corrosion and extend reliability of equipment in harsh seawater service.

REFERENCES:


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3. Optimized lean-Pd Titanium Alloys for Aggressive Reducing Acid and Halide Service Environments R.W. Schutz and Ming Xiao, RMI Titanium


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