

# Crevice Corrosion of Titanium in High Temperature-Concentrated Chloride Environments

Mohammed I. Abdulsalam

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Crevice corrosion of titanium is activated in concentrated chloride media at 100 °C. This was possible only with the tightest gap (0.005 cm) between Ti-Ti surfaces. No crevice corrosion was observed with greater gap dimensions. The design of the crevice led to the occurrence of two concentric circular rings of corroded areas, with many pits on them. After potentiostating in the passive region for 5 h in 25% NaCl (pH = 4.7)—where hydrogen evolution is thermodynamically prohibited—hydrogen gas bubbles were observed to egress out of the crevice mouth during ongoing crevice corrosion. This indicates that hydrogen evolution occurs within the crevice. The results are compatible with the occurrence of gradually increasing ohmic potential shift and localized acidification in the crevice electrolyte as judged by the measured gradual increase of the crevice corrosion current. The high acidity of the bulk electrolyte does not seem to be sufficient or even a necessary condition for crevice corrosion to occur.

**Keywords** acidification, chloride, crevice corrosion, high temperature, hydrogen bubbles, ohmic potential drop, titanium

## 1. Introduction

Titanium and its alloys provide excellent corrosion resistance in many aqueous environments. This is attributed to its ability to form a protective oxide film in the presence of air or water. The growth of this film is accelerated in oxidizing environments and its composition varies widely depending on the conditions (Ref 1-3). This film is very stable and is attacked only by a few substances including hot concentrated reducing acids. Conversely, the film is stabilized by the presence of oxidizing species (Ref 4, 5). Titanium is capable of healing this film almost instantaneously wherever moisture and oxygen are present because of its strong affinity for oxygen. In anhydrous or corrosive reducing conditions the protective film may not be regenerated if damaged (Ref 6, 7).

Titanium and its alloys are used widely in refineries as coolers and overhead condensers, e.g., in catalytic cracking, desulfurization, distillation,...etc. In some of these applications such as in shell and tube heat exchangers, air coolers, piping and pressure vessels, the resistance of titanium to corrosion becomes questionable. One factor that is believed to contribute to this is the presence of chloride salts in the crude oil. These salts can hydrolyze to produce hydrochloric acid. The corrosion behavior of titanium in such media has long been attracting the attention of researches as well as the titanium industry (Ref 8-16).

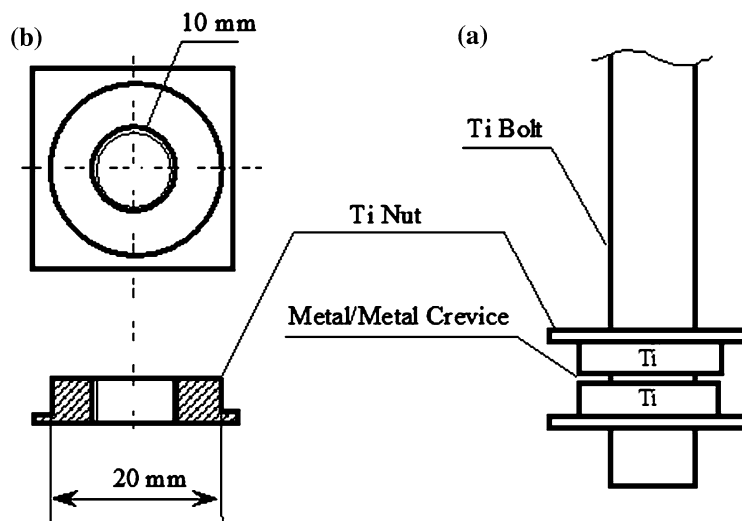
Some of the early corrosion failures of commercially pure Ti (grade 2) have been described (Ref 6). Grade 12 Ti (alloyed titanium) has been used in atmospheric crude distilling column overhead condensers up to about 170 °C. However, when this alloy was used as bundles for overhead/crude exchanger, leaks developed after 4 years. An investigation revealed localized corrosion. This was attributed to the lack of enough water to wash away the amine chloride salts that accumulated in the crevices between the tubes and baffles. At the elevated temperature, high acidity and chloride concentration, titanium could not maintain its passivity in the restricted crevice areas in the under deposit beneath the baffles.

The objective of this work is to study crevice corrosion of titanium at high temperature-concentrated chloride environments. In addition to its relevance to the oil industry, this work is also significant with regard to the application of titanium and its alloys in geothermal brine service (Ref 9, 16).

## 2. Experimental Procedure

A crevice was created between two nuts threaded onto a bolt, all made from commercially pure titanium. The crevice was made by finger-tightening the two nuts against each other on the bolt. A schematic diagram is shown in Fig. 1. This arrangement makes a metal/metal crevice between the adjacent surfaces of the two nuts. The crevice gap dimension was measured using an optical microscope. It was typically 0.005 cm. The bolt was designed in such a way as to eliminate crevice corrosion between the bolt and the nuts. It was machined down to a 3 mm thick slab in the region where the nuts are mounted. This made the gap between the bolt and most of the inner circumference of the nuts large enough so that crevice corrosion did not occur. It also exposed the crevice opening at the inner circumference of the nuts to the controlled potential and the bulk electrolyte. The nuts and bolt were examined after each experiment. In all the measurements

Mohammed I. Abdulsalam, Department of Chemical and Materials Engineering, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia. Contact e-mail: miabdul@yahoo.com.



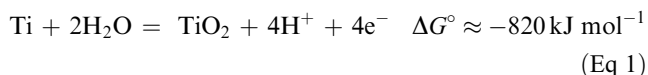
**Fig. 1** Schematic of the metal/metal crevice specimen. (a) Crevice setup and (b) top and side view of the titanium nut

reported in this work, no discernible crevice corrosion was detected on the threads between the bolt and the nuts nor on the internal crevice surface at crevice gap openings.

Both crevice surfaces were wet finished with #1500 SiC paper. The solution was deaerated by bubbling purified nitrogen for 30 min prior to running the experiment. A saturated calomel electrode (SCE) was used as a reference electrode. A platinum wire was used as a counter electrode. Measurements were performed at 80 and 100 °C at a potential of -200 mV (SCE) in an acid medium of pH = 0.6 and in NaCl medium of pH = 4.7.

### 3. Results and Discussion

Titanium is known to be highly reactive (Ref 2, 17, 18). Some 40 different reactions were reported at 25 °C covering a broad range of reduction potentials (Ref 18). The remarkable passivity of titanium is attributed to the formation of a protective film of TiO<sub>2</sub> on the titanium surface at room as well as at high temperatures:



This film is very stable by virtue of the very low value of its free energy of formation. It passivates the metal and diminishes its dissolution over a broad range of potential in various environments. While this oxide can be formed via many other reactions (Ref 2, 17, 18), there are several other oxides (TiO<sub>x</sub>, where  $x < 2$ ) which impart various degrees of passivity on the metal.

Under active potentials, or whenever the film breaks, Ti dissolves (Ref 3) to give Ti(OH)<sup>2+</sup>.



Reaction 2 indicates that the anodic dissolution (corrosion) of titanium leads to an increase in the acidity of the medium. If this were to occur in a restricted location (e.g., crevice), the

process is accompanied by progressive increase of acidity (decrease of pH), which promotes local dissolution of the metal, which further decreases the pH. This is the basis of the famous concept of autocatalytic nature of crevice corrosion.

The electrochemical behavior of titanium in aqueous media is also affected by the hydrogen evolution reaction (h.e.r)11 of which its equilibrium potential is determined by Nernst's equation. Therefore, higher acidity (lower pH) and lower values of  $P_{\text{H}_2}$  make  $E_{\text{H}_2/\text{H}^+}$  less negative (less cathodic). Table 1 lists the values of  $E_{\text{H}_2/\text{H}^+}$  as calculated using Nernst's equation for the different test conditions, using a residual value of  $P_{\text{H}_2} = 10^{-3}$  atm. Under potentials more negative (more cathodic) than  $E_{\text{H}_2/\text{H}^+}$ , h.e.r. proceeds in the forward direction and hydrogen is evolved in the form of gas bubbles which are dispersed in the electrolyte. If these bubbles were trapped within the electrolyte in a restricted location (crevice), the resistance of the electrolyte increases greatly and hence the flow of even a small current within this electrolyte produces a large potential drop.

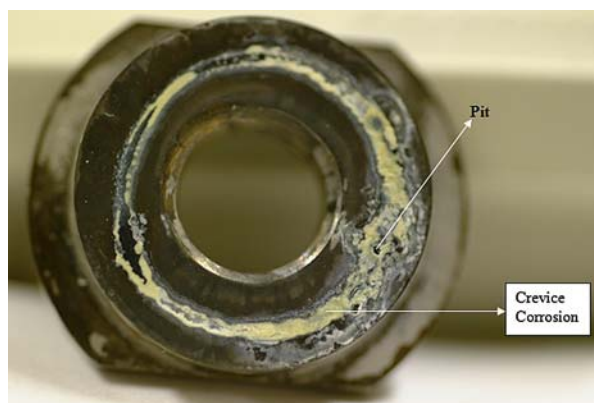
The results of crevice corrosion testing are summarized in Table 1. Evidently, the thermodynamic conditions of tests #1 and #2 are favorable for the evolution of hydrogen gas on the exposed titanium surface from the bulk electrolyte. This is in agreements with the measured cathodic currents produced by the titanium electrode throughout the tests, and the observation of gas bubbles evolving continuously. No crevice corrosion was observed in test #1, Fig. 2. On the other hand, test #2 produced crevice corrosion, as shown in Fig. 3. A white corrosion product resulted from test #2 while the electrolyte turned yellow. The only difference between tests #1 and #2 is that the concentration of chloride ions in test #2 is about an order of magnitude greater than that in test #1. Consequently, one concludes that the high acidity and the modest chloride concentration in test #1 were not enough to initiate crevice corrosion. Furthermore, the occurrence of crevice corrosion in test #2 is attributed to the high level of acidity and chloride concentration inside the crevice.

Under the condition of test #3, the external crevice surface is in the passive region, judged by the negligibly small passive anodic current produced for flat specimen with no crevice. Furthermore, under the controlling potential -200 mV (SCE) at

**Table 1** Details of the crevice corrosion tests on a tight titanium crevice, see text

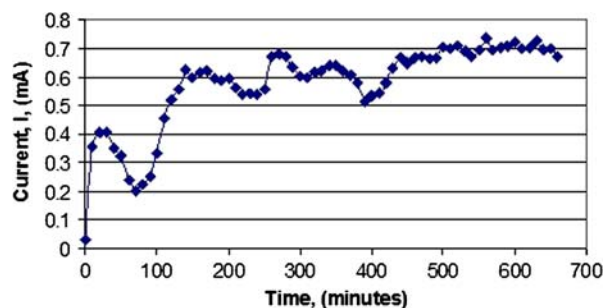
Conditions	Test #1	Test #2	Test #3
Electrolyte	1.5% HCl	1.5% HCl + 19%NaCl	25% NaCl
Temperature	80 °C	100 °C	100 °C
pH	0.6	0.6	4.7
$E_{H_2/H^+}$	-178 mV (SCE)	-174 mV (SCE)	-477 mV (SCE)
Duration	24 h	12 h	25 h
Current	~0.5 mA cathodic	~0.3 mA cathodic	Anodic current,
Result	No crevice corrosion, see Fig. 2	Crevice corrosion occurred, see Fig. 3	Crevice corrosion occurred, see Fig. 5

All tests were performed in deaerated electrolytes under a potential of, -200 mV (SCE)

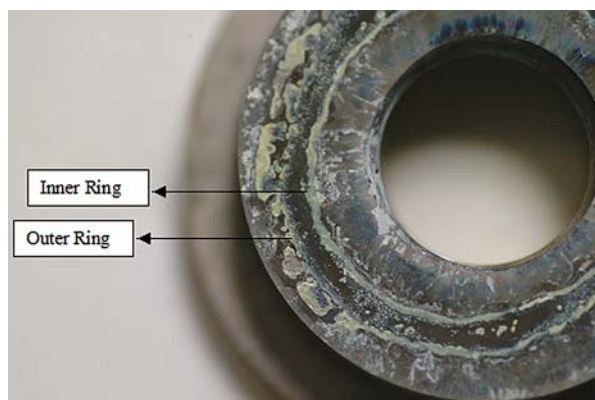
**Fig. 2** Photograph of the crevice surfaces after test #1, 1.5 % HCl at 80 °C**Fig. 3** Photograph of one side of the two attacked crevice surfaces after test #2, 1.5% HCl + 19% NaCl at 100 °C

the external surface of the crevice, the evolution of hydrogen at pH = 4.7 is thermodynamically unfavorable in view of the fact the equilibrium potential for h.e.r is -558 mV (SCE). Throughout the experiment, although we observed an anodic current started at the microampere range, it grew with time into the milliamper range, as shown in Fig. 4. This indicates the activity of crevice corrosion.

It has long been established (Ref 19) that when an electrochemical reaction occurs on a cracked surface, the potential changes with increasing distance within the crevice due to ohmic potential drop caused by the flow of ions within

**Fig. 4** Current-time transient during on-going crevice corrosion of titanium immersed in 25 wt.% sodium chloride NaCl at 100 °C, test #3

the crevice electrolyte. The extent of the potential shift within the crevice can be many hundreds of mV depending on the gap dimension of the crevice, the resistivity of the crevice electrolyte and the magnitude of the current (Ref 19-26). Therefore, in our case here we expect the potential deep inside crevices to shift from -200 mV (SCE). Evidently, If this shift in potential is large enough, the local potential deep inside the crevice might become more cathodic (negative) than the equilibrium potential for h.e.r. In this case hydrogen gas bubbles evolve inside the crevice and disperse in the highly constricted crevice electrolyte to increase its resistivity and hence progressively increase the potential drop. Furthermore, the resulting titanium ions that are trapped inside the crevice,



**Fig. 5** Photograph of one of the crevice sides after test #3. The two rings of the surface attack appear in the figure

are hydrolyzed to produce an acidic local environment, with a pH well below 1 (Ref 3), which destabilizes the protective film (Ref 26). The localized breakdown of this film under the more active local potentials and constricted acidified solution deep inside the crevice leads to anodic dissolution of titanium, similar to the condition shown in Fig. 4. Figure 5 illustrates the crevice corrosion which resulted from this test.

It is interesting to note that the pH of the bulk electrolyte in test #3 decreased during the test from an initial value of 4.7 to a final value of 2.7, attributed to the localized acidification inside the crevice. Another noteworthy observation is that for test #3 and after about 5 h we observed the egress of intermittent hydrogen gas bubbles off one location of the external crevice gap every about 10 s. Figure 6 displays the appearance of this location after test #3. The results indicate that, after the lapse of this time, conditions within the crevice have become favorable for hydrogen evolution ( $\text{pH} \approx 1$  and active potential). Hydrogen evolution cannot occur at the controlling potential at the external surface of the crevice  $-200 \text{ mV(SCE)}$  even at  $\text{pH} = 1$ . Consequently the potential must have shifted to a more cathodic value within the crevice in addition to the increased acidification, i.e., the process is accompanied by a potential shift and a pH gradient within the crevice electrolyte. A rough calculation reveals that a potential shift of about or greater than



**Fig. 6** Photograph of the crevice cell after test #3, 25 % NaCl at  $100 \text{ }^\circ\text{C}$

200 mV in addition to the pH shift from 4.7 to 1 are required to evolve hydrogen gas bubbles within the crevice in test #3. This combination of potential shift, acidification and chloride accumulation has often been cited as reasons for the stabilization of crevice corrosion in some alloys (Ref 19-26).

An important finding in our study is that crevice corrosion attacked the surface in two circular rings with some pits into them, and no attack in the other areas. This can be readily explained in view of the fact that our experimental setup geometry provided a crevice with two circular mouths facing the electrolyte; one is the outside rim of the specimen and the other is much smaller next to the titanium bolt. It was always noticed that the two concentric rings were not in the middle of the crevice area, but rather shifted closer to the inner circumference of the nuts. A possible interpretation is the operation of the IR drop mechanism in this system which predicts similar behavior. More work is needed to clarify this behavior.

## 4. Conclusions

The present work demonstrates crevice corrosion of titanium undergoes at  $100 \text{ }^\circ\text{C}$ . Crevice corrosion occurred in highly concentrated chloride environment and for tightest crevices. The high acidity of the bulk electrolyte does not seem to be sufficient or even a necessary condition for crevice corrosion to occur. The results show that localized acidification occurs inside the crevice and that significant ohmic potential shifts occur within the crevice electrolyte.

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