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May 24, 2000 Contract No. NRC-02-97-009 Account No. 20.01402.571

U.S. Nuclear Regulatory Commission ATTN: Dr. Tae Ahn Two White Flint North 11545 Rockville Pike Mail Stop T7 C6 Washington, DC 20555

Subject: Review of a paper—Effects of Environmental and Metallurgical Conditions on the Passive and Localized Dissolution of Ti-0.15Pd, Intermediate Milestone 01402.571.010

Dear Dr. Ahn:

Enclosed is a technical paper entitled Effects of Environmental and Metallurgical Conditions on the Passive and Localized Dissolution of Ti-0.15Pd. The investigations conducted by the CNWRA indicate that Ti-0.15Pd (Ti Grade 7), proposed as the primary construction material for the drip shield, is unlikely to suffer from localized corrosion in the form of pitting under reasonably attainable conditions in the repository. The most likely failure mode examined here was general passive corrosion, though hydrogen embrittlement may also occur (but has not been examined to date). Further work examining the effects of the Pd addition on the corrosion behavior of Ti is planned as is an examination of the possibility of hydrogen embrittlement. This paper is being submitted for your review as CLST Intermediate Milestone 01402.571.010. Please advise me of the results of your review, so that we can submit the paper for publication in a timely manner.

If you have any questions regarding this paper, please feel free to contact Sean Brossia at (210) 522-5797 or Gustavo Cragnolino at (210) 522-5538.

Sincerely yours,

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EFFECTS OF ENVIRONMENTAL AND METALLURGICAL CONDITIONS ON THE PASSIVE AND LOCALIZED DISSOLUTION OF Ti-0.15Pd

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ABSTRACT

The effects of chloride concentration, fluoride concentration, pH, temperature, and weldments on the corrosion behavior of Ti–0.15Pd (Ti Grade 7, UNS R52400) were examined. It was noted that even at elevated temperatures (165 °C), the breakdown and repassivation potentials in chloride solutions were well above 1 V_{SCE} in solutions containing 4 M Cl⁻. It was also observed that welded specimens exhibited lower breakdown and repassivation potentials than wrought specimens. Short-term tests examining the passive dissolution rate of Ti Grade 7 revealed that chloride concentration, pH, and applied potential had only a slight effect on passive dissolution rates. Fluoride additions to chloride solutions resulted in the appearance of a pseudo active/passive transition and a significant increase in the potential-independent current density, that was several orders of magnitude greater than typical passive current densities. Also of note was the observation that despite the use of creviced specimens, all corrosion attack took place on

the boldly exposed surfaces of the specimens. A model to explain this observation is presented. Keywords: titanium, titanium palladium alloys, localized corrosion, weldments

INTRODUCTION

The safety strategy adopted by the U.S. Department of Energy (DOE) for the proposed high-level nuclear waste (HLW) repository at Yucca Mountain (YM) relies on four key attributes for the unsaturated repository system, one of which is long waste package (WP) lifetimes.¹ In an effort to enhance WP lifetimes, the DOE is considering the use of a drip shield to divert incoming water away from the WP thereby minimizing the quantity of water that may contact the WP.² The primary material being considered by the DOE for construction of the drip shield is Ti, and specifically Pd-bearing Ti alloys [e.g., Ti Grades 7^{a} (UNS R52400) and 16^{b} (no UNS designation)]. Ti-Pd alloys are α Ti alloys that have similar mechanical properties to commercial purity (CP) Ti, but exhibit considerably better corrosion resistance than CP Ti.³

Ti alloys are known to exhibit excellent corrosion resistance under many conditions as a result of the spontaneous formation of a protective TiO_2 passive film, however, under highly reducing acidic conditions, Ti has been observed to suffer from significant corrosion. Given the likely prevailing groundwater chemistry in the YM region (near-neutral and oxidizing), a primary failure mechanism under anticipated repository conditions for Ti-Pd alloys is hydrogen embrittlement, possibly resulting from galvanic coupling to ferrous components in the repository or through the development of localized corrosion sites (crevices) in which an acidic, reducing environment develops. This possibility will be explored further in

^{*}Nominal Composition (max wt%): 0.03 N, 0.10 C, 0.015 H, 0.30 Fe, 0.25 O, 0.12-0.25 Pd, bal. Ti.

^bNominal Composition (max wt%): 0.03 N, 0.10 C, 0.015 H, 0.30 Fe, 0.25 O, 0.05 Pd, bal. Ti.

future work. In addition to hydrogen embrittlement, the possibility also exists for the concentration of detrimental species (e.g., chloride, fluoride) present in the groundwater to increase as a result of interaction with heated metal surfaces (from radionuclide decay) which would cause water evaporation. Furthermore, there is no information concerning the potential detrimental effects of fabrication methods, such as weldments, on the corrosion resistance of these materials. Thus, the goal of this work was to determine the effects of environmental and metallurgical conditions on the localized and passive dissolution of Ti Grade 7, with particular emphasis on determining parameters (e.g., breakdown and repassivation potentials, temperature, passive current density) which then would be utilized in long-term predictive modeling of material performance. This work will also aid in the development of suitable review methods for evaluating the DOE safety case for a high-level nuclear waste repository which may rely on the corrosion resistance of a Ti alloy drip shield. A sensitive, electrochemical-based examination of material performance is of particular importance given the heavy reliance of the DOE experimental program on immersion testing of materials.⁴ It may be difficult using such testing approach to effectively measure the localized corrosion susceptibility and passive dissolution rates of these materials.

EXPERIMENTAL APPROACH

All tests were performed using specimens machined from a 2.5-cm thick plate from a single heat of Ti Grade 7, the composition of which is shown in Table 1. Specimens were machined in the form of cylinders 6.3 mm in diameter and 48.6 mm in length or as standard crevice specimens in the form of blocks with dimensions of $19 \times 19 \times 12$ mm (length × width × thickness) with an 8-mm hole through the thickness to facilitate attachment of the crevice former. For crevice specimens, a serrated polytetrafluoroethylene

(PTFE) crevice former having 12 crevice feet was used and pressed against the flat portion of the specimen at a torque of 0.28 N·m. In the case of welded crevice specimens, the plate was cut into 1.25 cm thick sections and welded together using 10 passes per side. The composition of the weld wire used and the resulting weldment are also shown in Table 1. All specimens were wet polished to a 600 grit finish and ultrasonically cleaned in acetone and water prior to testing. All test solutions were made from reagent grade sodium or lithium salts, reagent grade acids and 18 M Ω ·cm water. For tests conducted in glass cells, after the bulk solution was made, the solution was introduced into the test cell, purged with high purity N₂ and the solution was heated to the desired temperature prior to introduction of the specimen to the cell. All tests used a Pt-coated Nb mesh counter electrode and a saturated calomel electrode (SCE) as a reference, connected into the cell through a salt bridge/Luggin probe to maintain the reference electrode at room temperature.

In the case of tests conducted at temperatures greater than 100 °C, a PTFE-lined type 316 L (UNS 531603) autoclave was used. In the autoclave tests, the solution and specimen were introduced simultaneously, then the solution was purged with high purity N_2 and heated to the desired temperature in the range from 95 to 165 °C prior to testing. Tests were conducted at 95 °C to serve as a basis for comparison of the autoclave results to the results observed from testing in the glass cells. A Pt-coated Nb mesh was used as a counter electrode and an internal Ag/AgCl (0.1 M KCl) reference electrode, similar to that discussed by Macdonald et al.^{5,6} and reviewed by Cragnolino,⁷ was used. All potentials shown from autoclave tests are reported versus SCE at 25 °C, using the conversions provided by Cobble.⁸

Both cyclic potentiodynamic and potentiostatic polarization tests were performed. Cyclic polarization tests were performed at a scan rate of 0.167 mV/s and were reversed at a current density of

 5 mA/cm^2 with the exception of tests conducted in fluoride solutions, in which case the scans were reversed at $1.0 \text{ V}_{\text{SCE}}$. Potentiostatic tests were performed to examine environmental effects on passive dissolution and to examine the effects of long-term polarization on the possible initiation of localized corrosion.

EXPERIMENTAL RESULTS

Figure 1 shows a typical polarization curve for this material in chloride only solutions, with high breakdown (E_{bd}) and repassivation (E_{rp}) potentials evident. Figure 2 summarizes the effects of chloride concentration and weldments on E_{bd} and E_{rp} determined from cyclic potentiodynamic polarization experiments performed at 95 °C. The typical attack morphology observed after polarization is shown in Figure 3. Note that some localized breakdown of the surface is evident, however the morphology is not hemispherical. Furthermore, under no conditions was attack observed under the crevice former, but rather all attack was observed on the boldly exposed surfaces of the specimens. As a result, the breakdown and repassivation potentials labeled in Figure 1 as E_{bd} and E_{rp} are not crevice and crevice repassivation potentials but are associated with the boldly exposed surface. Though the presence of weldments appeared to be slightly detrimental, when examined in the context of the variability (shown by the error bars) of E_{bd} and E_{rp} there is little difference between the wrought and the welded material. Consequently, Eq. 1 was fit to both sets of data (wrought and welded),

$$E_{crit} = E_{crit}^0 - B \log[Cl^-]$$
⁽¹⁾

where E_{crit} is the critical potential (either E_{bd} or E_{rp}), E_{crit}^{0} is the critical potential at 1 M chloride concentration, and B is the slope of the dependence of E_{crit} on the log of the chloride concentration. For

 E_{bd} , the slope was found to be approximately 1.82 V/decade [Cl⁻] with E_{bd}^{0} at 7.49 V_{SCE} and an r² of 0.84. For E_{rp} , the slope was 1.02 V/decade [Cl⁻] with an E_{rp}^{0} of 5.44 V_{SCE} and r² of 0.80. Slightly better fitting results were obtained for E_{rp} when the wrought and welded data sets were examined independently (r² increased to 0.87), however, given the overlapping variability ranges for most of the data sets they were examined as a single set. Even though the critical potentials for the welded and wrought materials were very similar, it should be noted that the location of corrosion attack was concentrated at the weldments for welded specimens. Furthermore, long-term (up to 6 weeks) potentiostatic polarization tests at potentials as high as 1.5 V_{SCE} did not result in any observable localized corrosion of Ti even in high chloride solutions, and negligible weight change was measured^c. This indicated that the specimen was passive throughout the testing period.

The effect of temperature on E_{bd} and E_{rp} for both wrought and welded specimens in 1 M and 4 M chloride is shown in Figures 4 and 5. As was observed at 95 °C, the welded specimens exhibited slightly lower critical potentials than did the wrought specimens. Further, increases in temperature resulted in a linear decrease in the critical potentials up to a certain point, then an abrupt decrease was observed, followed by a continued linear decrease with increasing temperatures. The critical temperature (T_{crit}) at which this abrupt decrease was observed was between 140 and 165 °C for E_{bd} and between 120 and 140 °C for E_{rp} . Again, however, the critical potentials observed were well above 1 V_{SCE} , with the lowest observed E_{rp} being 1.23 V_{SCE} for welded Ti Grade 7 at 165 °C. When exposed to 4 M chloride solutions, similar results were observed with only a shift towards lower potentials (as would be expected) noted.

^cMinimum, accurate weight change measurable was 0.05 mg, which roughly corresponds to a corrosion rate of 10⁻³ mm/yr for Ti Grade 7.

Furthermore, even at 165 °C in 4 M chloride, E_{rp} was still above 1 V_{SCE}.

To evaluate the passive behavior of Ti Grade 7 and the potential influences of environment on the rate of passive dissolution, a series of short-term (~24 h) potentiostatic experiments were performed. The results of these experiments are shown in Figures 6 and 7. Figure 6 shows the effects of applied potential on the passive dissolution rate measured in two different chloride solutions, 1 and 0.1 M ($pH \sim 6.5$), at 95 °C. Little effect of applied potential on the passive dissolution rate was observed. For example, in 0.1 M NaCl the passive dissolution rate at -0.25 V_{SCE} was 2.5 μ A/cm² whereas at +0.50 V_{SCE} the passive dissolution rate was $5.4 \,\mu$ A/cm². At $-0.25 \,V_{SCE}$, increasing the chloride concentration from 0.1 to 1 M resulted in an increase in the passive dissolution rate from 2.5 µA/cm² to 18.2 µA/cm². Error bars in Figures 6 and 7 represent the range of values observed through out the length of the test. Figure 7 shows the effects of applied potential and pH on passive dissolution in 1 M chloride at 95 °C. Both increases in the pH from 6.5 to 10.5 and decreases in the pH to 2.1 generally resulted in a decrease in the passive dissolution rate, especially at higher applied potentials. For example, at an applied potential of 0 V_{SCE} , the passive dissolution rate at pH 6.5 was nearly $30 \,\mu$ A/cm². By increasing the pH to 10.5 or decreasing the pH to 2.1, the passive dissolution rate decreased to 7.1 and 1.7 μ A/cm², respectively. Greater variability in the measured passive dissolution rate was also observed in both alkaline and acidic solutions compared to neutral solutions.

To confirm the results obtained and examine the effects of long-term polarization on the passive dissolution rate, an additional series of potentiostatic tests were performed. In general it was observed that the initial passive dissolution rates were high, but then decreased and eventually the measured current became cathodic for the remainder of the test. Figure 8 shows the results from a potentiostatic hold of Ti

Grade 7 in 1 M chloride at 95 °C and an applied potential of +0.5 V_{SCE} . After an initial period of anodic behavior, the current was observed to oscillate between cathodic and anodic before becoming fully cathodic after about 100 h. The nominal, steady-state current density was approximately 0.1 μ A/cm² (cathodic).

In addition to the likely presence of chloride in the proposed repository, the possibility exists for fluoride to also be present as it is known to exist at low concentrations (~0.1 mM) in the local groundwater at YM. Thus, the effect of fluoride on the polarization of Ti Grade 7 was examined. Shown in Figure 9 are three polarization curves for non-creviced specimens comparing the anodic behavior observed in 1 M NaCl, 1 M NaF, 1 M NaF + 1 M NaCl, and 1 M NaF + 0.1 M HCl solutions. Ti Grade 7 exhibited a considerably lower open circuit potential in all solutions containing fluoride and a pseudo active/passive transition with a subsequent potential independent current region with current densities considerably higher than those typically encountered during passive dissolution $(10^{-3} \text{ to } 10^{-1} \text{ as compared to } -10^{-6} \text{ A/cm}^2)$. It is also interesting to note that in the non-acidified fluoride solutions there existed a small area of passivity just noble of the open circuit potential, prior to a sharp increase in the current (similar to what is observed during localized corrosion) which then decreased after reaching a critical current density. Post-test examination of the specimens revealed extensive attack, but the attack was general.

Also noted in Figure 9 are two dashed horizontal lines which represent the range of steady state open circuit potentials for Ti measured in chloride solutions under air-saturated conditions.⁹ Using the maximum observed potential ($\sim -0.1 V_{SCE}$) as a reference point of comparison, the dissolution rate observed as a function of fluoride concentration was examined. Shown in Figure 10 is the dissolution rate in A/cm² (and converted to mm/y) observed at $-0.1 V_{SCE}$ as a function of fluoride concentration for both

wrought and welded Ti in 1 M chloride solutions. Also shown is the dissolution rate observed for wrought material in 0.1 M chloride. For comparison, the dissolution rate observed at $-0.1 V_{SCE}$ in 1 M chloride is also noted by the horizontal dashed line at 0.7 μ A/cm² (or ~ 8x10⁻³ mm/y). Changes in the chloride concentration and the presence of weldments did not significantly effect the observed dissolution rate. Of importance, however, is that there seems to be a critical fluoride concentration below which only a slight elevation in the dissolution rate compared to chloride only solutions is observed and above which much more significant dissolution rates are seen. This critical fluoride concentration ([F⁻]_{crit}) seems to be on the order of 0.05 to 0.1 M. Below [F⁻]_{crit} the dissolution rates were at most one order of magnitude larger than what was observed in chloride only solutions. Above [F⁻]_{crit} a marked increase to dissolution rates some three orders of magnitude greater were seen. In addition, when creviced specimens were polarized in these solutions, in contrast to chloride-only solutions, corrosion under the crevice former was observed.

DISCUSSION

The goal of this work was to determine the effects of environmental and metallurgical conditions on the localized and passive dissolution of Ti Grade 7, with particular emphasis on defining critical parameters which could be used in long-term predictive modeling of material performance. To accomplish this, a series of short-term potentiodynamic and potentiostatic tests were performed to establish the role of these variables on corrosion behavior and then were further examined through a limited set of longer experiments. The results are discussed in three sections: (i) localized corrosion in chloride solutions, (ii) passive dissolution, and (iii) effects of fluoride on corrosion behavior of Ti Grade 7.

Localized Corrosion in Chloride Solutions

Based on the results obtained from potentiodynamic polarization, it is clear that $E_{\rm bd}$ and $E_{\rm rp}\,$ for Ti Grade 7 are dependent on the chloride concentration, following the well recognized decrease with the logarithm of chloride concentration shown in Eq. 1. In the present work, a slope, B, of nearly 1.82 V/decade \cdot [Cl⁻] was observed for E_{bd} (Figure 2) for a chloride concentration range of 0.1 to 10 M at 95 °C. These values are considerably larger than those summarized previously by Smialowska¹⁰ of 0.11 V/decade for Ti alloys in bromide solutions. It should be noted, though, that the dependence of E_{bd} on chloride concentration for Pd-bearing Ti alloys has not been previously examined, with the majority of the work similar to this being conducted in other halide solutions. Ero followed a similar relationship to chloride concentration, but the slope of the dependence on chloride concentration was lower $(1.02 \text{ V/decade} [Cl^{-}])$. It should be noted that some deviation in expected behavior with the experiments conducted in 10 M chloride was noted. When these data were removed, the r^2 values for both E_{bd} and E_{rp} increased. The exact nature of this deviation is unclear, but it should also be noted that the activity of hydrogen ions is influenced by the chloride concentration,¹⁰ and thus a change in the measured pH for these solutions was also observed. It is possible, then, that at these high chloride concentrations there is a coupled effect between chloride concentration and hydrogen ion activity on the critical potentials. Other tests examining the effect of pH, however, did not reveal a strong dependence of E_{bd} and E_{rp} on pH with only a slight decrease in the measured critical potentials being observed.9 Similar results have been reported by Koizumi and Furuya11 for CP Ti in 0.53 M chloride at 200 $^\circ\text{C}$ in which a decrease in the pitting potential from 1.5 V_{SCE} at pH 7.2 to just over 1.3 V_{SCE} at pH 1.

Increasing the temperature also resulted in a decrease in the measured critical potentials for Ti Grade 7 (Figures 4 and 5) up to a certain critical temperature, T_{crit} , above which an abrupt decrease in the critical potentials was observed. At temperatures less than T_{crit} , E_{bd} and E_{rp} had temperature dependencies ranging from 20 to 33 mV/°C and 11 to 14 mV/°C for the wrought and welded specimens. The critical temperatures observed in the present case (between 140 and 165 °C for E_{bd} and between 120 and 140 °C for E_{rp}) are similar to the value of approximately 125 °C for E_{bd} in 1 M chloride reported by Posey and Bohlmann¹² for Ti Grade 7. It should be noted, however, that Posey and Bohlmann¹² observed a much stronger temperature dependence for E_{bd} at temperatures less than T_{crit} (approximately 70 mV/°C), but similar dependencies at temperatures above T_{crit} . The source of the differences is unclear, except that Posey and Bohlmann¹² examined the effect of temperature over a wider range than was used in the present study (minimum temperature by Posey and Bohlmann was 25 °C as opposed to the minimum of 95 °C examined here). At T_{crit} both E_{bd} and E_{rp} decrease significantly, by as much as 2.6 V_{SCE} , similar to that observed by Posey and Bohlmann.

Similar results were observed with regard to tests conducted in 4 M chloride solutions. In the case of these higher chloride solutions, the only significant change in material behavior as a shift in the critical potentials measured to less positive values as would be expected. In all cases, however, E_{rp} was again observed to be greater than 1 V_{SCE}, even at 165 °C. This further highlights that localized corrosion of this material under anticipated conditions at the proposed repository in chloride only solutions is unlikely.

Though not discussed in any detail thus far, the effect of welding on the localized corrosion resistance of Ti Grade 7 appears to be somewhat detrimental, though generally within the data scatter observed. Based on the examination of welding on the corrosion resistance of other materials, this would

be expected. But according to Donachie¹³ and Schutz,¹⁴ Ti weldments should have comparable corrosion resistance to the wrought material as the formation, structure and thickness of the TiO₂ passive film should be essentially independent of substrate microstructure. In the present case, however, this was not strictly observed and weldments did act as preferential sites for localized corrosion initiation (but again on the boldly exposed surface and not under the crevice former) even though no significant change in the critical potentials was observed. At first, one could argue that this observation was a consequence of Pd dilution within the weld bead. The composition of the weld wire and the weldment itself, though, seems to counter argue this point in that they were in fact slightly enriched with Pd compared to the base metal. Though not examined in any detail, it seems more likely that the reason for the observed detrimental effects of weldments is a result of differences in the grain structure of the weldment and the heat affected zones as compared to the base metal and possibly through an increased quantity of defects at these locations. Another possibility is segregation of Pd in the dendrites or interdendritic regions of the weldment. Each of these possibilities are being evaluated.

Previous results obtained indicated that a maximum corrosion potential (E_{corr}) on the order of -0.1 V_{SCE} is attainable, which is considerably below the repassivation potentials observed for Ti Grade 7.⁹ Furthermore, it seems unlikely (unless stray current effects of sufficient magnitude may result from improper grounding of electrical rails in the repository) that potentials outside the region of water stability are possible. The exception to this would be the possible formation of hydrogen peroxide (H₂O₂) through radiolysis. Neglecting the well known complexation ability of peroxide with Ti for the moment,¹⁵ addition of peroxide would not likely result in E_{corr} exceeding the repassivation potential of Ti Grade 7, except in highly concentrated H₂O₂ solutions at low pH. For example, at pH 0 and 1 M H₂O₂, the maximum

attainable potential without oxidation of peroxide according to thermodynamic calculations¹⁵ is roughly 1.6 V_{SCE} . Given the unlikelihood of achieving this high concentration of peroxide, this low pH, and the fact that the minimum temperature where this value would exceed the repassivation potential is 140 °C, it does not seem likely that localized corrosion of Ti Grade 7 would occur without significant polarization in chloride-only solutions.

Though it seems that localized corrosion of Ti Grade 7 will only occur under high overpotential conditions in chloride solutions, it was also observed that no corrosion was observed to occur under the PTFE crevice former. This is surprising given that Ti alloys have historically been considered more susceptible to crevice corrosion than to pitting corrosion. However, Beck¹⁷ has clearly delineated the differences between crevice and pitting corrosion of Ti alloys, and it has been demonstrated that for Ti alloys crevice and pitting corrosion do not operate via the same mechanism. Ti-Pd alloys have been shown to be nearly immune to crevice corrosion under extremely aggressive conditions.^{18,19} For example, Satoh et al.,¹⁸ observed no initiation of crevice corrosion on Ti Grade 7 in boiling 20% NaCl solutions at pH 4 after 720 h of exposure and in boiling 42 % MgCl₂ solutions after 240 h. In contrast, CP Ti was observed to suffer from severe crevice corrosion in as little as 92 and 15 h under identical conditions. Similarly, Schutz and Xiao¹⁹ did not observe crevice corrosion in either Ti Grades 7 or 16 after 30 d exposure in 20 % NaCl at pH2 and 260 °C nor in boiling 10% FeCl₃ solutions (102 °C). Though these cases are clearly not at the high potentials at which localized corrosion was observed in the present case, they clearly demonstrate the superior crevice corrosion resistance of Pd-bearing Ti alloys. Consideration of the model for pitting of Ti by Beck¹⁷ and Cotton²⁰ involves the migration and adsorption of chloride on the surface and Ti dissolution being controlled by mass transport of chloride to the pit base which may more easily occur on bold surfaces since the diffusion path to the corrosion site. Furthermore, if crevice corrosion of an externally polarized Ti specimen would occur via IR drop in the acidified solution causing a portion of the crevice interior to lie on the active nose of the polarization curve,²¹ the enhanced resistance of Ti-Pd alloys to reducing, acidified environments compared to other Ti alloys would suggest that passivity would be maintained within the crevice. As such, though crevice corrosion of other Ti alloys may be observed, IR drop into a Ti-Pd crevice may not have a detrimental effect on performance as indicated by the absence of an active-passive loop for Ti Grade 7 in acidic solutions.

Passive Dissolution in Chloride Solutions

As a result of the unlikelihood of achieving conditions for localized corrosion of freely corroding Ti Grade 7 in chloride-only solutions, the effects of environmental and electrochemical conditions on passive dissolution were examined. Initial work focused on examining the effects of chloride concentration, pH, and applied potential through short-term potentiostatic tests. In general, increased chloride concentrations from 0.1 to 1 M resulted in an increase in the passive dissolution rate, whereas acidification or alkalinization of the solution tended to decrease the passive dissolution rate (Figures 6 and 7). Applied potential generally had a minor effect on passive dissolution, as would be expected given that over the potential range examined the thermodynamically stable species is TiO₂.²²

Increases in the chloride concentration did result in a slight increase in the measured dissolution rate. In all cases, though, the increase was less than a factor of 7 and at an applied potential of +0.25 V_{SCE} the difference was only a factor of 2. The precise reasoning for the slight increase in passive dissolution with increased chloride concentration is unclear. Work on pure Ti thin films has shown that changes in chloride concentration had little to no effect on the passive dissolution rate.²³ Furthermore, extensive industrial experience with Ti in geothermal and desalination applications has not revealed any significant effects of chloride concentration on the passive dissolution of Ti alloys.²⁴ It seems likely that the observed increases in the present study could very well be a consequence of the short experimental times used (24 hr/test). In addition, considering the variability observed during the pseudo steady-state period of these tests, the relative differences decrease to less than a factor of 3 and in some cases no difference was observed. Thus, the observation that chloride concentration influences the passive dissolution rate of Ti Grade 7 may originate in the experimental approach taken.

Changes in the pH tended to have a slight decreasing effect on the passive dissolution rate, especially at higher applied potentials. This may indicate a slight enhancement in the stability of the passive film. Examination of the Ti-H₂O E-pH diagram,²² however, does not show that any changes would be expected as the thermodynamically stable species over the range of applied potentials and pH values examined here. As was the case for the effect of chloride concentration, though, the differences observed here, especially when the variability in the measured passive dissolution rate is taken into consideration, are relatively small (only between 2 and 8 at a maximum at 0 V_{SCE}). Considering these small differences, the observed effect of pH may also be a consequence of the short experimental times used. Furthermore, others have similarly observed that pH exhibited no or only a slight influence on the passive dissolution rate of Ti alloys. For example, the passive dissolution rate of Ti-15V-3Cr was found to only change by a factor of 2 on decreasing the pH from near neutral to $1.^{25}$ Other work by these authors on pure Ti thin films revealed that pH had no effect on passive dissolution rate.²³

Based on the maximum steady state open circuit potential of $\sim -0.1 V_{SCF}$ measured in previous work,⁹ a nominal dissolution rate of 15 µA/cm² can be estimated in 1 M chloride (without pH adjustment). This equates to an approximate corrosion rate of 0.13 mm/yr. Given the DOE plans to utilize a 15 mm thick Ti drip shield, this would roughly correspond to a life expectancy of 115 vr, considerably shorter than the life span desired by the DOE of several thousands of years.⁴ Longer-term tests (Figure 8), however, revealed that the high currents observed in the short-term tests were not sustainable. In fact the net current measured during the course of the results shown in Figure 8 are anodic only over 8% of total experiment time of just over 598 h. For the rest of the time, the specimen was cathodic with a mean current density of $0.12\,\mu\text{A/cm}^2$. Furthermore, though the current densities measured in the short-term experiments are in line with those reported by Beck,²⁶ it also seems likely that a portion (perhaps even a majority) of the current measured during the short-term tests is not associated with passive dissolution but rather with passive film growth which was indirectly confirmed using EIS. Unlike Ni-Cr alloys and stainless steels whose passivity is governed by a thin Cr film which attains a constant thickness in a relatively short time, the passive film on Ti tends to grow with time. Though these corrosion rates are only approximate and only validated over a short period of time relative to expected engineering service, it appears that the corrosion rates observed during short-term tests are not likely sustainable for longer periods of time and that changes in chloride concentration, pH, and applied potential likely also do not have a significant effect on expected performance over long time periods. Longer-term tests (up to several years) may be necessary to gain confidence in the values and observations made here for use in performance assessment modeling of expected repository performance.

Effect of Fluoride on Corrosion Behavior

Another environmental variable to consider with respect to the corrosion behavior of Ti Grade 7 in the proposed repository is the presence of fluoride. Fluoride is present in the local ground water chemistry at levels approaching 0.1 mM.²⁷ Work examining the possibility of concentration effects through repeated evaporation and re-wetting cycles has estimated that this concentration can increase to at least 0.2 M in the presence of crushed tuff.²⁸ Though it is known that fluoride acts as a complexant for Ti, the typical concentration ranges that have been examined have been generally in the mM range.^{29,30} In addition, there is little information on the effects of higher fluoride concentrations on the corrosion behavior of Pdbearing Ti alloys. With the possibility of enhanced concentration of fluoride being present as a result of dripping of water onto drip shields which are at elevated temperatures, a series of experiments were performed.

In both the 1 M fluoride solution and the fluoride-chloride solution an initial passive region was observed prior to a current increase similar to that which is associated with a breakdown potential for localized corrosion. Under all conditions studied, though, general dissolution of the specimens was observed. Thus, the current increase observed after the initial passive region in fluoride solutions is not associated with localized corrosion. Rather, further increases in the potential for fluoride solutions resulted in the attainment of a critical current density (peak current density) after which increases in the potential resulted in decreases in the current density, similar to an active/passive transition. The peak current density of approximately 0.1 A/cm^2 was observed in all solutions. The potential-independent current density at higher potentials in these solutions ranged from 10^{-3} to 0.1 A/cm^2 , which is considerably higher than the passive current density observed in chloride-only solutions. Furthermore, given the magnitude of these

currents, this region likely is not truly passive. It is possible that these high current densities are limited by transport of TiF_6^{2-} through a porous corrosion layer on the surface, similar to the mass transport conditions encountered in electropolishing. Another possibility, which has been proposed in the literature for this apparent mass transport limited dissolution region,^{31–33} is the transport of HF to the metal surface as a rate determining step in the reaction sequence shown in Eq. 2,

$$\mathrm{Ti}_{\mathrm{passive film}}^{3+} + 2\mathrm{HF} \rightarrow \mathrm{TiF}_{2}^{2+} + 2\mathrm{H}^{+}$$
(2)

In any event, it is clear that the presence of fluoride above a critical concentration resulted in marked changes in polarization behavior and dissolution rate.

Examination of the effect of fluoride concentration on the dissolution rate at a constant potential (Figure 10) revealed that there existed a critical fluoride concentration above which the increase in dissolution rate compared to chloride-only solutions was significant. The existence of a critical fluoride concentration is in line with what has been observed by others and in some cases is comparable. Boere,³⁴ for example, observed a decrease in the polarization resistance of CP-Ti in 0.2 M NaCl by a factor of over 30 when the fluoride concentration was increased from 10 mM to 30 mM, in agreement with the nearly two order of magnitude increase in the dissolution rate observed in the present work when the fluoride concentration was above 50 mM. In cases where acidified solutions were utilized, the critical fluoride concentration tended to be lower. It seems in the present case, then, that the higher critical fluoride concentration necessary as compared to acidified solutions has to do with the formation of HF in the solution via Eq. 3,

$$H^+ + F^- \leftrightarrow HF$$
 (3)

and enhanced HF production at the dissolving Ti surface when H^+ is produced from Eq. 2 and reacts with free F⁻ to form HF via Eq. 3 as proposed by Mandry and Rosenblatt.³¹ It is possible that the high fluoride concentrations examined here will not occur in the proposed repository because of calcium fluoride solubility limitations (~ 0.2 mM), because silica has been claimed to reduce the concentration of free fluoride in flue gas scrubber environments.^{29,35} However, fluoride solubility possibly may not be limited by calcium fluoride precipitation at elevated pH (~10), but rather by sodium fluoride precipitation as Ca will preferentially precipitate out as calcium carbonate. Therefore, it is clear that the detrimental role of fluoride on the corrosion behavior of Ti Grade 7 cannot be neglected.

Also of importance was the observation that crevice corrosion was observed for Ti-Gr7 in fluoride solutions which exhibited an active passive transition. Though not all of the corrosion attack was located under the crevice former (i.e., some attack was also observed on the boldly exposed surfaces), the presence of corrosion under the crevice former is a distinguishing feature compared to the results observed in chloride only solutions. The attack under the crevice former may, in this case, be a result of the added mass transport limitation provided by the crevice former allowing an increased buildup of HF via Eq. 3 and further exacerbated by hydrolysis of Ti cations which are similarly constrained by the crevice former. That localized corrosion of Ti Grade 7 in the form of crevice corrosion is observed in the presence of fluoride at reasonably attainable potentials may indicate that localized corrosion of this material may be possible in such mixed fluoride-chloride systems under possible repository conditions. This then suggests that further examination of the maximum attainable free fluoride concentration possible be examined as well as the

possibility that monitoring of the fluoride content of incoming ground water at the proposed repository may be necessary.

CONCLUSIONS

- 1. Localized breakdown of the passive film on Ti Grade 7 in chloride solutions observed only at high potentials (> $1 V_{SCE}$) even under conditions of high chloride concentration or high temperature.
- 2. Welded specimens tended to have lower breakdown and repassivation potentials than did the wrought material under identical conditions.
- 3. All corrosion attack was observed to be present on the boldly exposed areas of the specimen and not under the crevice former.
- 4. Short-term experiments were not observed to accurately represent the longer term corrosion behavior of Ti Grade 7.
- 5. Environmental and electrochemical variables generally did not significantly influence the short-term passive dissolution rate and long-term experiments showed that the majority of the current measured after the first 48 h was cathodic.
- 6. Additions of fluoride (at relatively high concentrations) to chloride solutions resulted in a significant change in the polarization behavior of Ti Grade 7, most notably the appearance of a pseudo active/passive transition and a significant increase in the potential-independent current density, that is several orders of magnitude greater than typical passive current densities.
- 7. The results of this work did not identify susceptibility of Ti Grade 7 to localized corrosion under anticipated repository conditions.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Material Safety and Safeguards, Division of Waste Management under contract No. NRC-02-97-009 in performing this work. The views presented herein are an independent product of the authors and the Center for Nuclear Waste Regulatory Analyses (CNWRA) and do not necessarily reflect the regulatory position of the NRC. Technical assistance provided by Mr. S. Clay, Mr. J. Spencer and Ms. F. Daby (Southwest Research Institute) for some of the experimental work and SEM microscopy are gratefully acknowledged.

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TABLE 1

Material	C	Fe	N	0	H	Pd	Ti
Base Plate	0.019	0.115	0.007	0.140	0.005	0.15	bal.
Weld Wire	0.027	0.030	0.002	0.046	0.002	0.18	bal.
Weld Metal	0.026	0.080	0.005	0.100	0.003	0.16	bal.

Composition of Ti Grade 7 base material, weld wire, and weldments used in the current study (wt%)

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Figure 1: Potentiodynamic polarization curve for a creviced Ti Grade 7 specimen in 10 M LiCl at 95 °C. Note no attack was observed under the crevice former with all corrosion attack occurring on the boldly exposed surfaces.

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Figure 3: SEM micrograph of localized breakdown observed after polarization of Ti Grade 7 in chloride only solutions.

Figure 4: Effect of temperature on the breakdown potential of wrought and welded Ti Grade 7 in 1 and 4 M NaCl.

Figure 5: Effect of temperature on the repassivation potential of wrought and welded Ti Grade 7 in 1 and 4 M NaCl.

Figure 6: Effect of chloride concentration and applied potential on the short-term passive dissolution rate of Ti Grade 7.

Figure 7: Effect of pH and applied potential at 1 M chloride concentration on the short-term passive dissolution of Ti Grade 7.

Figure 8: Passive current density of Ti Grade 7 in deaerated, 1 M NaCl at 95 °C and an applied potential of + 0.5 V_{SCE} . The horizontal lines represent the likely range of passive dissolution rates observable over long time periods.

Figure 9: Effect of fluoride on the anodic polarization behavior of Ti Grade 7 at 95 °C. Note the horizontal lines at \sim -0.1 and \sim -0.3 V_{SCE} bound the steady state open circuit potentials measured in air-saturated chloride solutions at 95 °C.

Figure 10: Effect of fluoride concentration on the dissolution rate measured at $-0.1 V_{SCE}$ for both wrought and welded Ti Grade 7 in 1 M NaCl and wrought Ti Grade 7 in 0.1 M NaCl. For comparison, the dissolution rate in 1 M NaCl without fluoride is shown.







Brussia L. Chagnelon Fig 2



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Applied Potential, V_{SCE}





Time, h