GATEKEEPER
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Acidizing Effects of Titanium Grade 29 Tapered Stress Joints

Titanium (Ti) alloys are attractive to subsea oil and gas operators due to their high strength, low density relative to steel, and innate corrosion resistance. The current primary application for Ti alloys has been in tapered stress joints (TSJs). Ti stress joints are a primary and sole barrier to loss of a riser and release of hydrocarbons into the environment. Therefore, the integrity of the TSJ is of utmost importance, and integrity loss of a TSJ carries a very high inherent risk.

While Ti alloys are heralded for their superior corrosion resistance, there are some environments in which Ti is susceptible to corrosion or environmentally-assisted cracking (EAC). This is particularly seen during acid stimulation (acidizing) of offshore wells. Acidizing involves pumping acid into a wellbore or geologic formation that is capable of producing oil and/or gas. The purpose of acidizing is to improve a well's productivity or injectivity after production has declined [4]. Spent acid is then produced through the Ti TSJ. Depending on acid properties, this acid can have an impact on the long-term mechanical integrity of the TSJ, potentially leading to general corrosion, hydrogen embrittlement, and premature failure. Corrosion inhibitors are typically mixed with the acid to prevent piping and tubing from corroding in the presence of fresh acids; however, these inhibitors must be effective with the given pipe material and remain effective for the duration of the acidizing.

There are two grades of Ti currently utilized for TSJ manufacture: Grade 23 and Grade 29. Gr23 is a more economic choice, but it does not perform as well in sour service or in temperatures above 167°F (75°C), which precludes it from use in most deep water offshore fields.

Currently the most common utilized Ti Alloy in TSJs is Gr29. The Gr29 alloy is more robust due to the platinum group metals, such as ruthenium (Ru), that are added to enhance the crevice and stress corrosion temperature limits for the alloy to over 500°F (260°C) in sour service and high chloride environments by shifting the hydrogen ion reduction kinetics [3]. As high pressure and high temperature (HPHT) wells become more common, the need for high strength materials that can withstand sour and chloride-containing fluids at high temperature grows, which makes Gr29 Ti a good candidate for many areas of offshore oil and gas systems. This GATEKEEPER will address the viability, concerns, and recommended future work associated with acidizing corrosion issues of Ti Gr 29 in TSJs in offshore oil and gas.

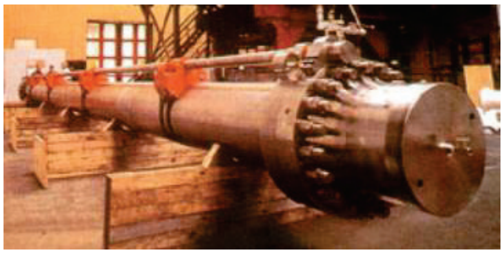
Acid-Related Integrity Threats to Titanium TSJs

As production profiles decline, it is common for operators to pump specific acids into wells to stimulate production by dissolving sand and minerals. Most operators do not consider acidizing when selecting materials for a field because it is a "process upset" condition, typically lasting no longer than 24 hours at a time. However, short-term intermittent use does not guarantee that the acidizing will have minimal or no effect on the materials.

Ti alloys are particularly susceptible to acids with high hydrochloric acid (HCl) content or any hydrofluoric acid (HF) content. Table 1 highlights the resistance or compatibility of Ti Gr 29 to common acidizing fluids. From this data, it is evident that Ti is particularly resistant to organic acids, but is not resistive to HF or HCl over 10 wt%; these acids will lead to corrosion and possible pitting.

Sodium molybdate or potassium pyroantimonate may inhibit corrosion of Ti in HCl, but not in HF [5]. Sodium molybdate inhibits the anodic reaction by surface adsorption, preventing the Ti from diffusing through the layer. However, it requires dissolved oxygen or an oxidant to form a protective film [6]. With aging wells, more frequent acidizing may jeopardize the reliability of Ti parts.

Acid compatibility screening studies in which GATE has participated, have shown that corrosion rates of the Gr 29 Ti can be extremely rapid in spent acids, but are highly dependent on acid composition, acid concentration, and the presence of inhibitors. No evidence of cracking has been found in short-term testing, however, embrittlement of the Ti alloy may remain a long-term threat and this may increase with each acid exposure. More studies are needed to more accurately frame the likelihood of TSJ failure due to acidizing jobs over an extended period.



Section of a Drilling Riser Made From Ti-6Al-4V [10]

Ti Alloys Gr23 & Gr29

Grade	23	29
Al (wt%)	5.5-6.5	5.5-6.5
V (wt%)	3.5-4.5	3.5-4.5
Ru (wt%)	0	0.08-0.14
O (max wt%)	0.08	0.08
Fe (max wt%)	0.03	0.03
C (max wt%)	0.0125	0.015
N (max wt%)	0.25	0.25
H (max wt%)	0.13	0.13
Yield Strength, 0.2% offset - ksi (MPa)	115 (793)	110 (759)

Comparing Ti Alloys to Alternatives [8,9]

Material	Density – lb/in^3 (g/cm^3)	Yield Strength – ksi (MPa)	Tensile Strength – ksi (MPa)
Ti 23	0.160 (4.43)	115 (790)	125 (860)
Ti 29	0.160 (4.42)	120 (828)	130 (897)
X65	0.283 (7.82)	65 (448)	77 (531)
AISI 420 (13Cr)	0.282 (7.80)	197 (1360)	294 (2025)
2205 DSS	0.282 (7.80)	66.7 (460)	109 (750)

Acid	Resistant/Compatible?
12% HCl + 3% HF	NO
9% HCl + 1% HF	NO
12-32% HCl	NO
<12% HCl with inhibitor	YES
10% Acetic	YES
10% Formic	YES
10% Acetic + 10% Formic	YES

Table 1: Ti Gr 29 in Acid [7]

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Ti Alloy Corrosion Tolerance

Ti alloys are treated as completely corrosion resistant in the oil and gas production environments, thus Ti alloy parts are designed with little or no corrosion tolerance. This assumption is safe under normal operating conditions, but in cases of frequent acidizing, acids can potentially corrode Ti beyond its tolerance or cause hydrogen embrittlement until its required strength and ductility for the operation is lost. Certain acid combinations can lead to corrosion issues such as pitting, hydrogen embrittlement, etching, or intergranular attack, which may compromise the integrity of Ti structures. These issues need to be adequately addressed in future design considerations.

Hydrogen Embrittlement

One major threat of acidizing to Ti TSJ integrity is hydrogen embrittlement. Hydrogen embrittlement occurs when hydrogen ions diffuse into the metal, forming hydrogen gas bubbles within the metal. This process creates pressure in the metal, reducing the ductility, toughness, and tensile strength of the material.

It is also possible for Ti to undergo embrittlement by reacting with free hydrogen ions to form Ti hydrides. These hydrides are very brittle and, if they form to a significant extent, operational stresses will lead to brittle cracking of the hydride surface layers. With the addition of acid to the fluid in the pipe, the pH is lowered and more hydrogen ions are available for diffusion into the Ti. High temperature wells have increased susceptibility to hydrogen embrittlement because diffusion increases with increasing temperature.

The embrittlement of Ti may be dependent upon the solubility and diffusivity of the alloy and its microstructure. Gr 29 consists of α and β phases, with composition dependent upon the forging and heat treatment process.

Hydrogen embrittlement by any mechanism increases the chance of brittle failure. Ti is subject to fatigue failure, and hydrogen embrittlement lowers the fatigue life after a certain penetration thickness. Lowered fatigue life can lead to crack propagation and premature failure.

Proposed Solutions

While acid compatibility issues may exist related to Ti alloys used in upstream operations, both small and large-scale testing can help define the problem, and options such as control of process conditions or use of acidizing inhibitors can help mitigate these issues.

Inhibitors can prevent the corrosion of metals in hostile environments. The effectiveness of an inhibitor is related to its protection as well as its availability; an inhibitor must protect against corrosion and be active in the system for the duration of the acidizing. Inhibitors are commonly used in acid jobs to protect ferrous alloys during acid injection in the system, but these inhibitors are not always equally effective for mitigating Ti alloy corrosion. The inhibitors may also not remain effective against "spent" acid being produced after acidizing is complete.

Sodium molybdate or potassium pyroantimonate inhibitors have been shown to protect Ti Gr 29 from <10 wt% HCl acids [7]. Ti Gr 29 requires no inhibitor for most non-acidizing environments up to 400°F (204°C), but work must be done to improve the inhibitors if they are to be used in more severe conditions.

During acid flowback, inhibitor may be injected upstream of the riser and therefore not reach the Ti alloy. This issue can be alleviated by a few options:

- Employ a corrosion inhibitor injection point upstream of the riser to protect the Ti TSJ
- Develop new inhibitors specifically geared toward protecting Ti from acid corrosion.
- Utilize a separate, designated flowline with a non-Ti flex joint when acidizing in order to prevent acid contact with the TSJ. This separate piping run would allow for separate handling and targeted inhibition of acidizing, prolonging the life-cycle of the TSJ.

More frequent examination of Ti alloy parts used in new environments and applications would further the understanding of the long-term effect of the environment on the alloy's integrity. Unfortunately, most non-destructive evaluations (NDEs) are impractical in tapered non-ferrous parts such as TSJs. It would be beneficial to develop new NDE methods to adequately monitor the parts for general corrosion, hydrogen embrittlement, and cracking.

As operators only began using Ti TSJs in the late 1990s, they are relatively new in the industry and most, if not all, of the original parts are still in service. Performing a thorough inspection of a decommissioned TSJ would also help ascertain a better understanding of acidizing effects on these parts.

Recommendations

Aging Ti TSJs pose a potential issue for operators who need to understand their end-of-life use. The long-term effects of flowing spent acidizing chemicals through Ti TSJs has not been fully explored or understood. The eventual decommissioning and inspection of a Ti TSJ that has seen contact with acidizing fluids during its service life would shed light on the effects of acidizing in Ti TSJs. Metallurgical analysis of flow-wetted surfaces for pitting, hydrides, etching, and intergranular attack, fatigue life analysis, and mechanical property testing would be extremely beneficial to understanding the long-term consequences of intermittent acidizing and would give a new perspective on the future of Ti alloys in subsea applications.

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