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U.S. Nuclear Regulatory Commission  
ATTN: Mrs. Deborah A. DeMarco  
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Subject: Programmatic review of a paper

Dear Mrs. DeMarco:

Enclosed is a paper entitled "Effect of Palladium on the Localized and Passive Dissolution of Titanium," to be presented at the NACE 2001 Conference on March 11-16, 2001 in Houston, TX. Please advise me of the results of your programmatic 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 Gustavo Cragnolino at (210) 522-5539 or Sean Brossia at (210) 522-5797.

Sincerely yours,

  
Budhi Sagar  
Technical Director

BS:NS:jg

Enclosure

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# Effect of Palladium on the Localized and Passive Dissolution of Titanium

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## ABSTRACT

The effects of palladium (Pd) additions on the localized and uniform corrosion of titanium (Ti) were examined by comparing the corrosion behavior of Ti Grade 2 (UNS R50400) to that of Pd-bearing Ti Grade 7 (UNS R52400). Pd additions were found to increase the pitting ( $E_{pit}$ ) and repassivation ( $E_{rp}$ ) potentials such that  $E_{pit}$  for Ti Grade 2 was significantly lower than  $E_{rp}$  for Grade 7 in chloride ( $Cl^-$ ) solutions. Under conditions where Ti Grade 2 was found to be susceptible to crevice corrosion, Ti Grade 7 was observed to be immune. Though Pd additions did significantly affect the localized corrosion resistance of Ti, Pd did not appear to influence the passive corrosion rate nor did it mitigate the deleterious effects of fluoride ( $F^-$ ). The effect of Pd on Ti can be explained through the effects Pd has on the hydrogen evolution reaction.

Keywords: Titanium, palladium,  $F^-$ , hydrogen evolution, pitting corrosion, crevice corrosion, passive corrosion

## INTRODUCTION

The U.S. Department of Energy (DOE) is responsible for the permanent disposal of high-level nuclear waste (HLW) generated by power plant, research, and defense reactor operations. Current plans call for the emplacement of the waste into dual container waste packages constructed from an inner container of Type 316 Nuclear Grade (similar to Type 316LN, UNS S31653) and an outer container of Alloy 22 (UNS N06022). The safety strategy currently proposed by the DOE relies on several key attributes to maintain public health and safety, one of which is long waste package lifetime.<sup>1</sup> In an effort to increase waste package lifetimes, the DOE is

considering the use of a drip shield to divert incoming water away from the container thereby minimizing the quantity of water that may come in contact with the container.<sup>2</sup> The primary material being considered by the DOE for construction of the drip shield is Pd-bearing Ti alloys [e.g., Ti Grades 7 and 16 (no UNS designation)].

Ti-Pd alloys are  $\alpha$ -Ti alloys and, as with all Ti alloys, are known to exhibit excellent corrosion resistance in many aqueous environments as a result of the spontaneous formation of a protective  $\text{TiO}_2$  passive film. It has been generally accepted that Ti alloys tend to be highly resistant to pitting corrosion in chloride ( $\text{Cl}^-$ ) solutions, but can more readily undergo crevice corrosion. Previous work by the authors<sup>3,4</sup> indicated that Ti-Pd alloys were immune to crevice corrosion in oxidizing  $\text{Cl}^-$  solutions in line with the reported performance of Pd-bearing Ti alloys.<sup>5,6</sup> It was speculated that the lack of crevice corrosion was a consequence of the absence of an active/passive transition for Ti Grade 7 even in highly aggressive solutions. To further evaluate this possibility, testing of Ti Grade 2 was initiated to serve as a basis for comparison to Grade 7, as more information on the corrosion behavior of Grade 2 (and other similar Ti alloys) has been published than for Pd-bearing Ti alloys, and as a way to better understand the role of Pd on the localized and passive corrosion of Ti alloys under potential repository conditions.

## EXPERIMENTAL APPROACH

All tests on Ti Grade 7 were performed using specimens machined from a single 2.5 cm thick plate. Ti Grade 2 specimens were either machined from a 0.95 cm thick plate for crevice specimens or from a 0.95 cm diameter rod for cylindrical specimens. The compositions for each material are 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  $\times$  width  $\times$  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 for one side and a solid PTFE block was used for the other. The crevice formers were pressed against the flat portion of the specimen at a torque of 0.28 N·m. 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 $\Omega$ ·cm water. Unless intentionally acidified, the solution pH was found to be near neutral for all conditions studied. After the bulk solution was made, the solution was introduced into the test cell, purged with high purity  $\text{N}_2$ , and heated to the desired temperature prior to introduction of the specimen to the cell. All tests used a Pt-coated Nb mesh or graphite rod counter electrode and a saturated calomel electrode (SCE) as a reference, introduced into the cell through a salt bridge/Luggin probe to maintain the reference electrode at room temperature.

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<sup>2</sup>, with the exception of tests conducted in  $\text{F}^-$  solutions and solutions simulating the solution chemistry of a propagating crevice, in which case the scans were terminated at 1.0 V<sub>SCE</sub>. Potentiostatic tests were performed to examine the effects of environmental and electrochemical variables on passive dissolution and to examine the effects of long-term polarization on the possible initiation of localized corrosion.

## EXPERIMENTAL RESULTS

Figure 1 summarizes the effects of chloride concentration on  $E_{\text{pit}}$  and  $E_{\text{rp}}$  determined from cyclic potentiodynamic polarization (CPP) experiments performed at 95 °C for Ti Grades 2 and 7. The typical attack morphology observed after polarization is shown in Figure 2. Note that localized corrosion is evident; however, the morphology of the attack is extremely irregular. Furthermore, under no conditions was attack observed under the crevice former during CPP testing, but rather all attack was observed on the boldly exposed surfaces of the specimens. As a result, the breakdown and repassivation potentials are not associated with crevice corrosion despite the use of creviced specimens. Both Ti Grades 2 and 7 exhibited a dependence of  $E_{\text{pit}}$  and  $E_{\text{rp}}$  on  $\text{Cl}^-$  concentration according to Eq. 1,

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

where  $E_{\text{crit}}$  is the critical potential (either  $E_{\text{pit}}$  or  $E_{\text{rp}}$ ),  $E_{\text{crit}}^0$  is the critical potential at 1 M chloride concentration, and  $B$  is the slope of the dependence of  $E_{\text{crit}}$  on the log of the chloride concentration. The values for  $E_{\text{crit}}^0$  and  $B$  are summarized in Table 2. In general, the primary difference between Ti Grade 2 and Grade 7 was  $E_{\text{crit}}^0$  (i.e., the curve offset) with only slight differences observed in the slope of the curves. For example,  $E_{\text{rp}}^0$  and  $B_{\text{rp}}$  for Grade 7 were 5.61  $V_{\text{SCE}}$  and 1.02  $V/p\text{Cl}^-$ , whereas for Grade 2 they were 0.72  $V_{\text{SCE}}$  and 1.06  $V/p\text{Cl}^-$ . Furthermore,  $E_{\text{rp}}$  for Grade 7 was observed to be greater than  $E_{\text{pit}}$  for Grade 2. Except at low  $[\text{Cl}^-]$  ( $\leq 0.1$  M), this difference was on the order of 4.5 V. At lower  $[\text{Cl}^-]$ , Grade 2 exhibited a transition to much higher critical potentials, but these potentials were still less than those measured for Grade 7.

As no crevice corrosion of Grade 2 was observed in the CPP tests and Grade 2 is known to be susceptible to crevice corrosion,<sup>7,8</sup> a series of potentiostatic experiments was conducted. The potential chosen was 0  $V_{\text{SCE}}$ , which was found to be a readily achievable open circuit potential ( $-0.3$  to 0  $V_{\text{SCE}}$ ) under air-saturated conditions<sup>4</sup>. If no crevice corrosion initiated under the conditions studied, then the tests were used as a measurement of the long-term passive corrosion rate. Figure 3 shows the results of potentiostatic holds in deaerated solutions at 95 °C. Crevice corrosion initiated on Grade 2 held at 0  $V_{\text{SCE}}$  in 5 M  $\text{Cl}^-$  after an induction time of  $\sim 32$  hr. This induction time was measured from the start of the experiment to the point at which the current density exceeded 1  $\mu\text{A}/\text{cm}^2$  and was observed to continue increasing. The morphology of the crevice attack is shown in Figure 4. In this case, attack was general in nature, and clearly crevice corrosion did not initiate as pits that coalesced together. Also shown in Figure 3 are the passive dissolution rates for Grade 2 in 1 M  $\text{Cl}^-$  and Grade 7 in 5 M  $\text{Cl}^-$ . The inset figure shows an expanded view of the current axis. For both Grade 2 in 1 M  $\text{Cl}^-$  and Grade 7 in 5 M  $\text{Cl}^-$  the measured currents were quite low, averaging 0.099 and 0.074  $\mu\text{A}/\text{cm}^2$  respectively over the nearly 1200 hr of the experiment thus far. It should also be noted that on occasion the net current became cathodic.

Because crevice corrosion was observed in Ti Grade 2 in a relatively short time (32 hr) in 5 M  $\text{Cl}^-$  and Ti Grade 7 did not experience crevice corrosion under similar conditions (at least up to  $\sim 1200$  hr), the cathodic and anodic polarization behaviors of Ti Grades 2 and 7 were examined in a simulated crevice solution (deaerated, 5 M  $\text{Cl}^-$ , 0.1 M HCl, 95 °C). Figure 5 shows the cathodic polarization curves for Ti Grades 2 and 7 with Ti Grade 7 exhibiting a higher open circuit potential. During cathodic polarization, evolution of gas, assumed to be  $\text{H}_2$ , was observed. For both materials, an activation controlled region was observed that was then followed by a mass transport limited region. The cathodic Tafel slope observed for Ti Grade 2 was  $-100$  mV/decade. Ti Grade 7

exhibited a cathodic Tafel slope of  $-27$  mV/decade at low overpotentials that transitioned to a slope of  $-138$  mV/decade at higher overpotentials. Anodic polarization of Ti Grade 2 (Figure 6) resulted in the observation of an active/passive transition, with a peak current of nearly  $8 \times 10^{-4}$  A/cm<sup>2</sup> prior to decreasing to  $\sim 2 \times 10^{-5}$  A/cm<sup>2</sup>. Anodic polarization of Ti Grade 7 exhibited essentially passive behavior at all potentials above the corrosion potential. Furthermore, there was little difference in the observed passive current for either material, but the passive current density did decrease with increasing polarization. Post-test examination of the specimens revealed that they had undergone general corrosion with no evidence of pitting noted.

In addition to the likely presence of Cl<sup>-</sup> ions in the water contacting the drip shield, the possibility exists for free F<sup>-</sup> ions to also be present as it is known to exist at low concentrations ( $\sim 0.1$  mM) in the local groundwater at YM and has been shown to reach higher concentrations on repeated dryout and rewetting.<sup>9</sup> Thus, the effect of F<sup>-</sup> on the polarization of Ti was examined. Shown in Figure 7 are two polarization curves for non-creviced Ti Grade 7 specimens comparing the anodic behavior observed in 1 M NaCl and 1 M NaF + 1 M NaCl solutions. As can be seen, Ti Grade 7 exhibited a considerably lower open circuit potential on the addition of F<sup>-</sup> 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 ( $10^{-3}$  to  $10^{-1}$  as compared to  $\sim 10^{-6}$  A/cm<sup>2</sup>). It is also interesting to note that a small area of passivity just noble of the open circuit potential was observed in many of the Cl<sup>-</sup> + F<sup>-</sup> solutions, 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 generalized in nature.

Using a reasonably achievable open circuit potential ( $0$  V<sub>SCE</sub>) as a reference point of comparison, the dissolution rate observed as a function of [F<sup>-</sup>] was examined. Shown in Figure 8 is the current density measured from CPP tests at  $0$  V<sub>SCE</sub> as a function of [F<sup>-</sup>] for both Ti Grades 2 and 7 in 1 M chloride solutions. For comparison, the dissolution rate at  $0$  V<sub>SCE</sub> in 1 M chloride is represented by the horizontal dashed line at  $0.9$   $\mu$ A/cm<sup>2</sup>. A slight difference in the measured dissolution rates was observed, particularly at low [F<sup>-</sup>]. For example, at [F<sup>-</sup>]  $< 0.01$  M, the dissolution rate of Ti Grade 2 was in general a factor of 3 greater. For both Ti Grades 2 and 7 there also seemed to be a critical [F<sup>-</sup>] below which only a slight increase in the dissolution rate compared to chloride only solutions is observed and above which significant dissolution rates are seen. This critical [F<sup>-</sup>] ([F<sup>-</sup>]<sub>crit</sub>) seemed to be around 0.05 M. Potentiostatic polarization at  $0$  V<sub>SCE</sub> at  $95$  °C in 1 M Cl<sup>-</sup>, however, showed little difference in the long-term dissolution rates at 0.01 and 0.1 M F<sup>-</sup> (Figure 9). Although the initial current on polarization for Ti Grade 7 was a factor of 23 greater in 0.1 M F<sup>-</sup> than in 0.01 M (in line with CPP results in Figure 8), after  $\sim 20$  hr a quasi-steady state was achieved in which there was little difference in terms of [F<sup>-</sup>] or material. For example, the average current densities for Ti Grades 2 and 7 at 0.01 M F<sup>-</sup> were 29.1 and 26.4  $\mu$ A/cm<sup>2</sup> and at 0.1 M F<sup>-</sup> the current density of Ti Grade 7 was 38.8  $\mu$ A/cm<sup>2</sup>.

## DISCUSSION

The objective of this work was to examine the role of Pd on the localized and passive dissolution of Ti alloys to gain a better understanding of how Ti-Pd alloys would behave in the proposed HLW repository at YM. To accomplish this, a series of CPP tests was used to establish the differences between the materials in terms of pitting corrosion resistance in Cl<sup>-</sup> solutions and differences in dissolution rate in Cl<sup>-</sup> + F<sup>-</sup> solutions. These tests were augmented through the use of longer-term potentiostatic polarization measurements to examine crevice corrosion

susceptibility and to measure passive corrosion rates. The results are discussed in two sections: localized corrosion and uniform corrosion.

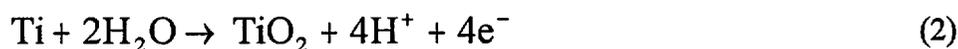
## Localized Corrosion

Based on the results obtained from CPP tests, it is clear that  $E_{\text{pit}}$  and  $E_{\text{tp}}$  for Ti Grades 2 and 7 are dependent on the chloride concentration, following the well established decrease with the logarithm of chloride concentration shown in Eq. 1. In the present work, the slope,  $B$ , was greater than 1.3 V/pCl<sup>-</sup> for both Ti alloys for a [Cl<sup>-</sup>] range of 0.1 to 10 M at 95 °C. These values are considerably larger than those observed by Beck<sup>10</sup> of 0.11 V/pBr<sup>-</sup> for Ti alloys in bromide solutions and by Koizumi and Furuya<sup>11</sup> in chloride solutions at 200 °C (0.1 V/pCl<sup>-</sup>). It should be noted, however, that little has been published in the area of the effects of [Cl<sup>-</sup>] on  $E_{\text{pit}}$  and  $E_{\text{tp}}$  compared to the effects of [Br<sup>-</sup>] and temperature, especially with respect to Pd-bearing Ti alloys.  $E_{\text{tp}}$  followed a similar relationship to [Cl<sup>-</sup>], but the slope of the dependence on chloride concentration was lower (slightly larger than 1.0 V/pCl<sup>-</sup>). In no cases, however, was attack observed under the crevice former with all attack being located on the boldly exposed surfaces of the specimen.

Previous results<sup>4</sup> indicated that a corrosion potential ( $E_{\text{corr}}$ ) on the order of 0 V<sub>SCE</sub> is attainable, which is considerably below the repassivation potentials observed for Ti Grade 7 and is still below those measured for Ti Grade 2 except at very high [Cl<sup>-</sup>] (~ 5 M) at 95 °C. Furthermore, it seems unlikely (unless stray current effects of sufficient magnitude may result from improper grounding of electrical rails in the proposed repository) that potentials outside the region of water stability are possible. The exception to this would be the possible formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) through radiolysis. Neglecting the well known complexation ability of peroxide with Ti for the moment,<sup>12</sup> addition of peroxide would not likely result in  $E_{\text{corr}}$  exceeding the repassivation potential of Ti Grade 7, except in highly concentrated H<sub>2</sub>O<sub>2</sub> solutions at low pH. Ti Grade 2 could experience pitting at potentials within the stability region of water at [Cl<sup>-</sup>] higher than about 0.5 M, but again the  $E_{\text{tp}}$  predicted from these measurements would be considerably higher than the open circuit potentials measured, and another source of oxidants (beyond O<sub>2</sub>) would likely be needed for pitting to occur.

Though it seems that localized corrosion of Ti Grades 2 and 7 only occurs at high overpotentials in chloride solutions, it was also observed that no corrosion occurs under the PTFE crevice former. This seemed to be a surprising result given that Ti alloys have historically been considered more susceptible to crevice corrosion than to pitting corrosion. To evaluate this further, potentiostatic crevice experiments were conducted at an applied potential of 0 V<sub>SCE</sub>. Ti Grade 2 experienced crevice corrosion after an incubation time of 32 hr in 5 M Cl<sup>-</sup>, whereas Ti Grade 7 remained immune to crevice corrosion under the same conditions for at least 1200 hr (Figure 3). If one assumes the explanation put forth by Beck<sup>10</sup> that crevice and pitting corrosion of Ti alloys do not operate via the same mechanism (i.e., crevice corrosion does not initiate through the coalescence of individual pits inside the crevice) and that crevice corrosion occurs with Ti dissolving in the Ti<sup>3+</sup> state and pitting occurs with Ti dissolving in the Ti<sup>4+</sup> state, then the role of Pd on both pitting and crevice corrosion can be explained by coupling the general pitting model put forth by Galvele<sup>13</sup> with the pitting model for Ti put forth by Beck<sup>10</sup> and Cotton.<sup>14</sup>

Galvele's model<sup>13</sup> for pitting involves the localized acidification at the corrosion site, in this case through Eq. 2,



such that the product of the metal dissolution rate,  $i$ , and the diffusion distance,  $x$ , exceed a critical value (for most materials this seems to be  $10^{-6}$  A/cm). In Galvele's model,  $\text{Cl}^-$  acts to accelerate the metal dissolution reaction, and  $E_{\text{crit}}$  is the overpotential needed to drive the metal dissolution reaction such that sufficient hydrolysis occurs and the local pH drop results. The  $\text{H}^+$  ions that are produced according to Eq. 2 can, in addition to lowering the local pH, also diffuse away into the bulk environment, be absorbed by the metal lattice, or be evolved as  $\text{H}_2$  gas. Pd is a known catalyst for the hydrogen evolution reaction (HER), with a reported exchange current density ( $i_0$ ) of  $10^{-3}$  A/cm<sup>2</sup> compared to  $6 \times 10^{-9}$  A/cm<sup>2</sup> for Ti.<sup>15</sup> Thus, it would be reasonable to assume that  $i_0$  for HER would be greater on Ti Grade 7 than on Grade 2. Furthermore, Pd has a high affinity for H, such that a considerable fraction of H can be absorbed into the Pd lattice (up to  $\text{PdH}_{0.6}$ ).<sup>16</sup> Thus, one could argue that the overpotential needed to achieve the critical pH for sustained pit growth on Ti Grade 7 would be greater than on Ti Grade 2 because of the catalytic effect Pd has on HER and increasing  $\text{H}_{\text{abs}}$ , thereby decreasing the effective  $\text{H}^+$  ion concentration. This would translate into a higher  $E_{\text{pit}}$  and  $E_{\text{tp}}$  as was observed.

Similarly, the increase in  $i_0$  promoted by the Pd addition could render Ti Grade 7 effectively immune to crevice corrosion.<sup>5,6</sup> For example, Satoh et al.,<sup>5</sup> 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%  $\text{MgCl}_2$  solutions after 240 h. In contrast, CP Ti (similar to Grade 2) was observed to suffer from severe crevice corrosion in 92 and 15 h under identical conditions. Similarly, Schutz and Xiao<sup>6</sup> did not observe crevice corrosion in Ti Grade 7 after 30 d exposure in 20% NaCl at pH 2 and 260 °C nor in boiling 10%  $\text{FeCl}_3$  solutions (102 °C). If one assumes that Pd will not influence the anodic dissolution behavior of Ti and will only influence the cathodic reaction kinetics, then one would expect to observe an increase in the open circuit potential for Ti Grade 7 compared to Grade 2 in a simulated crevice solution. As shown in Figure 6, this is indeed the case. Note that little difference was in fact observed in the passive region of the polarization curves lending credence to the argument that the main role of Pd is through alteration of the cathodic kinetics. This is further brought out by consideration of the cathodic polarization curves for Ti Grades 2 and 7 (Figure 5). Ti Grade 2 exhibited a cathodic Tafel slope of  $-100$  with Ti Grade 7 exhibiting a cathodic Tafel slope of  $-27$  mV/decade at low overpotentials and  $-138$  mV/decade at high overpotentials. Though a detailed study of the HER mechanism on each material was not conducted<sup>a</sup>, based on these Tafel slopes and the relationship between the Tafel slope,  $b$ , and the transfer coefficient,  $\alpha$ , shown in Eq. 3,

$$b = \frac{2.303RT}{\alpha F} \quad (3)$$

where  $R$  is the Universal Gas constant,  $T$  is temperature and  $F$  is Faraday's constant, some conclusions can be drawn. First, the HER can be broken down into the reaction steps shown in Eq. 4–6,




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<sup>a</sup>To conclusively confirm the HER mechanisms, one would still need to know the stoichiometric number (the number of times the rate determining step takes place each time the reaction sequence occurs once), the reaction order (the dependence of reaction rate on  $[\text{H}^+]$ ), and the dependence of H surface coverage on applied potential.



where these represent the discharge, recombination, and electrodic desorption reaction steps. The values of  $\alpha$  for each of the reaction steps are 0.5, 2.0, and 1.5 at low  $H$  coverage ( $\theta_H$ )<sup>15</sup> resulting in Tafel slopes (at 95 °C) of -146, -36.5, and -48.7 mV/decade. In the present case then, the likely rate determining step (rds) on Ti Grade 2 is the discharge reaction step (-100 vs. -146 mV/decade) and on Ti Grade 7 at low overpotentials the rds is likely recombination (-27 vs -36.5 mV/decade). At higher overpotentials, it seems likely that the Pd addition to Ti acts in similar fashion as Pt in that as  $\theta_H$  approaches unity the rds changes to electrodic desorption. At high  $\theta_H$ ,  $\alpha$  for electrodic desorption is 0.5<sup>16</sup> which results in a Tafel slope of -146 in comparison to the -138 mV/decade observed here. This conclusion is in agreement with the mechanisms for HER proposed by Fukuzuka et al.<sup>17</sup> for Ti Grade 2 (rds = discharge) but does not agree with their mechanism for Grade 7 (rds = electrodic desorption at low  $\theta_H$ ). This difference in reaction mechanisms is likely a result of the difference in environments examined between Fukuzuka et al.<sup>17</sup> (2% HCl at 70 °C) and the present case. Thus, it appears that Pd acts to increase  $i_0$  and decrease the cathodic Tafel slope (e.g., lower overpotential needed to achieve similar reaction rates) such that the cathodic reaction line no longer intercepts the anodic dissolution line below the active/passive transition but intersects in the passive range. The consequence of this is that IR drop in the crevice on Ti Grade 2 puts a portion of the crevice in the active nose and rapid dissolution occurs. In Ti Grade 7, IR drop into the crevice does not significantly increase the dissolution rate, and eventually the interior of the crevice will be cathodic and generate  $H_2$  gas or will lead to increased concentrations of  $H_{\text{abs}}$  in the metal lattice. If Pd accumulates on the metal surface as dissolution proceeds, as has been reported,<sup>18-21</sup> then the cathodic reaction kinetics could be further enhanced (e.g.,  $i_0$  may increase further) resulting in an additional increase in the open circuit potential and thereby causing the disappearance of the slight active/passive transition observed in the present case.

The explanation given thus far would account for the differences in the crevice corrosion behavior of the materials and explains the relative positions of the critical potentials for pitting corrosion. It does not, however, account for the observation that pitting occurred only on the boldly exposed surfaces and did not occur under the crevice former. If one neglects the argument by Beck<sup>10</sup> that crevice corrosion and pitting corrosion of Ti occur by different mechanisms and focus solely on the model put forth by Galvele<sup>13</sup>, the presence of the crevice former should assist in the stabilization of pits as the diffusion length is increased. This would then imply a lower metal dissolution rate is needed and thereby decrease the potential needed to achieve localized corrosion. Thus, one would expect  $E_{\text{crev}} < E_{\text{pit}}$ , as is seen with stainless steels and Ni-based alloys<sup>22</sup>. By expanding on the role of  $Cl^-$  beyond that assumed by Galvele's model to that proposed by Beck<sup>10</sup> and Cotton<sup>14</sup>,  $Cl^-$  migration and adsorption at the pit embryo may be a critical step that is partially hindered by the presence of the crevice former by making the diffusion path longer. Thus, there may be a combined effect of local acidification coupled with  $Cl^-$  migration and adsorption such that the presence of a crevice aids the former but hinders the latter such that pitting cannot nucleate and grow under the crevice. Clearly, though, based on the results reported by Beck<sup>10</sup> and the observation in the present work that crevice corrosion does not initiate as pits, as shown in Figure 4, indications are that crevice corrosion and pitting corrosion of Ti alloys occur by different mechanisms, which is contrary to the case for most materials.

## Uniform Corrosion

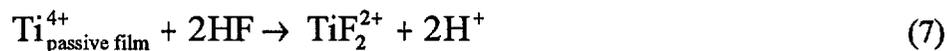
In addition to  $\text{Cl}^-$ , another environmental variable to consider with respect to the corrosion behavior of Ti in the proposed repository is the presence of  $\text{F}^-$  in the local groundwater chemistry that has been observed to approach levels as high as 0.2 M during repeated evaporation/rewetting cycles.<sup>9</sup> Although it is known that  $\text{F}^-$  acts as a complexant for Ti, the typical concentration ranges that have been examined have been generally in the mM range.<sup>23,24</sup> In addition, there is little information on the effects of Pd on the corrosion behavior of Ti in the presence of  $\text{F}^-$ . Thus, the possibility that Pd may be beneficial for passive corrosion and corrosion in the presence of  $\text{F}^-$  was investigated. Uniform, passive corrosion was observed in  $\text{Cl}^-$  only solutions, whereas much more rapid uniform corrosion was observed in the presence of  $\text{Cl}^- + \text{F}^-$ . If localized corrosion in the form of either pitting or crevice corrosion does not occur, then the next most likely corrosion mode would be uniform passive dissolution.

The passive corrosion rates of both Ti Grade 2 and 7 were quite comparable under the conditions studied here. Previous work demonstrated that environmental variables, such as  $[\text{Cl}^-]$  and pH, did not have a significant influence on the passive corrosion rate of Ti.<sup>4,25-27</sup> Thus, direct comparison of the passive dissolution rates on Ti Grade 2 in 1 M  $\text{Cl}^-$  and Ti Grade 7 in 5 M  $\text{Cl}^-$  can be made. Little difference between the passive corrosion rate of these materials was observed, with an average dissolution rate of  $0.099 \mu\text{A}/\text{cm}^2$  (or  $8.6 \times 10^{-4} \text{ mm/y}$ ) for Ti Grade 2 and  $0.074 \mu\text{A}/\text{cm}^2$  ( $6.4 \times 10^{-4} \text{ mm/y}$ ) for Ti Grade 7. The exact nature of the periodic fluctuations in the measured current are unclear; however, the values being measured are near the resolution limit of the instrument used. In any event, it is evident that Pd does not play a significant role in determining the passive corrosion rate of Ti. The most likely explanation for this is that Pd does not alter the anodic dissolution curve but simply alters cathodic reaction kinetics. More specifically, Pd alters the HER reaction kinetics, as discussed above. Thus, in oxidizing conditions where the dominant cathodic reaction is not HER, Pd does not play a significant role in altering either the anodic dissolution curve or the cathodic kinetics, and thus little effect is observed.

This explanation that Pd does not play a role in determining the passive corrosion of Ti in oxidizing conditions is in line with the reported benefits of Pd in reducing environments. For example, Okazaki et al.,<sup>18</sup> Shida and Kitayama,<sup>19</sup> and Shimogori et al.<sup>20</sup> all report increases in the concentration of Pd in the passive film on Ti during corrosion, in some cases increasing by as much as a factor of 5.<sup>19</sup> It was also noted that the Pd concentration in the passive film on Ti increased with increasing exposure to the solution, and concomitantly the Ti dissolution rate was observed to decrease.<sup>20</sup> It should be noted, however, that all these observations were based on exposures to high concentrations of HCl at elevated temperature, and it seems likely that the accumulation of Pd in the passive film is through rapid, active dissolution of Ti. The subsequent decrease in the corrosion rate over time is then easily explained in terms of the discussion provided above with regard to crevice corrosion of Ti Grade 7. Thus, it appears that in mildly oxidizing, near neutral  $\text{Cl}^-$  solutions Pd does not influence the passive corrosion of Ti.

The addition of 1 M  $\text{F}^-$  to 1 M  $\text{Cl}^-$  significantly altered the anodic behavior of Ti Grade 7 (Figure 7). On polarization from open circuit, 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  $\text{F}^-$  solutions is not associated with localized corrosion. Rather, further increases in the potential for  $\text{F}^-$  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. A peak current density of

approximately  $0.1 \text{ A/cm}^2$  was observed in all solutions with the potential-independent current density at higher potentials ranging from  $10^{-3}$  to  $0.1 \text{ A/cm}^2$ , irrespective of material. These potential-independent currents were 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  $\text{TiF}_6^{2-}$  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,<sup>28-30</sup> is the transport of HF to the metal surface as a rate determining step in the reaction sequence shown in Eq. 7,



In any event, it is clear that the presence of  $\text{F}^-$  resulted in marked changes in the anodic behavior and dissolution rate, basically shifting the anodic dissolution curve to higher currents, thereby also decreasing the open circuit potential.

Examination of the effect of  $[\text{F}^-]$  on the dissolution rate at  $0 \text{ V}_{\text{SCE}}$  from CPP tests (Figure 8) seemed to indicate that a critical  $[\text{F}^-]$  existed, above which a significant increase in dissolution rate was observed. This critical  $[\text{F}^-]$  was  $\sim 0.05 \text{ M}$  for both Ti Grades 2 and 7, indicating that the Pd additions in Ti Grade 7 did not alter the corrosion behavior significantly. The existence of a critical  $[\text{F}^-]$  is in line with what has been observed by others in other short term tests. Boere,<sup>31</sup> for example, observed a decrease in the polarization resistance of CP-Ti (similar to Ti Grade 2) in  $0.2 \text{ M NaCl}$  by a factor of over 30 when the  $[\text{F}^-]$  was increased from  $10 \text{ mM}$  to  $30 \text{ mM}$ , in reasonable agreement with the observed increase by a factor of 7 for Ti Grade 2 at  $[\text{F}^-]$  above  $50 \text{ mM}$ . In cases where acidified solutions were utilized, the critical  $[\text{F}^-]$  tended to be lower. It seems that the higher critical  $[\text{F}^-]$  necessary as compared to acidified solutions is related to the formation of HF in the solution via Eq. 8,



and enhanced HF production at the dissolving Ti surface when  $\text{H}^+$  is produced from Eq. 7 and reacts with free  $\text{F}^-$  to form HF via Eq. 8 as proposed by Mandry and Rosenblatt.<sup>28</sup> Subsequent longer-term potentiostatic testing of Ti Grades 2 and 7 at  $0 \text{ V}_{\text{SCE}}$ , however, did not reveal a significant difference between  $[\text{F}^-]$  of  $0.01$  and  $0.1 \text{ M}$  (Figure 9). Furthermore, no significant difference in the dissolution rates for Ti Grade 2 or 7 at the same  $[\text{F}^-]$  was observed. Thus, it seems likely that Pd additions do not significantly alter the corrosion behavior of Ti in the presence of  $\text{F}^-$ .

Given that Pd does not seem to influence the passive corrosion rate in  $\text{Cl}^-$  solutions nor does it seem to mitigate the detrimental effects of  $\text{F}^-$ , it would appear that the only role that Pd plays as an alloying element is by altering the cathodic reaction kinetics. If only cathodic kinetics are affected, then one would not expect a change in the passive current density in  $\text{Cl}^-$  solutions, but open circuit potential would be expected to change. In air-saturated conditions (as would be expected in the proposed repository), little or no effect on the open circuit potential would be expected as the dominant cathodic reactant under most conditions would be  $\text{O}_2$ , and Pd does not appear to alter the oxygen reduction reaction. Because  $\text{F}^-$  shifts the anodic dissolution curve to higher currents and promotes active dissolution by forming  $\text{TiF}_6^{2-}$  which is more stable than  $\text{TiO}_2$ , Pd likely does not alter this in

any foreseeable way. Given the shift in open circuit to lower potentials with the shift in the anodic curve, however, Pd may play a small role in decreasing the open circuit potential. Anodic polarization by the presence of oxidizing species (e.g.,  $\text{Fe}^{3+}$ ,  $\text{H}_2\text{O}_2$ ), however, would alter that behavior and any beneficial effects of Pd would likely be lost.

## SUMMARY AND CONCLUSIONS

Based on the observation that Pd additions resulted in increasing  $E_{\text{pit}}$  and  $E_{\text{rp}}$  and conveyed immunity to crevice corrosion in  $\text{Cl}^-$  solutions but did not alter the passive dissolution rate in mildly oxidizing  $\text{Cl}^-$  solutions, nor did Pd mitigate the deleterious effects of  $\text{F}^-$  on the anodic behavior of Ti, the following mechanism was proposed. The addition of Pd to Ti results in increasing the exchange current density and decreasing the Tafel slope for the hydrogen evolution reaction. Such changes would raise the potential required to achieve sufficient Ti dissolution in pit embryos to sustain hydrolysis and attain the critical pH for pit propagation. These changes also explain the immunity of Ti Grade 7 to crevice corrosion as a result of shifting the open circuit potential of Ti above the active/passive transition in the crevice solution. Such changes to the hydrogen evolution reaction would presumably not alter the passive current density in mildly oxidizing solutions as the primary governing cathodic reaction would not be hydrogen evolution. Furthermore, since  $\text{F}^-$  appears to alter anodic dissolution kinetics Pd additions, again, significantly mitigate this effect.

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TABLE 1 – Composition of Ti Grades 2 and 7 used in the current study (wt%).

Material/Specimen	C	Fe	N	O	H	Pd	Ti
Grade 2 – cylindrical specimens	0.011	0.080	0.006	0.150	0.0015	–	bal.
Grade 2 – crevice specimens	0.032	0.080	0.002	0.110	0.0019	–	bal.
Grade 7 – all specimens	0.009	0.115	0.007	0.140	0.005	0.155	bal.

TABLE 2 – Parameters for Eq. 1 measured in the present study.

Material	$E_{pit}^0$ (V <sub>SCE</sub> )	$B_{pit}$ (V/pCl <sup>-</sup> )	$E_{rp}^0$ (V <sub>SCE</sub> )	$B_{rp}$ (V/pCl <sup>-</sup> )
Ti Grade 7	7.69	2.00	5.61	1.02
Ti Grade 2, [Cl <sup>-</sup> ] > 0.1 M	1.08	1.30	0.72	1.06
Ti Grade 2, [Cl <sup>-</sup> ] < 0.1 M	4.26	1.83	3.11	1.77

## Figure Captions

Figure 1: Effect of chloride concentration on the pitting ( $E_{pit}$ ) and repassivation ( $E_{rp}$ ) potentials for Ti Grades 2 and 7 in deaerated solutions at 95 °C.

Figure 2: SEM micrograph showing morphology of pitting attack after cyclic potentiodynamic polarization testing of Ti Grade 2 in deaerated 1 M NaCl at 95 °.

Figure 3: Current density as a function of time for creviced Ti Grades 2 and 7 in 5 M chloride solutions and creviced Ti Grade 2 in 1 M chloride solution. All tests conducted under deaerated conditions at 0  $V_{SCE}$  and 95 °C. Inset figure shows expanded view of passive currents measured.

Figure 4: SEM micrograph of crevice corrosion on Ti Grade 2 after polarization at 0  $V_{SCE}$  in 1 M chloride at 95 °C.

Figure 5: Cathodic polarization curves for Ti Grades 2 and 7 in deaerated 5 M chloride + 0.1 M HCl at 95 °C. Dotted lines represent linear regression lines used to calculate cathodic Tafel slopes.

Figure 6: Anodic polarization curves for Ti Grades 2 and 7 in deaerated 5 M chloride + 0.1 M HCl at 95 °C.

Figure 7: Polarization curves for Ti Grade 7 in the presence and absence of 1 M fluoride under deaerated conditions at 95 °C.

Figure 8: Effect of fluoride concentration on the dissolution rate of Ti Grades 2 and 7 at a potential of 0  $V_{SCE}$  (results taken from cyclic potentiodynamic polarization tests in 1 M NaCl at 95 °C).

Figure 9: Effect of long-term potentiostatic polarization at 0  $V_{SCE}$  on the dissolution rate of Ti Grades 2 and 7 in the presence of fluoride.

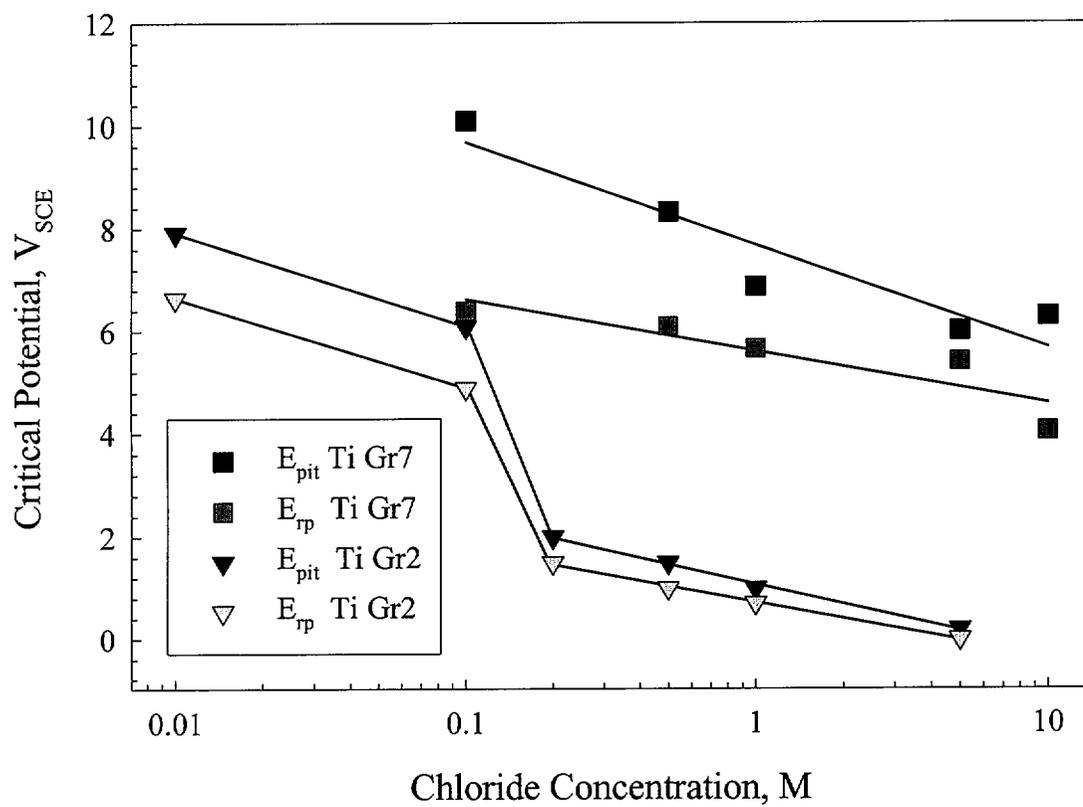


Figure 1

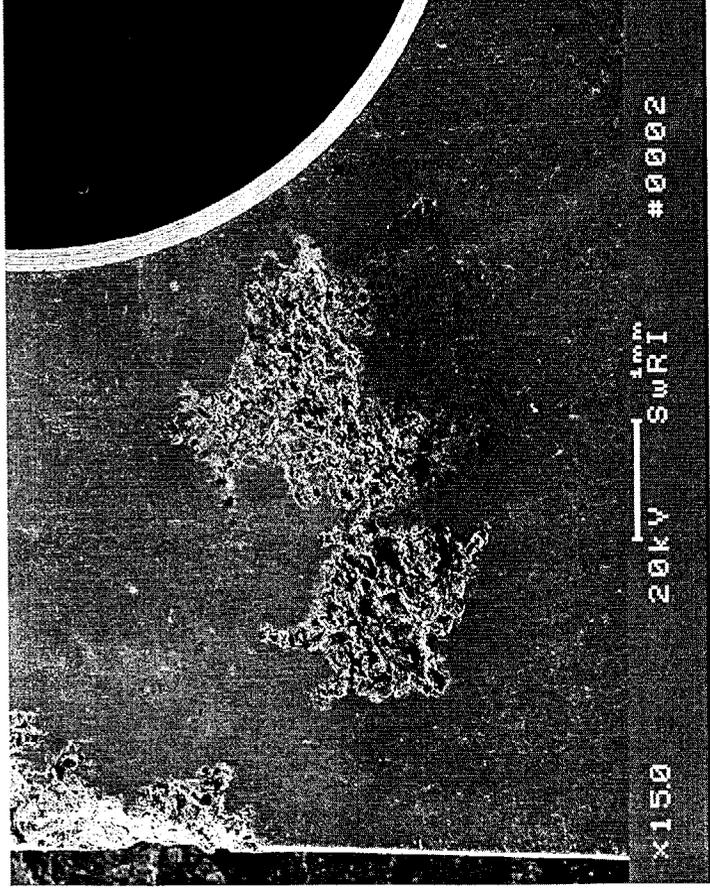


Figure 2

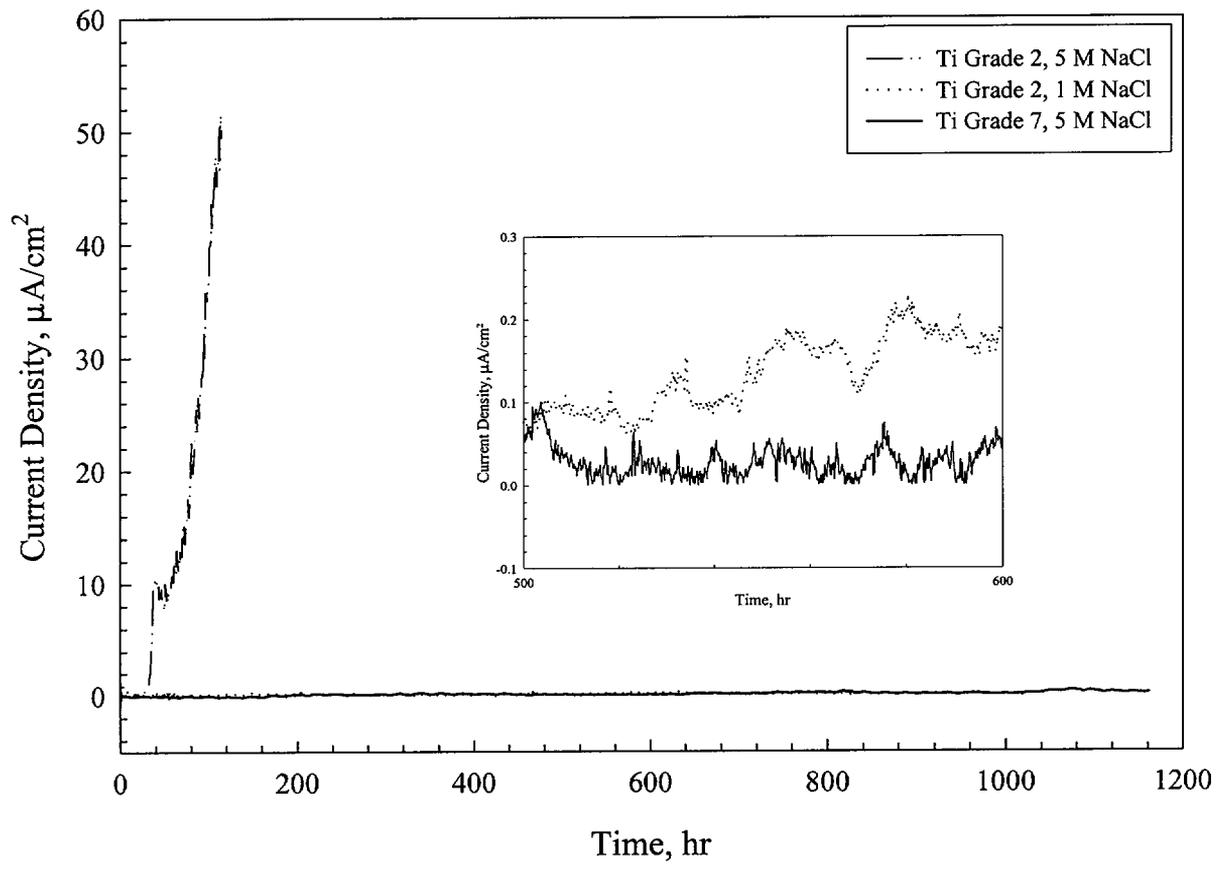


Figure 3

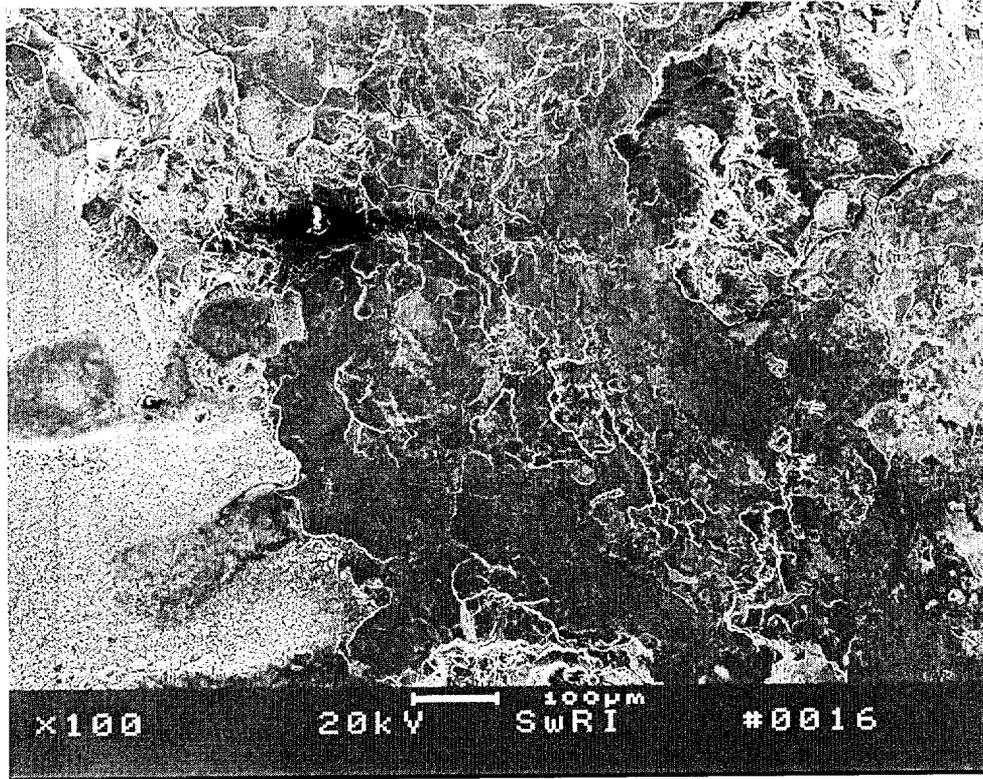


Figure 4

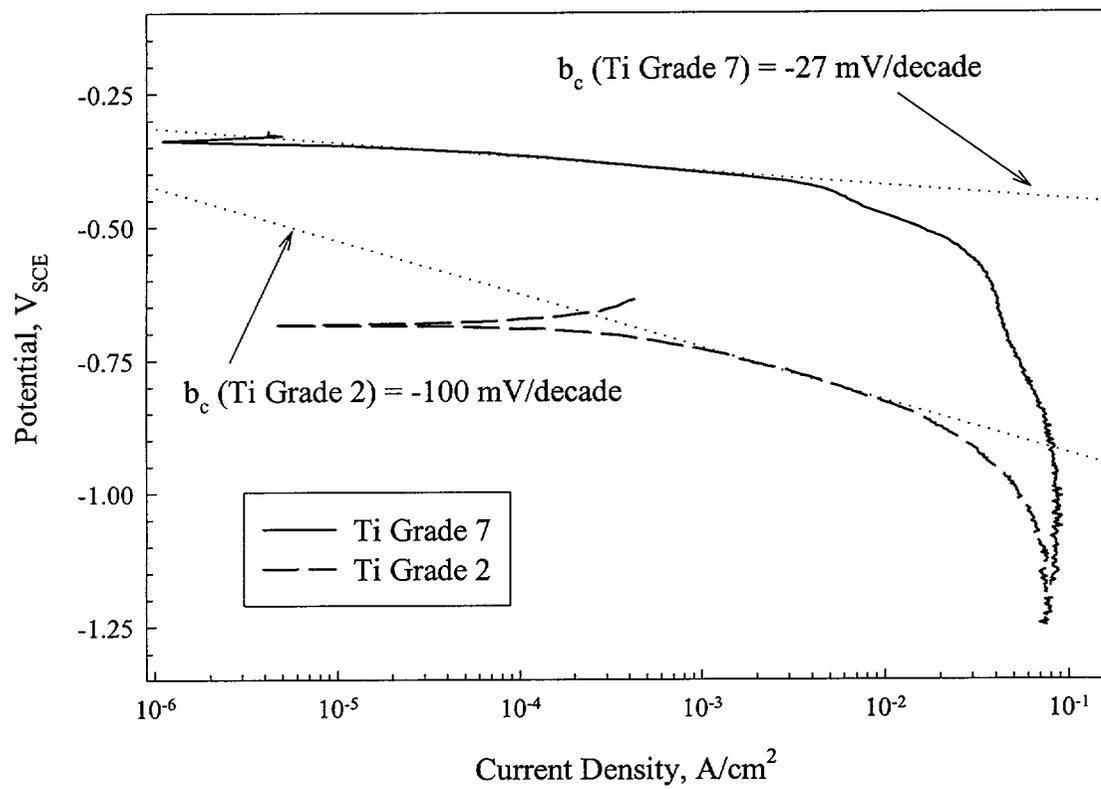


Figure 5

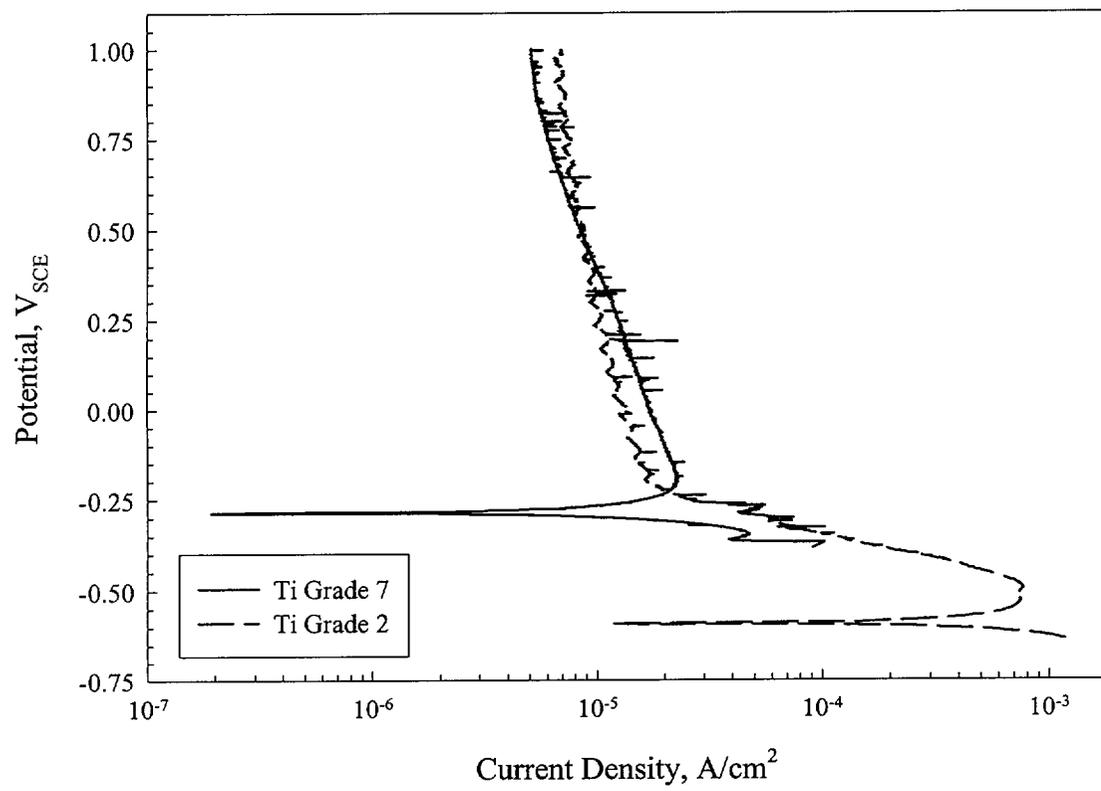


Figure 6

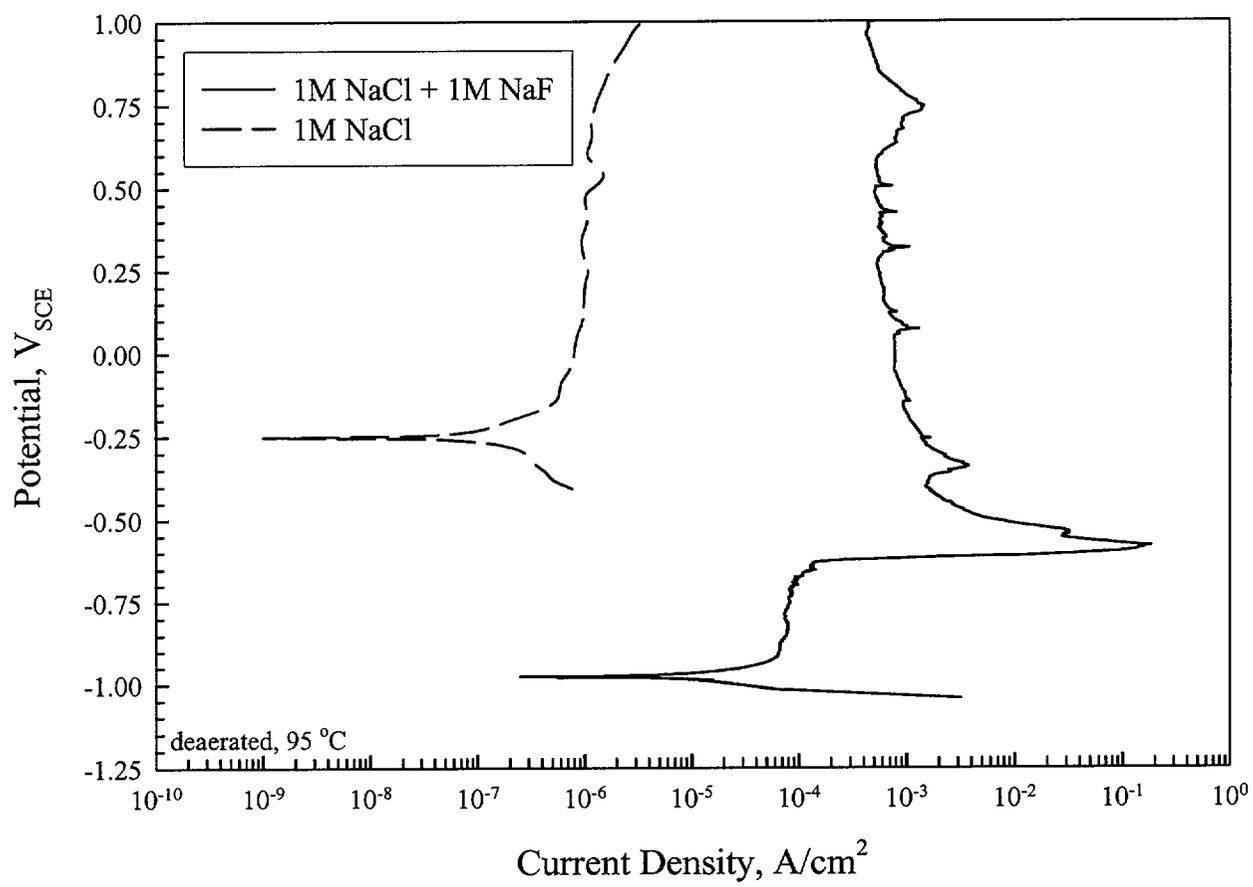


Figure 7

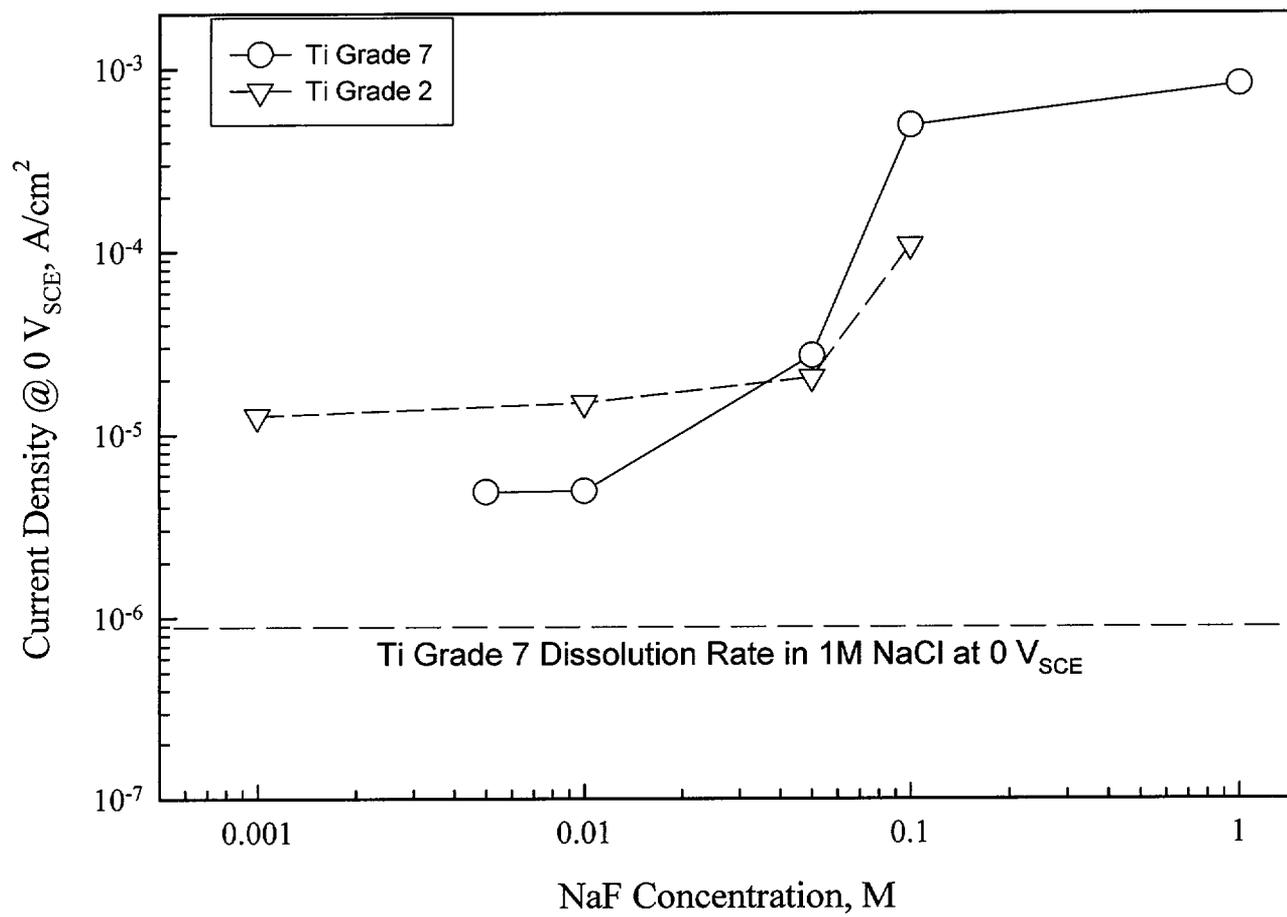


Figure 8

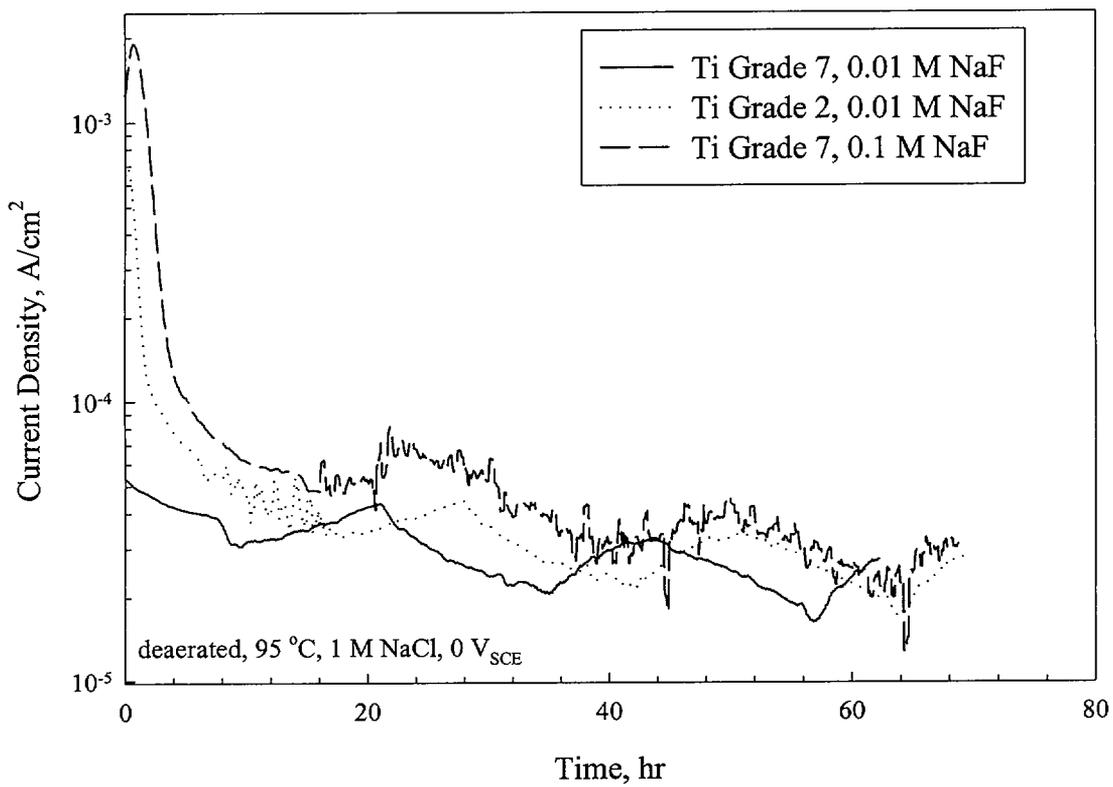


Figure 9