Titanium alloys are often selected for industrial applications because of their superior corrosion resistance to chloride- and other halide-containing environments. As temperatures increase, however, crevice corrosion generally becomes the limiting mode of corrosion for many titanium alloys when crevices exist or occur in these environments. Therefore, it is vital that the designer and user understand the primary factors which influence titanium's susceptibility to crevice corrosion, and recognize the conditions under which crevice attack is possible. This paper not only reviews these factors and provides environmental guidelines, but also outlines practical, effective strategies for prevention of titanium alloy crevice corrosion.

Titanium alloys may be subject to localized attack within tight crevices, known as crevice corrosion, when exposed to hot chloride, bromide, iodide, fluoride, or sulfate-containing aqueous solutions. Crevices can stem from adhering process stream deposits or scales (ie. salt deposits), metal-to-metal joints (ie. poor joint design or tube-to-tubesheet joints), or gasket-to-metal flange and other seal joints. Severe mechanical damage of metal surfaces, such as heavy scratches or gouges, can produce heavy metal laps or smears under which crevice corrosion can occur. Crevice attack on titanium typically generates irregularly-shaped pits, as shown in Figure 1, which are often filled or covered with voluminous, adhering, tenacious, and grey/off-white-colored titanium dioxide corrosion products. The microstructure of sectioned and polished crevice pits generally exhibits a surrounding layer of titanium hydride precipitates in alpha or near-alpha titanium alloys, which are by-products of the cathodic hydrogen reduction reaction within crevices.

Crevise corrosion may also take the form of highly-circular pits involving minimal apparent TiO2, corrosion product scale formation. This less-common form of attack can result when a titanium surface has been gouged, scratched, smeared, and embedded with iron, carbon steel, or low alloy steel.

Crevice Corrosion Mechanism

The mechanism for crevice corrosion of titanium alloys is similar to that for stainless steels, in which oxygen-depleted, reducing-acid conditions form within tight crevices. Finite titanium surface oxidation (Reaction (1)) within crevices consumes dissolved oxygen or other oxidizing species from crevice solutions faster than diffusion from the outside bulk solution can replenish them. As a result, metal potentials within crevices become active (negative) to open-exposed metal surfaces, creating an electrochemical cell in which creviced surfaces become anodic and corrode (Reaction (2)) as shown in Figure 2.

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**Fig. 1:** Examples of crevice corrosion attack on C.P. titanium tubing in hot chloride brine service.

**Fig. 2:** Schematic showing the mechanism of titanium crevice corrosion in hot aqueous chloride media.
Chlorides diffuse into the crevice and concentrate to maintain mass balance with the increasing concentration of dissolved titanium ions as crevice corrosion proceeds. The titanium chlorides formed are unstable and readily hydrolyze to form titanium oxide corrosion products and more acid (Reaction (3)), allowing the corrosion process to proceed autocatalytically within the crevice. Studies have determined that pH values as low as 0-1 may develop within active crevices.  

$$\text{(1) } 2 \text{Ti}^+ + 2 \text{H}_2\text{O} \rightarrow 2 \text{TiO}_2 + 4 \text{H}$$  
$$\text{(2) } 2 \text{Ti}^+ + 5 \text{HCl} + 2 \text{H}_2\text{O} \rightarrow 2 \text{TiCl}_3 + 2 \text{H}_2\text{O} + 7 \text{H}$$  
$$\text{(3) } \text{TiOCl}_2 + 2 \text{TiCl}_3 + 4 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{Ti}_2\text{O}_3 + 8 \text{HCl}$$  

**Influencing Factors**

The primary factors that are recognized to significantly influence initiation and propagation of crevice corrosion of titanium alloys include temperature, solution chemistry and pH, physical nature of the crevice, alloy composition, metal surface condition, and metal potential. Although most of these factors are highly interactive, a synopsis of their principal effect on crevice corrosion is presented.

**Temperature**

Susceptibility to and severity of crevice corrosion generally increases with increasing temperature, and is highly dependent on pH, as indicated in Figure 3 for NaCl media. A practical minimum threshold temperature for crevice corrosion of titanium alloys is approximately 70°C regardless of pH or solution chemistry. Somewhat reduced temperature thresholds (40-60°C) for unalloyed titanium have been reported with very special salt-impregnated gasket materials in laboratory tests.

**Solution Chemistry/pH**

Crevice corrosion of titanium is only known to occur in chloride, bromide, iodide, fluoride, and sulfate solutions. pH/temperature guidelines for chloride, bromide, and iodide media are generally similar, whereas pH/temperature thresholds for fluoride-rich solutions may be somewhat reduced. Crevice attack is enhanced as halide concentration increases, although studies reveal that susceptibility to attack may be a maximum in the 1-2M range, unless solutions are aerated, oxygenated, or chlorinated. Chloride concentration attack threshold lies between 100-1000 ppm, depending on temperature, pH, and the cathodic depolarizers present. Pure sulfate solutions tend to be somewhat more benign, with crevice attack limited to higher sulfate concentrations (>1%) and temperatures (>82°C). The effect of cation type, if not oxidizing (ie. Na⁺, K⁺, NH₄⁺, Mg²⁺, Ca²⁺), is rather insignificant, with the exception of Mg²⁺, Ca²⁺, Zn²⁺, and Al³⁺ salts which may hydrolyze to form HCl at higher concentrations and temperatures and aggravate localized attack.

Cathodic depolarizers, such as dissolved oxidizing species and H⁺ ions, dramatically stimulate crevice corrosion initiation and propagation. Decreasing solution pH strongly increases susceptibility to crevice attack, as Figure 3 indicates. Table 1 presents approximate critical pH values for crevice corrosion.
of various commercial Ti alloys in hot NaCl-based brines. Crevice corrosion in chloride media is stifled at pH levels above 10.5. Dissolved oxygen in solution dramatically enhances susceptibility to crevice corrosion, even at levels on the order of tenths of a ppm. Oxygenated or aerated solutions aggravate attack by providing cathodic depolarization and increasing the anode to cathode potential of the crevice cell. On the other hand, totally deaerated, neutral or alkaline brines (devoid of oxidizing species) may not induce significant crevice corrosion of titanium. Other cathodic depolarizers which also encourage crevice corrosion include the cationic oxidizing species listed in Table 2. This table also lists certain oxidizing anionic species which may diffuse into crevices and inhibit attack in halide-containing solutions.

### Table 1: Critical pH values for crevice corrosion of titanium alloys in hot (≥ 90°C) NaCl brines.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Max. pH at Which Attack Occurs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>10-10.5</td>
</tr>
<tr>
<td>C.P. T1</td>
<td>9.5-10</td>
</tr>
<tr>
<td>Ti-550</td>
<td>3</td>
</tr>
<tr>
<td>Gr. 12 T1</td>
<td>2.5</td>
</tr>
<tr>
<td>Ti-6Al-2Sn-4Zr-6Mo</td>
<td>2</td>
</tr>
<tr>
<td>Gr. 7 or 11 T1</td>
<td>0.7-0.8</td>
</tr>
<tr>
<td>Ti-15Mo-5Zr</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

### Table 2: Dissolved oxidizing species which may accelerate or inhibit crevice corrosion of titanium in hot halide solutions.

#### Accelerate Attack
- Fe^{3+}, Cu^{2+}, Ni^{2+}, Ti^{4+}
- Ce^{4+}, Sn^{4+}, VO_2^{2+}, Te^{4+}, etc.
- Se^{4+}, Hg^{2+}, Pt^{2+}, etc.
- Pd^{2+}, Ru^{2+}, Ir^{3+}, Rh^{3+}, etc.
- Au^{3+}, O_2, Cl^-,

#### Inhibit Attack
- OCl^-, ClO_3^-, ClO_4^-,
- NO_3^-, Cr_2O_7^{2-}, MoO_4^{2-},
- MnO_4^-, S_2O_3^{2-}, VO_4^{3-},
- VO_3^-, IO_3^-, WO_4^-,

### Nature of the Crevice

Initiation of crevice corrosion of titanium alloys requires extremely tight and reasonably deep crevices. Crevice gap (or width) must be less than 1.5 x 10^{-3} cm with a crevice depth greater than 1 cm depending on the crevice gap. The extremely tight (< 5 x 10^{-2} cm) crevices created by certain fluorocarbons (i.e. Teflon® or Viton®) and certain sealants against metal surfaces result in more consistent attack initiation, and greater susceptibility to attack under less aggressive pH/temperature conditions. Rubber, asbestos, EPDM, PVC, epoxy, nylon, and silicone rubber gasket-metal crevices exhibit somewhat reduced susceptibility to attack. Carbon-filled or graphite-impregnated sealants and carbon felt may avert crevice attack depending on the severity of conditions. Litharge-cured Viton aggravates titanium crevice corrosion, compared to MgO-cured Viton grades. Fluorine-release from powdered or reprocessed (non-virgin) fluorocarbons may induce localized attack as well.

Titanium metal to metal crevices are generally much less susceptible to attack than gasket to metal crevices due to their inherently larger crevice gaps (typically ≥ 1 x 10^{-3} cm). Crevices created by contact of two dissimilar titanium alloys can assume the crevice corrosion resistance of the more noble (resistant) alloy as a result of galvanically-induced anodic protection. For example, a crevice formed between grade 2 and 7 titanium contacting surfaces will behave similar to an all grade 7 titanium metal crevice. Furthermore, crevices formed between titanium and a number of common dissimilar metals may also resist crevice corrosion as indicated in Table 3.

### Table 3: Influence of dissimilar metal crevice members on the crevice corrosion resistance of C.P. titanium in hot chloride brines.

<table>
<thead>
<tr>
<th>Attack</th>
<th>Precious Metals (Pt,Pd,Ru,Ir,Rh)</th>
<th>Copper Alloys (Brass &amp; Bronzes)</th>
<th>Cu-Ni Alloys</th>
<th>Nickel Alloys (Monel,625,C-276)</th>
<th>Ni-Stainless Steels (304,316)</th>
<th>Magnesium</th>
<th>Gold*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibit</td>
<td>Aluminum Alloys</td>
<td>Zinc</td>
<td>Silver</td>
<td>Niobium</td>
<td>Molybdenum</td>
<td>Tin</td>
<td>Lead</td>
</tr>
</tbody>
</table>

*Not effective in Cl_2 sat. brines.
Crevice corrosion may also be favored under adherent chloride, sulfate, and siliceous deposits or scales on titanium metal surfaces. These scales can support highly acidic reducing conditions within deposit-metal crevices. Conversely, crevice attack will not occur under alkaline salt deposits such as carbonates. Scales containing significant amounts of oxidizing compounds, such as iron oxides (rust), also inhibit crevice corrosion by passivating creviced metal surfaces.18

Alloy Composition

The alloying elements which promote passivation of titanium in hot reducing acids similarly enhance titanium alloy crevice corrosion resistance. Thus, small (at least 0.08 wt. %) precious metal (Pt, Pd, Ru, Ir) alloying additions impart significant crevice improvements,3,19,20 as indicated by grade 7 titanium (Ti-0.15Pd) performance in Figure 3. Nickel (> 0.5 wt. %)3,8,3,19 and/or molybdenum (> 3 wt. %)14,19 also significantly expand the range of temperatures and pH's where crevice attack can be avoided. Commercial titanium alloys with improved crevice corrosion resistance are grades 7, 11, and 12 titanium, and certain high strength Mo-containing alloys14 including the Ti-3Al-8V-6Cr-4Zr-4Mo and Ti-6Al-2Sn-4Zr-6Mo alloys. Although interstitial content (O, N, C) has little influence on alloy resistance, there is evidence suggesting that small increases in iron content mitigate crevice attack on C.P. titanium alloys.11 Higher strength titanium alloys alloyed with Al, V, Sn, and Zr exhibit crevice corrosion resistance almost equivalent to the C.P. grades. However, resistance diminishes as Al content increases above 3%.14

Metal Surface Condition

Flat, smooth, and low-RMS titanium metal surfaces result in tighter crevices, and, thus, enhanced susceptibility to crevice corrosion relative to roughened surfaces. Smooth, heavily-pickled, or highly-polished surfaces are, therefore, less desirable than ground or sandblasted surfaces in creviced metal situations. Although anodized surfaces are comparable in resistance to pickled surfaces, surfaces with thermal oxide films (air-annealed above 400°C) will exhibit significantly improved crevice corrosion resistance.8,21

Metal Potential

Impressed anodic potentials on titanium metal crevices will enhance the onset of crevice corrosion4,8 by promoting crevice acidification from the oxidation reaction: Ti + 2 H₂O + TiO₂ + 4 H⁺ + 4e⁻. Although cathodic potentials may inhibit crevice corrosion below -0.4V (vs SCE)7, total cathodic protection may not be possible under severe crevice conditions.

Strategies for Prevention

There are a number of practical strategies for effectively avoiding crevice corrosion on titanium alloy equipment and components. These strategies may be categorized as: proper alloy selection, precious metal surface treatments, other metallic/metallic oxide coatings, thermal oxidation, noble alloy contact, and surface pickling (for smeared surface iron). Selection of a fully resistant titanium alloy is generally preferred from a long-term performance reliability and life cycle cost standpoint, particularly as section size decreases. On the other hand, localized surface treatments may be more practical and cost-effective when very thick wall sections (> 20mm) are involved or when existing equipment requires upgrading or remedies.

Proper Alloy Selection

General guidelines for titanium alloy selection in alkali metal and dilute alkali-earth metal chloride solutions can be inferred from Figure 3, when crevices are anticipated in service. Grade 7 (or 11) (Ti-Pd) is favored in hot (> 70°C) acidic chloride, bromide, or iodide solutions, in the pH range of 0.8-3.0 (ie. Cl₂- sat. brines or heavy metal chloride solutions). Over the pH range of 3 to 12, grade 12 titanium may be preferred over Ti-Pd for cost reasons. The compatibility and inter-weldability of these alloys with C.P. grades permit local, selective integration of more resistant titanium alloy components (ie. flanges, joints, etc.) into C.P. titanium equipment to maximize cost-effective use. Where high strength
is required, the titanium alloys containing > 3% Mo can be expected to resist crevice attack down to the pH 1-2 range.  

Precious Metal Surface Treatments

Precious metal or precious metal oxide coatings on titanium alloy surfaces offer crevice corrosion resistance approaching that of the Ti-Pd alloy. The most common precious metals applied to titanium are palladium, platinum, and ruthenium, and their oxides. Thermal diffusion coatings of these metals are readily applied by firing in an air furnace after coating titanium with modified metal chloride solutions. The resultant coating (~0.1-10µ thick) is typically a mixture of titanium and precious metal oxides, depending on firing temperature.

Other methods of applying these precious metals on titanium surfaces include electroplating, brush-plating and ion-implantation. The electroplating and brush plating involves cathodic deposition from aqueous metallic chloride solutions to form metal layers on the order of 0.003-0.01mm thick. Brush plating permits spot or localized electroplating in the field by swabbing a simple hand-held anode. Palladium implantation generates Pd-rich surface layers on the order of 0.5µ or less in thickness. However, this method can be relatively costly and requires that the component be small enough to fit into the implantation chamber.

Other Metallic/Metallic Oxide Coatings

Other, but less costly, coatings which inhibit crevice corrosion in hot halide solutions include those containing metallic nickel or copper, their oxides (NiO, CuO), and/or the Fe₂O₃ and MoO₃ oxides. In very finely powdered form, these materials can be painted in thin layers on titanium crevice surfaces in slurry form. Alternatively, these powders can be formulated into sealants such as silicone or EPDM rubber. For example, a 5 wt. % addition of Ni metal/NiO (1:1 or 2:1) blended into EPDM gaskets effectively prevents crevice attack of C.P. titanium in hot, low pH, Cl₂-sat. brines. Crevice corrosion resistant surfaces may also be produced by a simple anodizing treatment in a molybdate solution. Finely-powdered conductive forms of carbon also effectively inhibit crevice corrosion when formulated (25-50 wt. %) into organic binders such as epoxy.

Thermal Oxidation

Improved crevice corrosion resistance is afforded from thermal oxide films formed when titanium alloys are heated in air at 450°-800°C for 2-10 minutes. Increasing temperature or time at temperature within this range results in thicker, more protective (rutile TiO₂) oxide films. Thermal oxide films offer superior resistance compared to anodized or as-pickled surfaces, but avoidance of mechanical damage or plastic metal strain is required for optimum protection. Long-term protection in hot low-pH brines may be limited, and should mainly be considered for the least resistant titanium alloys under mildly aggressive or borderline crevice corrosion conditions.

Noble Alloy Contact

Crevice corrosion in metal to metal contact points, joints, and seals can be averted by incorporation of a more noble alloy member into the crevice. The more noble alloy member would anodically protect the other less-resistant creviced titanium alloy number through the galvanic couple within the crevice. Effective noble metal crevice members include the precious metals, the more resistant titanium alloys (i.e. grades 7, 11, and 12), and most copper and nickel alloys. Other dissimilar metals which inhibit titanium crevice corrosion when creviced together with C.P. titanium are listed in Table 3. These metal combinations have particular relevance to tube to tubesheet joints of heat exchangers, where copper, stainless steel, or nickel alloy tubesheets often contact C.P. titanium tubing. However, possible aggravated attack of the non-titanium member of these galvanic couples should be considered as well.

Surface Pickling

If the presence of galled-or smeared-in surface iron is suspected on titanium equipment, it should be removed to prevent possible localized attack in hot halide service. This surface iron contamination can be removed with a light 5-10
minute pickle in near ambient temperature 35-5 or 12-1 vol % HNO₃-HF solution, followed by water flushing. This procedure, which removes on the order of 0.03mm from the metal surface, is more effective than either anodizing or pure HNO₃ pickling. Heavy damaged or gouged and cut surfaces may require longer pickle times to remove heavy metal laps or smears under which crevice attack may initiate.¹

Summary
A review of the relative influences of six primary factors on the susceptibility of titanium alloys to crevice corrosion is presented. These, often interacting, factors include temperature, solution chemistry/pH, nature of the crevice, alloy composition, metal surface condition, and metal potential. A number of practical methods for effectively preventing titanium alloy crevice attack are offered as well, all of which promote titanium passivation through ennoblement within crevices.

References