$\cancel{D}$T# 47518
QA:NA 4/13/06

UCRL-PROC-218716

COMPARATIVE CORROSION BEHAVIOR OF TWO PALLADIUM-CONTAINING TITANIUM ALLOYS

Tiangan Lian
Lawrence Livermore National Laboratory
7000 East Ave, L-631
Livermore, California, 94550 USA

Takashi Yashiki
Kobe Steel, Ltd.
Osaka, 541-8536 Japan

Takenori Nakayama
Kobe Steel, Ltd.
Kobe, 651-2271 Japan

Tomoaki Nakanishi
Kobe Steel, Ltd.
Kobe, 657-0845 Japan

Raul B. Rebak
Lawrence Livermore National Laboratory
Livermore, California, 94550 USA

ABSTRACT

The ASTM standard B 265 provides the requirements for the chemical composition of titanium (Ti) alloys. It is planned to use corrosion resistant and high strength titanium alloys to fabricate the drip shield at the proposed Yucca Mountain Repository. Titanium grade (Gr) 7 (R52400) and other Ti alloys are currently being characterized for this application. Ti Gr 7 contains 0.15% Palladium (Pd) to increase its corrosion performance. In this article we report results on the comparative short term corrosion behavior of Ti Gr 7 and a Ruthenium (Ru) containing alloy (Ti Gr 33). Ti Gr 33 also contains a small amount of Pd. Limited electrochemical testing such as polarization resistance and cyclic potentiodynamic curves showed that both alloys have a similar corrosion behavior in the tested environments.

Keywords: Ti Gr 7, Ti Gr 33, corrosion, chloride, fluoride

INTRODUCTION

In its current design, the drip shields for the high-level nuclear waste containers for the Yucca Mountain repository will be mainly made using Ti Gr 7 (R52400) [1]. Ti Gr 7 is a highly corrosion resistant alloy, especially because it contains 0.15% palladium (Pd) [2].

A higher strength structural support titanium alloy such as Ti Gr 24 or Gr 29 [2] will also be used for the fabrication of the drip shield.

Titanium and Ti alloys have excellent corrosion resistance due to the presence of a highly adherent and continuous oxide film that develops on the surface of the fabricated components [3]. If the film is damaged, the high affinity of Ti for oxygen causes this film to reform instantly even in presence of small amounts of oxygen or moisture. This protective oxide film is basically TiO_2. The addition of small amounts of alloying elements (2-3%) to titanium does not alter the protective stability of the oxide film on Ti [3]. Also the addition of small amounts of platinum group metals (PGM) such as Pd, Ru, etc. reduces considerably the general corrosion rate of Ti in reducing acids [3-5]. Some Ti alloys may be susceptible to crevice corrosion under certain conditions; however, Ti alloys are practically immune to pitting corrosion in chloride solutions under most practical applications. It has been suggested that the susceptibility to crevice corrosion is due to the formation of low pH reducing solution under occluded conditions, where the corrosion rate of Ti is higher than in oxidizing conditions [5]. Halide and sulfate containing solutions may induce crevice corrosion in Ti at temperatures higher than 70°C [5]. Anodic polarizations of Ti Gr 7 in chloride and fluoride containing solutions at 95°C have shown that the presence of fluoride

1

produces significantly higher current densities at potentials above the corrosion potential [6]. The presence of fluoride may have also rendered Ti Gr 7 more susceptible to crevice corrosion under anodic polarizations [6].

Ti alloys have a broad range of application in the industry as corrosion resistant materials. Uses include seawater, wet chlorine, chlorinated organic compounds and oxidizing acids (e.g. nitric and chromic acids). Some of the media in which Ti should not be used include hydrofluoric acid, dry chlorine and hot pure sulfuric acid solutions.

The goal of this study was to determine whether a Ti Gr 33 low-Pd (0.01%) titanium alloy would have corrosion resistance similar to the more expensive Ti Gr 7 in both chloride and fluoride containing environments. The focus of this testing program was on the susceptibility of the alloys to localized corrosion. Therefore, only artificially creviced specimens were used.

EXPERIMENTAL

Electrochemical Tests

Table 1 shows the nominal chemical composition of the Ti Gr 33 and Ti Gr 7 specimens prepared for the tests.

Table 1. Nominal Chemical Composition (in wt.%) of Ti Gr 33 and Ti Gr 7 Alloys. The Balance of the composition is Titanium (>99%)

Element →	Ni	Cr	Pd	Ru	Fe
Alloy ↓					
Ti Gr 33	0.44	0.16	0.010	0.032	0.05
Ti Gr 7	-	-	0.17	-	0.067

Element →	C	O	N	H
Alloy ↓				
Ti Gr 33	0.008	0.102	0.003	0.0092
Ti Gr 7	0.006	0.084	0.004	0.0003

The composition of Ti Gr 7 and Ti Gr 33 are given in ASTM standard B 265. According to B 265, the composition of Ti Gr 33 is similar to Ti Gr 34. The main difference between Ti Gr 7 and Ti Gr 33 compositions is that the latter contains small amounts of Ru, Ni, Cr and also a lower content of Pd than Ti Gr 7. The alloy Ti Gr 33 used here is also known as AKOT.[1]

---

[1] AKOT is a registered trademark of Kobe Steel Ltd.

The specimens used for corrosion testing were prism crevice assemblies (PCA). These specimens were 19×19×9.5 mm with a hole in the middle to attach the crevice formers (CF) (Figure 1). The specimens were fabricated in Kobe (Japan) and tested in Livermore (CA). Each specimen was wet ground with 600-grit SiC paper, and then ultrasonically cleaned in de-ionized water just before testing. Each specimen was then sandwiched by a pair of serrated ceramic crevice formers (ASTM G 48), using a Ti bolt and nut to apply the desirable tightness or torque (70 in-lb). Part of Ti bolt was sleeved with Teflon tubing to prevent the Ti bolt from making electrical contact with the test specimen. The specimen was then mounted in a specimen holder with electrical connection to run the polarization studies (Figure 1b). The final exposed surface area for the specimen after the crevice assembling was 14.06 cm².

A three-electrode cell (Figure 1a), with a capacity of one liter, was used for all the experiments. Approximately 900 mL of electrolyte solution was used in each test. A saturated silver/silver chloride (Ag/AgCl, pre-filled with 4 M KCl saturated with AgCl) reference electrode was used for measuring the potential of the working electrode. A solution bridge with a Luggin probe was used to maintain an ionic conductive path between the working electrode and the reference electrode, while a cooling jacket was used to maintain the reference electrode at near room temperature. A platinum (Pt) rod or sheet was used as a counter electrode. The electrochemical cell assembly was placed in a heating mantle to maintain the temperature of the test solution. A condenser was used to prevent solution evaporation. The electrochemical polarization measurements were conducted through a commercial potentiostat that was integrated with a desktop computer and the companion software.

The test solutions used in this study were 1 mol/L (or 1 M) NaCl brines. To study the effects of fluoride, 0.1 mol/L NaF was added into the NaCl brines. The solution pH was adjusted prior to each test to pH values of 4 or 8. The test temperature was 95°C. N_2 gas purging was used to de-aerate the test solutions. Gas purging began at least one-half hour before the specimens were placed into the solution. The test specimens were stabilized for 1 or 2 hour in the test solution before the electrochemical measurements were started.

Cyclic potentiodynamic polarization (CPP) measurements were performed to assess the localized corrosion susceptibility of both Ti Gr 7 and Ti Gr 33 in NaCl brines with and without the presence of fluoride. A potential scan rate of 600 mV per hour was used for all polarization measurements (0.167 mV/s). The CPP technique is described in ASTM G 61 (7). Open-circuit potential (OCP) immersion tests were also performed to evaluate the resistance of the Ti alloys to corrosion as a function of time both in pure NaCl solutions and in fluorinated

salt solutions. In these tests, the specimens were exposed to the test solution for up to two weeks. The free corrosion potential (E_{corr}) was monitored as a function of time, and polarization resistance (Rp) measurements were performed at various time increments during the exposure period. Post-test surface examinations determined the severity of corrosion in each tested specimen.

The corrosion rate was estimated from the polarization resistance tests using the following formulas given in ASTM standards G 59 and G 102 (7)

$$i_{corr} = \frac{1}{R_p} \times \frac{b_a \cdot b_c}{2.303(b_a + b_c)}$$

$$CR(\mu m / yr) = k \frac{i_{corr}}{\rho} EW$$

Where k is a constant (3.27×10^{-3} mm g/μA cm yr). The Tafel constants b_a and b_c were assumed to be $\pm$ 120 mV/decade, the density (ρ) of both titanium alloys was taken as 4.54 g/cm³ and the equivalent weight (EW) as 11.98.

RESULTS

Table 2 shows a description of the tests conducted and the outcome of the testing results. Table 3 shows results from the cyclic polarization tests including characteristic potentials such as breakdown potentials for both Ti alloys in each of the three tested solutions. Table 3 also shows the corrosion potentials and the corrosion rates under deaerated conditions for the twelve specimens listed.

Corrosion Rate of Ti Gr 33 and Ti Gr 7

Table 3 and Figures 2-3 show the corrosion rate for both Ti Gr 33 and Ti Gr 7 at the free corroding potential in three different electrolyte solutions at 95°C. Figure 2 shows that in 1 M NaCl pH 4 solution the corrosion rate of both Ti alloys are in the same order and between 0.5 and 0.6 µm/year. Figure 3 shows that in the pH 8 solutions, the corrosion rate of both Ti alloys is higher in the solution containing fluoride ions. The corrosion rates in Table 3 and Figures 2-3 are for short immersion times and may not be representative of the behavior of the Ti alloys for longer immersion times.

Anodic Polarization in NaCl Solutions

Based on the cyclic polarization measurement results (Figure 4), both Ti Gr 33 and Ti Gr 7 alloys showed excellent resistance to localized corrosion in acidic (pH 4) 1M NaCl solutions at 95°C. Ti Gr 33 and Ti Gr 7 had an identical

electrochemical behavior up to a potential of 1 volt. Above 1 volt their polarization behavior was slightly different but these high potentials are of little interest for corrosion applications since they are above the stability of water. For example, Table 3 shows that the breakdown potential E20 for Ti Gr 7 was approximately 100 mV higher than for Ti Gr 33. However, E20 had a potential beyond the range of interest for practical purposes. No localized corrosion was observed on either Ti Gr 33 or Ti Gr 7 specimens after the tests (Table 2) even though the specimens were polarized to very high potentials of near 5 volts. Only discoloration was observed on the surface.

Figure 1a. Set-up for Electrochemical Testing

Figure 1b. Specimen for Electrochemical Testing

Figure 5 shows the anodic polarization in near neutral (pH 8) 1M NaCl solutions only up to a potential of 1.5 V (for clarity purposes). The anodic behavior of both types of materials (Ti Gr 7 and Ti Gr 33) were practically identical. Both specimens show low passive currents and an extended passive region approximately 1500 mV wide. Ti Gr 7 had a higher value of E20 than Ti Gr 33 (Table 3) but for both metals the E20 values were well above a relevant potential for industrial applications. After the tests, both types of specimens showed slight discoloration but a total absence of localized corrosion in spite of the high applied potential (Table 2).

Figure 6 shows the comparison between the polarization curves for Ti Gr 33 in 1 M NaCl at pH 4 and pH 8. The corrosion potential was slightly higher in the pH 4 solution but the passive current density was practically the same in pH 4 and 8 solutions. Table 3 shows that for both Ti alloys the short-term E_{corr} was higher in the pH 4 solution than in the pH 8 solution.

Table 3 also shows that the breakdown potential E20 was slightly higher in the pH 8 solution than in the pH 4 solution
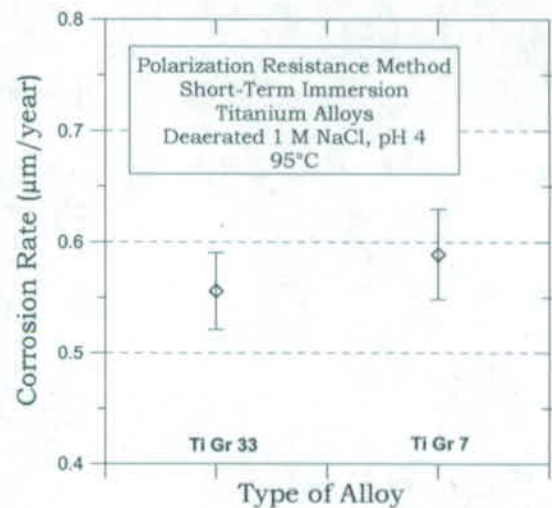

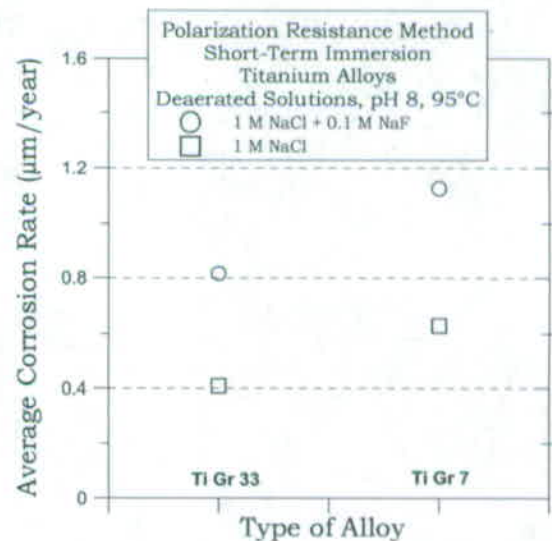**Figure 2.** Corrosion Rate in 1 M NaCl pH 4

Figure 3. Corrosion Rate in 1 M NaCl and 1 M NaCl + 0.1 M NaF pH 8

Anodic Behavior in Fluoride-Containing Solutions

Figure 7 shows the cyclic polarization curves of both titanium materials in 1 M NaCl + 0.1 M NaF pH 8 solution at 95°C. Due to the effect of the added fluoride, the maximum polarization in Figure 7 was only approximately 0.2 V compared to Figures 4-6 (in pure NaCl solutions) in which the

4

polarization was in the order of 5 volts. Figure 7 shows that the polarization behavior of both materials (Ti Gr 7 and Ti Gr 33) was the same in the fluorinated solution.
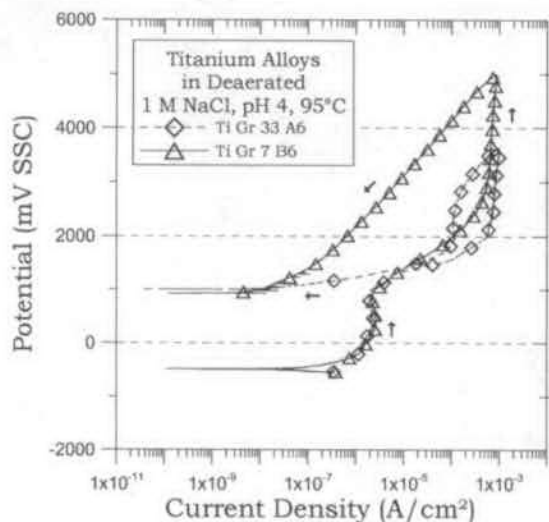
environment the current density increases continuously above the corrosion potential, that is, the passive behavior of Ti in pure NaCl solution practically disappears when fluoride is added.

Figure 4. Polarization Curves in 1 M NaCl pH 4

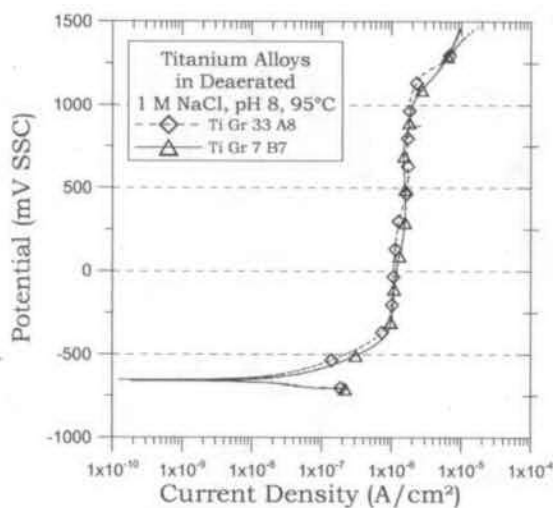**Figure 6.** Polarization Curves in 1 M NaCl pH 4 and 8

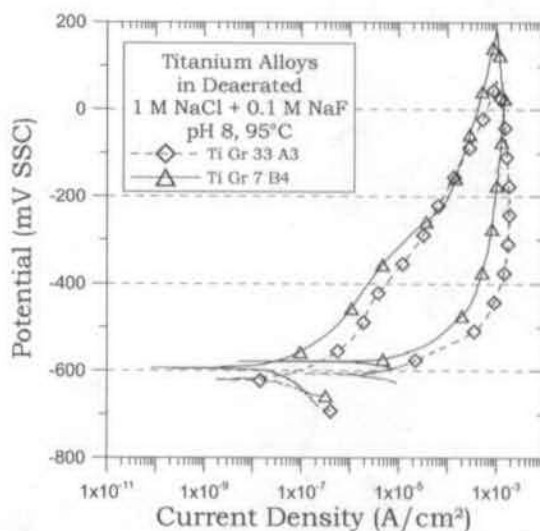**Figure 5.** Polarization Curves in 1 M NaCl pH 8

Figure 7. Polarization Curves in 1 M NaCl + 0.1 M NaF

Figure 8 shows comparatively for Ti Gr 33 the difference in the polarization behavior for 1 M NaCl with and without fluoride. From Figure 8, the destructive nature of fluoride on the passive film on titanium is apparent. In the fluoride-containing

Figure 8. Polarization Curves in 1 M NaCl and 1 M NaCl + 0.1 M NaF, pH 8 Solutions

It was apparent that the attack along the edges of the crevice formers was shallower for the Ti Gr 33 specimen.

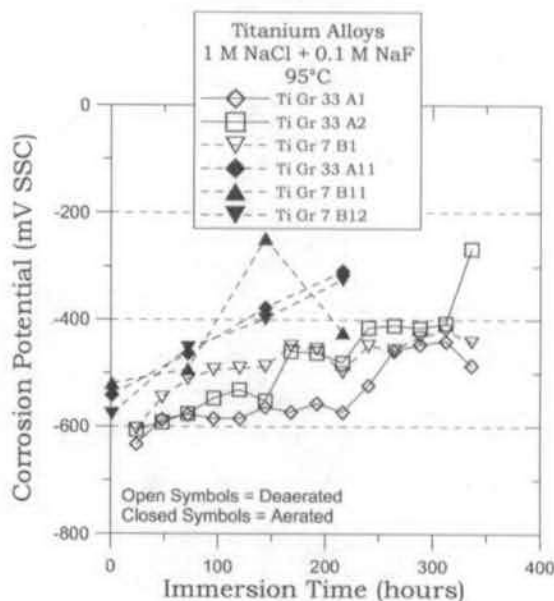**Figure 9.** Corrosion Potential vs. Time in 1 M NaCl + 0.1 M NaF pH 8

Open Circuit Potential Tests in Fluoride-Containing Solutions

Specimens of Ti Gr 33 and Ti Gr 7 were immersed in both aerated and deaerated 1 M NaCl + 0.1 M NaF solutions for more than ten days. The specimens were exposed at their free corroding potentials, that is, external polarization was not applied. The open circuit potential or corrosion potential was monitored as a function of time (Figure 9). At the same time, the resistance to polarization of the specimens was monitored at regular intervals. The polarization resistance was converted to corrosion rates (Figure 10). Figures 9 shows that the E_{corr} of the specimens immersed in the aerated solutions were higher than in the deaerated solutions. In both cases the E_{corr} slightly increased as the time increased. Figure 10 shows that the specimens immersed in the aerated solutions had an initial higher corrosion rate than the specimens immersed in the deaerated solutions; however, as the time increased the corrosion rate of the former decreased. Figure 10 also shows that both Ti Gr 33 and Ti Gr 7 specimens had a similar behavior in the tested fluorinated solutions. Table 2 shows that both Ti Gr 33 and Ti Gr 7 specimens suffered crevice corrosion even under open circuit conditions when exposed to fluorinated solutions. The observations in the open-circuit immersion tests revealed that corrosion attack without the external polarization was mostly along the crevice formers edges, and that the general corrosion on the bulk surfaces was relatively minimal.

Constant Potential Tests in Fluorinated Solutions

The susceptibility of crevice corrosion attack in fluoride-containing solutions was also confirmed using potentiostatic polarization measurements. In these tests a constant potential of −0.25 V (Ag/AgCl) was applied for sixty hours while the output current was recorded. Figure 11 shows that both materials behaved similarly. In the first hour of testing the current density increased and peaked at approximately 1 mA/cm². After this short initial period the current decreased and remained approximately constant for times longer than 10 hours. Figure 11 shows that the dissolution current was approximately the same for both Ti Gr 7 and Ti Gr 33. After 10-h exposure the dissolution rate of Ti Gr 7 was slightly higher than the dissolution rate of Ti Gr 33. Both Ti Gr 33 and Ti Gr 7 materials showed corrosion attacks along the edge of crevice teeth, and on the bulk surface away from the crevice regions as well (Table 2).

Remarks and Recommendations

The comparison of the relative corrosion resistance of Ti Gr 33 and Ti Gr 7 was made in a relative narrow electrolyte chemistry range. The findings here may not be applicable in other environments with very different water chemistries. It is likely

that the pure NaCl solution was too benign for both alloys and the solution containing 0.1 M NaF was too aggressive. Therefore, the corrosion behavior between these two alloys could not be discriminated.

Other important corrosion properties for Ti Gr 33 and Ti Gr 7 not studied are the effect of pre-filming and resistance to hydrogen-related degradation. For drip shield applications, the effect of pre-filming (pre-oxidation) under the initial hot (~200°C) dry conditions and resistance to hydrogen absorption, hydride formation, and hydrogen embrittlement may be equally important as the resistance to general and crevice corrosion under non pre-filmed conditions.
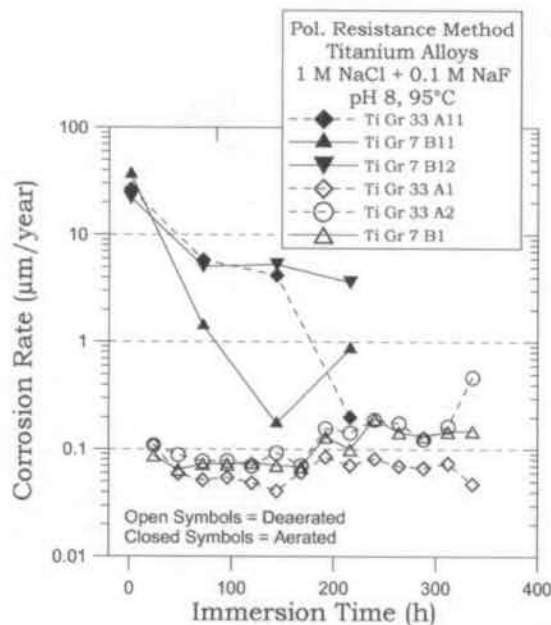

Figure 10. Corrosion Rate vs. Time in 1 M NaCl + 0.1 M NaF pH 8

Summary and Conclusions

This corrosion study on Ti Gr 33 and Ti Gr 7 materials can be summarized as follows

- Ti Gr 33 and Ti Gr 7 showed similar corrosion resistance in NaCl solutions with and without fluoride
- Both Ti Gr 33 and Ti Gr 7 are resistant to crevice corrosion in 1 M NaCl solutions
- Both Ti Gr 33 and Ti Gr 7 are susceptible to crevice corrosion in fluoride-containing aqueous solutions in the as-polished starting conditions.
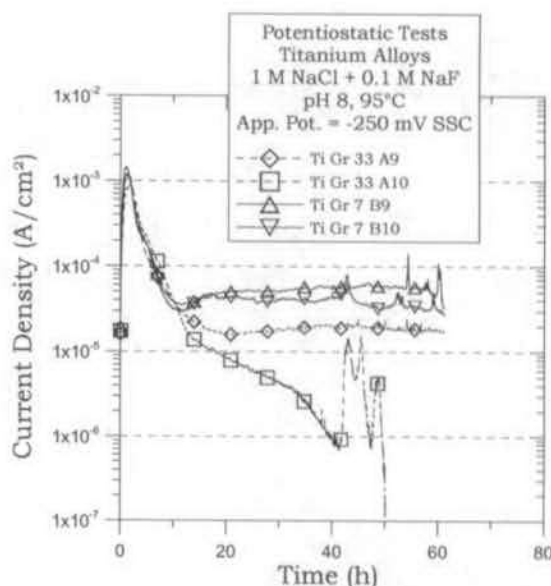

Figure 11. Constant Potential Tests in 1 M NaCl + 0.1 M NaF pH 8

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

REFERENCES

1. G. M. Gordon, Corrosion, 58, 811 (2002).

2. ASTM International, Annual Book of ASTM Standards, Volume 02.04 "Non-Ferrous Metals" Standard B-575 (West Conshohocken, PA: ASTM International, 2004).

3. R. W. Schutz, "Corrosion of Titanium and Titanium Alloys' in Metals Handbook, Volume 13B, p. 252 (ASM International, 2005).

4. Y. Sugizaki, K. Ueda, T. Yashiki, K. Mori, H. Yano and H. Satoh, Proc. Of the 4th International Offshore and Polar Engineering Conference, Vol. IV, p. 238 (The International Society of Offshore and Polar Engineers, 1994).

5. R. W. Schutz, Corrosion, 59, 1043 (2003).

6. C. S. Brossia and G. A. Cragnolino, Corrosion 57, 768 (2001).

7. ASTM International, Annual Book of ASTM Standards, Volume 03.02 "Wear and Erosion; Metal Corrosion" p. 91 (West Conshohocken, PA: ASTM International, 2004).

Table 2. Listing of the Electrochemical Tests and Results

Specimen ID	Test Environment	Test Description	Observations after the Tests
A1 (Ti Gr 33) A2 (Ti Gr 33) B1 (Ti Gr 7) B1 (Ti Gr 7)	1M NaCl + 0.1M NaF, pH 8, 95°C, de-aerated with N_2	2-week long immersion tests while OCP and (periodically) PR monitoring	General Corrosion and Crevice Corrosion
A11 (Ti Gr 33) A12 (Ti Gr 33) B11 (Ti Gr 7) B12 (Ti Gr 7)	1M NaCl + 0.1M NaF, pH 8, 95°C, Aerated with CO_2-free air	10-day long immersion tests while OCP and (periodically) PR monitoring	General Corrosion and Crevice Corrosion
A3 (Ti Gr 33) A4 (Ti Gr 33) B3 (Ti Gr 7) B4 (Ti Gr 7)	1M NaCl + 0.1M NaF, pH 8, 95°C, de-aerated with N_2	Cyclic Potentiodynamic Polarization	Crevice Corrosion
A5 (Ti Gr 33) A6 (Ti Gr 33) B5 (Ti Gr 7) B6 (Ti Gr 7)	1M NaCl, pH 4, 95°C, de-aerated with N_2	Cyclic Potentiodynamic Polarization	No localized corrosion
A7 (Ti Gr 33) A8 (Ti Gr 33) B7 (Ti Gr 7) B8 (Ti Gr 7)	1M NaCl, pH 8, 95°C, de-aerated with N_2	Cyclic Potentiodynamic Polarization	No localized corrosion
A9 (Ti Gr 33) A10 (Ti Gr 33) B9 (Ti Gr 7) B10 (Ti Gr 7)	1M NaCl + 0.1M NaF, pH 8, 95°C, de-aerated with N_2	Potentiostatic tests. Applied potential of −0.25 V (Ag/AgCl)	Crevice Corrosion
Polarization resistance tests were carried out before each one of the cyclic or potentiostatic tests were started. The polarization resistance tests were used to estimate the corrosion rate of the alloys (See Table 3)			

Table 3. Parameters from Cyclic Polarization Curves In Deaerated Electrolytes

Specimen ID	Alloy	E_{corr}, 1-2 h (mV, SSC)	Corrosion Rates (μm/year) After 1-2 h Immersion	E20 (mV, SSC)	E200 (mV, SSC)	ER10 (mV, SSC)	ER1 (mV, SSC)	ERCO (mV, SSC)
1M NaCl + 0.1 M NaF, 95°C, pH 8								
A3	Ti Gr 33	-652	1.257, 1.177, 1.205	-323	-120	-592	-607	NA
A4	Ti Gr 33	-702	2.732, 7.117, 4.694[A]	-322	-93	-616	NA	NA
B3	Ti Gr 7	-674	1.852, 1.354, 1.558	-247	45	NA	NA	NA
B4	Ti Gr 7	-671	1.146, 1.032, 1.022	-282	-113	-565	-578	-578
1 M NaCl, 95°C, pH 4								
A5	Ti Gr 33	-507	0.5493, 0.5469, 0.5456	1415	1793	NA	NA	NA
A6	Ti Gr 33	-486	0.5859, 0.5051, 0.6028	1406	1733	1423	1222	NA
B5	Ti Gr 7	-505	0.6152, 0.635, 0.6066	1516	2183	3046	2038	NA
B6	Ti Gr 7	-485	0.5412, 0.5992, 0.5368	1561	2221	3132	2178	NA
1 M NaCl, 95°C, pH 8								
A7	Ti Gr 33	-619	0.5754, 0.521, 0.4173	1467	1947	NA	NA	NA
A8	Ti Gr 33	-650	0.3908, 0.2769, 0.2713	1480	1976	1587	NA	NA
B7	Ti Gr 7	-696	0.4651, 0.4166, 0.3834	2647	NA	4070	2522	NA
B8	Ti Gr 7	-500	1.131, 0.7413, 0.6442	2420	NA	4012	2654	NA
All Specimens finished with 600 grit paper before testing. NA = Not Available or Not Applicable. E_{corr} is the corrosion potential before starting the polarization tests, the corrosion rate was obtained using the polarization resistance method and fitting the curves between ±10 mV around the corrosion potential putting current in the Y-axis, E20 and E200 are the potentials in the forward scan for which the current density reaches 20 and 200 μA/cm² respectively. They represent values of breakdown potentials. ER10 and ER1 are the potentials in the reverse scan for which the current density reaches 10 and 1 μA/cm². ERCO is the potential at which the reverse scan crosses over the forward scan. ER10, ER1 and ERCO represent values of repassivation potentials. [A]These values are not representative and were ignored in the average value of corrosion rate reported in the plots.								