

CORROSION OF SIMILAR AND DISSIMILAR METAL CREVICES IN THE ENGINEERED BARRIER SYSTEM OF A POTENTIAL NUCLEAR WASTE REPOSITORY

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Abstract

Crevice corrosion is considered possible if the corrosion potential (E_{corr}) exceeds the repassivation potential for crevice corrosion (E_{rcrev}). In this study, potentiodynamic polarization was used to determine the E_{rcrev} of similar and dissimilar metal crevices in the engineered barrier system of the potential Yucca Mountain repository in 0.5 M NaCl, 4 M NaCl, and 4 M MgCl₂ solutions at 95 °C [203 °F]. The results were compared with data previously obtained using crevices formed between Alloy 22 and polytetrafluoroethylene. It was observed that, except for Type 316L stainless steel, all other metal-to-metal crevices were less susceptible to crevice corrosion than the corresponding metal-to-polytetrafluoroethylene crevices. Measurements of galvanic coupling were used to evaluate the crevice corrosion propagation behavior in 5 M NaCl solution at 95 °C [203 °F]. The crevice specimens were coupled to either an Alloy 22 or a Titanium Grade 7 plate using metal or polytetrafluoroethylene crevice formers. For all the tests using a polytetrafluoroethylene crevice former, crevice corrosion was initiated at open circuit potential by the addition of CuCl₂ as an oxidant, whereas no crevice corrosion was initiated for all the tests using Alloy 22 or Titanium Grade 7 metals as crevice former. However, crevice corrosion propagation was found to be very limited under such test conditions.

Keywords: Alloy 22, crevice corrosion, corrosion potential, crevice corrosion repassivation potential, Titanium Grade 7, 316L stainless steel

Introduction

The possible waste package design for the disposal of high-level waste at the potential repository in Yucca Mountain, Nevada, may consist of an outer container made from Alloy 22 (Ni–22Cr–13Mo–4Fe–3W), and an inner container made of Type 316 nuclear grade stainless steel (low C–high N–Fe–18Cr–12Ni–2.5Mo). The waste package may rest on an emplacement pallet fabricated from Alloy 22. Additionally, an inverted U-shaped drip shield, fabricated with Titanium Grade 7 (Ti–0.15 Pd) and Titanium Grade 24 (Ti–6Al–4V–0.06Pd), may be extended over the length of the emplacement drifts to prevent seepage water and rockfall from contacting the waste packages.

Metal-to-metal crevices may be formed by contact between the drip shield and the waste package outer container as a result of mechanical disruption (or failure) of the drip shield. Metal-to-metal crevices may also exist between the waste package outer container, the inner

container, and between the outer container and the emplacement pallet. Water chemistry contacting the engineered barrier materials depends on the seepage water composition and the evolution of the water chemistry within the emplacement drifts. Retention of aggressive solutions in occluded crevice areas between similar or dissimilar metal components could lead to crevice corrosion. To provide parameter values for U.S. Department of Energy (DOE) to model the potential waste package degradation processes, Ikeda and Quinn (2003) studied the corrosion behavior of dissimilar metal crevices in the potential engineered barrier system in simulated concentrated ground water solutions at elevated temperature. The results indicated that a limited degree of acidification occurred in the Alloy 22 to Titanium Grade 7 and Alloy 22 to Titanium Grade 16 crevices during the experiment. However, under the test conditions the total crevice corrosion observed was limited. Additional studies by the DOE to investigate the effect of crevice-forming materials are underway (Payer, et al., 2005).

The crevice corrosion abstraction in the U.S. Nuclear Regulatory Commission/Center for Nuclear Waste Regulatory Analyses (NRC/CNWRA) Total-system Performance Assessment code is based on a critical potential model (Mohanty, et al., 2002). Crevice corrosion is considered possible if the corrosion potential (E_{corr}) of a metal in a given environment exceeds the repassivation potential for crevice corrosion (E_{rcrev}). Numerous short-term tests have been conducted to measure the E_{corr} and the E_{rcrev} as a function of metallurgical and environmental conditions using metal-to-polytetrafluoroethylene crevices (Dunn, et al., 2005a,b). Polytetrafluoroethylene is commonly used to form metal-to-plastic crevice due to its chemical inertness, deformability and moderate rigidity. Upon torque, polytetrafluoroethylene deforms slightly and fills the small voids created by the surface roughness of the specimen, which results in a better occluded region and consistent crevice. It is demonstrated that the tests results are more consistent by using polytetrafluoroethylene to form crevice than using ceramic (Evans, et al., 2005; Ilevbare, et al., 2005).

The objective of this work is to evaluate the role of realistic similar and dissimilar metal-to-metal crevices on the corrosion behavior of Type 316L stainless steel, Titanium Grade 7, mill-annealed Alloy 22, and welded plus solution annealed Alloy 22 in simulated Yucca Mountain groundwaters. Crevice corrosion initiation and propagation of similar and dissimilar metal crevices were studied as a function of solution chemistry, crevice tightness, metal combinations, and crevice specimen-to-crevice washer surface area ratios.

Experimental

1. Materials and Crevice Assemblies

The chemical composition of the heats of mill-annealed Alloy 22, Alloy 622 weld filler metal used for welding, Type 316L stainless steel, and Titanium Grade 7 used in this study are shown in Table 1. The corrosion potential and the crevice corrosion repassivation potential based on ASTM G-78 (American Society for Testing and Materials International, 2005a) were measured on a multiple-crevice assembly. In this assembly, the crevice specimen with a surface area of approximately 11.6 cm² [1.80 in²] [Figure 1(a)] was sandwiched between two serrated crevice washers with 24 plateaus [Figure 1(b)], and machined from mill-annealed Alloy 22 (Heat 2277-3-3266, Table 1) or Titanium Grade 7 (Heat CN 2775, Table 1) using a bolt and nut machined from the same material as the crevice washer [Figure 1(b)]. The combined surface area of the test fixture including crevice washer, bolt, and nut was approximately 39.3 cm² [6.09 in²]. In addition to mill-annealed Alloy 22, welded plus solution annealed Alloy 22 specimens also were

used to evaluate the effect of fabrication processes on the corrosion performance of Alloy 22. Welded specimens were produced from a plate using gas tungsten arc welding with a double U-groove joint geometry {25.4-mm-thick [1-in-thick] Alloy 22 Heat 2277-3-3292 and Alloy 622 filler metal Heat WN 813, Table 1}. The location of the weld is shown in Figure 1(a). Solution-annealing of the as-welded specimens was performed at 1,125 °C [2,057 °F] for 20 minutes, followed by water quenching.

Five types of crevices and two degrees of crevice tightness were evaluated (in each of the following, the first material was the crevice specimen and the second material was the crevice washer): (i) Type 316L stainless steel to mill-annealed Alloy 22, (ii) mill-annealed Alloy 22 to mill-annealed Alloy 22, (iii) welded plus solution annealed Alloy 22 to mill-annealed Alloy 22, (iv) mill-annealed Alloy 22 to Titanium Grade 7, and (v) welded plus solution annealed Alloy 22 to Titanium Grade 7. The torques applied to the assembly were 0.35 N·m [3.1 in·lb] and 8.4 N·m [75 in·lb]. The low and high torques were close to ASTM specifications (American Society for Testing and Materials International, 2005a) and were used to simulate different degrees of crevice tightness. For these assemblies, the surface area ratio of the crevice specimen to the test fixture (crevice washers, bolt, and nut) was approximately 1:3.

To observe the effect of the crevice washer surface area on values of E_{corr} and E_{rcrev} for crevice types (iii), (iv), and (v), serrated washers with flanges, Figure 1(c) and (d), were used to increase the surface area. The crevice specimen-to-test fixture area ratios were approximately 1:18 and 1:10 respectively for Titanium Grade 7 and Alloy 22 test fixtures.

2. E_{corr} and E_{rcrev} Measurements

E_{corr} and E_{rcrev} measurements were conducted in a three-electrode glass test cell, which consisted of the crevice assembly as the working electrode, platinum as the counter electrode, and a saturated calomel electrode as the reference. The reference electrode was connected to the solution through a water-cooled Luggin probe with a porous glass tip to maintain the reference electrode at room temperature. To compare the results with E_{corr} and E_{rcrev} measurements using metal-polytetrafluoroethylene crevices in chloride solutions (Dunn, et al., 2005a), most of the measurements were performed in 4 M NaCl solution at 95 °C [203 °F]. Limited tests were carried out in 0.5 M NaCl and 4 M MgCl₂ solutions at 95 °C [203 °F].

The crevice assembly was immersed in CO₂-free air saturated solution to monitor the E_{corr} using a potentiostat for 48–96 hours, which allowed E_{corr} to reach a steady state. After the E_{corr} measurement was completed, the solution was deaerated for two hours with high purity N₂. This step was followed by the measurement of E_{rcrev} in a deaerated solution using a combination of potentiostatic and cyclic potentiodynamic polarization (Dunn, et al., 2005a). In this method, the potential of the specimen was scanned from the open circuit potential to a higher potential at a scan rate of 0.1 mV/s, held at that potential for 8 hours, and then scanned down to -700 mV_{SCE} with a scan rate of 0.0167 mV/s. The hold potential was limited to potentials below the onset of transpassive dissolution of Alloy 22 or the potential that results in active metal dissolution. The corresponding current density is approximately $1 \times 10^{-3} \text{ A}\cdot\text{cm}^{-2}$ [0.93 A·ft⁻²]. For tests using Alloy 22 as the crevice specimen in 0.5 M and 4 M NaCl solutions, the maximum value of the hold potential was 550 mV_{SCE}, whereas for tests using Type 316L stainless steel as the crevice specimen or in 4 M MgCl₂ solution, the hold potential was lower depending on the current density. The E_{rcrev} is defined as the potential at which the current density remains below $2 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ [$1.9 \times 10^{-3} \text{ A}\cdot\text{ft}^{-2}$] on the reverse scan of the polarization curve (Dunn, et al.,

2005a). The current density was obtained from the measured current divided by the combined crevice assembly surface area, including crevice specimen, crevice washer, bolt, and nut. Duplicate tests were run for all conditions studied.

3. Crevice Corrosion Initiation and Propagation

Crevice corrosion initiation and propagation in aerated 5 M NaCl at 95 °C [203 °F] were evaluated by galvanically coupling the crevice specimen to either an Alloy 22 or a Titanium Grade 7 large plate. The large plate, acting as a cathode, was connected to the specimen through a potentiostat functioning as a zero-resistance ammeter. The area ratio of the crevice specimen to the plate was approximately 1:14. Crevice washers fabricated from metal or polytetrafluoroethylene [Figure 1(b)] were used to form crevices. The materials and electrochemical test cells were similar to those used for E_{corr} and E_{rcrev} measurements. After tests had been set up, the galvanic couple between the crevice specimen and the large plate was left under open circuit conditions to observe crevice corrosion initiation and propagation. For selected tests where localized corrosion was not initiated by coupling to the large plate, 2×10^{-4} M CuCl_2 solution was added to 5 M NaCl solution as an oxidant to initiate crevice corrosion. The potential of the galvanic couple and the galvanic current density were monitored throughout the tests using a multi-channel potentiostat. In the current setup, positive current corresponds to anodic current from the crevice specimen. The galvanic coupling technique and the addition of CuCl_2 solution as an oxidant was previously used to measure the localized corrosion propagation rate of Alloy 22¹ (He and Dunn, 2005).

Results

The experimental results are divided into three parts: (i) E_{corr} and E_{rcrev} measurement in 4 M NaCl solution, (ii) E_{corr} and E_{rcrev} measurement in 0.5 M NaCl and 4 M MgCl_2 solutions, and (iii) galvanic coupling tests in 5 M NaCl solution. All the results were obtained at 95 °C [203 °F].

1. E_{corr} and E_{rcrev} Measurements in 4 M NaCl Solution at 95 °C [203 °F]

Table 2 summarizes E_{corr} and E_{rcrev} values measured at 95 °C [203 °F] in 4 M NaCl solution for the following metal-to-metal crevice assemblies: (i) Type 316L stainless steel to mill-annealed Alloy 22 (Tests 1–4 in Table 2), (ii) mill-annealed Alloy 22 to mill-annealed Alloy 22 (Tests 5–9 in Table 2), (iii) welded plus solution annealed Alloy 22 to mill-annealed Alloy 22 (Tests 10–18 in Table 2), (iv) mill-annealed Alloy 22 to Titanium Grade 7 (Tests 19–28 in Table 2), and (v) welded plus solution annealed Alloy 22 to Titanium Grade 7 (Tests 29–38 in Table 2). Table 3 summarizes measured E_{corr} values of uncreviced Alloy 22 and stainless steel specimens and E_{rcrev} values of metal-to-polytetrafluoroethylene crevices under the same test conditions (Dunn, et al., 2005a). E_{corr} values of uncreviced Titanium Grade 7 and stainless steel measured in this study are also included in Table 3. Figure 2 shows the average E_{rcrev} values where crevice corrosion was not observed at each test condition in Table 2, and E_{rcrev} values where crevice corrosion was observed (Tests 7, 19, 22, and 31 in Table 2), along with the E_{rcrev} values from Table 3 for comparison.

¹He, X. and D.S. Dunn. "Alloy 22 Localized Corrosion Propagation in Chloride-Containing Waters." *Corrosion*. Accepted for Publication. 2006.

1.1 Type 316L Stainless Steel-to-Alloy 22 Crevice Couples

For Type 316L stainless steel coupled to mill-annealed Alloy 22 (Tests 1–4 in Table 2), the measured E_{corr} exceeded the E_{crev} by about 20 mV. The E_{crev} measured at 0.35 N·m [3.1 in·lb] torque was only few minivolts lower than that measured at 8.4 N·m [75 in·lb] (Figure 2); the difference is not considered to be significant. The E_{crev} values measured from Type 316L stainless steel-to-mill-annealed Alloy 22 crevices (Table 2) were close to that measured from the Type 316L stainless steel-to-polytetrafluoroethylene crevices ($-348 \text{ mV}_{\text{SCE}}$ in Table 3). Consistent with the observed low E_{crev} values, crevice corrosion was observed on nearly all of the crevice sites on the Type 316L stainless steel specimen at both applied torque values, whereas no corrosion was observed on Alloy 22 crevice washers. These observations suggest that the stainless steel is susceptible to crevice corrosion under such conditions, but the susceptibility is not highly affected by the crevice forming material.

Figure 3 shows the corrosion potential measured from uncreviced Alloy 22 and Type 316L stainless steel, and Type 316L stainless steel-to-Alloy 22 crevice. The E_{corr} of uncreviced Alloy 22 was higher than that of Type 316L stainless steel, which is consistent with the reported galvanic series in flowing sea water (ASM International, 1987). The E_{corr} of the crevice couple was close to that of the uncreviced Type 316L stainless steel, which suggests that the corrosion potential of the crevice couple is dominated by the behavior of stainless steel under this condition.

1.2 Mill-Annealed Alloy 22 to Mill-Annealed Alloy 22 Crevice Couples

For mill-annealed Alloy 22 to mill-annealed Alloy 22 couples (Tests 5–9 in Table 2), the E_{corr} values at both torque values were in the range of -200 to $-140 \text{ mV}_{\text{SCE}}$ —somewhat lower than the corrosion potential of the uncreviced Alloy 22 (Table 3). The difference is not considered to be significant considering that, in the measurement of corrosion potential of uncreviced specimens, longer times were allowed for passive film to age and hence, the corrosion potential shifted to more noble values. After E_{crev} measurement, it was observed that only one of the 120 crevice sites (5 specimens $\times$ 24 sites per specimen) showed corrosion on the crevice specimen (Test 7 in Table 2), and in one case, corrosion occurred on the Alloy 22 nut used to assemble the crevice (Test 8 in Table 2). However, corrosion was only observed at the higher torque. Figure 4 shows the current and potential as a function of time during potentiodynamic polarization and potentiostatic hold for Tests 7 and 9. For Test 7, several current spikes were observed during the forward scan and reverse scan that were not present in Tests 8 and 9 (Test 8 is not shown). Although crevice corrosion was observed in Test 7, the E_{crev} values were significantly higher than the E_{crev} values measured with Alloy 22-to-polytetrafluoroethylene crevice, as shown in Figure 2. Consistently, the Alloy 22-to-Alloy 22 crevices exhibited less corrosion sites than the Alloy 22-to-polytetrafluoroethylene crevices.

1.3 Welded Plus Solution Annealed Alloy 22 to Mill-Annealed Alloy 22 Crevice Couples

Previously, it was reported that waste package fabrication processes such as welding and postweld heat treatment might render Alloy 22 susceptible to localized corrosion (Dunn, et al., 2005a,b). Both beneficial and detrimental effects of solution annealing of Alloy 22 were reported to be attributed to microstructural and compositional variations in the welds (Bechtel

SAIC Company, LLC, 2003). The detrimental effects were mainly related to mechanical properties. The E_{corr} and E_{rcrev} measured for welded plus solution annealed Alloy 22 to mill-annealed Alloy 22 couples (Tests 10–18 in Table 2) were similar to those measured from mill-annealed Alloy 22 to mill-annealed Alloy 22 galvanic couples (Tests 5–9 in Table 2). No crevice corrosion was observed on any of the specimens or the crevice assembly. The E_{rcrev} values were significantly higher than those of the welded plus solution annealed Alloy 22-to-polytetrafluoroethylene crevice ($-41 \text{ mV}_{\text{SCE}}$ in Table 3). No effect on E_{rcrev} values was observed by increasing the torque or surface area of the crevice washer.

1.4 Mill-Annealed Alloy 22 to Titanium Grade 7 and Welded Plus Solution Annealed Alloy 22 to Titanium Grade 7 Crevice Couples

Figure 5 shows the E_{corr} of mill-annealed Alloy 22 to Titanium Grade 7 crevice couples (Tests 20, 21, 22, 23, 25, and 27 in Table 2) measured in air-saturated solution, along with E_{corr} of uncreviced Alloy 22 and Titanium Grade 7 (for clarity, only one set of data is shown in Figure 5 for uncreviced Alloy 22 and Titanium Grade 7). After the crevice couples were immersed in solution, the corrosion potential shifted to more noble values for all tests. The end potentials were in a range of $-200 \text{ mV}_{\text{SCE}}$ to $0 \text{ mV}_{\text{SCE}}$ after several days. The E_{corr} values of the uncreviced Alloy 22 and Titanium Grade 7 specimens were within E_{corr} range of the crevice couples. No obvious difference was observed between the E_{corr} of uncreviced Alloy 22 and Titanium Grade 7 specimens or the Alloy 22 to Titanium Grade 7 couples.

Post-test examination of the mill-annealed Alloy 22 to Titanium Grade 7 crevice couples revealed that 16 of 240 crevice sites (10 specimens $\times$ 24 sites per specimen) showed corrosion after the repassivation potential measurement. Crevice corrosion was only observed when the crevice specimen (mill-annealed Alloy 22) to crevice washer (Titanium Grade 7) area ratio was 1:3. For crevice specimen-to-crevice washer area ratios of 1:18 (Tests 25–28 in Table 2), no corrosion was observed regardless of the crevice tightness, which is consistent with the observed high repassivation potential.

Figure 6 shows the potentiodynamic polarization curves for Tests 19, 20, 22, and 23 in Table 2. No positive hysteresis was observed for Tests 20 and 23 in the high potential region. The corrosion observed for Tests 19 and 22 was probably due to the current peak observed at approximately $200 \text{ mV}_{\text{SCE}}$ during the reverse scan. Subsequent tests (Tests 20, 21, 23, and 24 in Table 2) with a fresh specimen and repolished Titanium Grade 7 crevice washers did not result in crevice corrosion and no such peak was observed. The only difference between these tests is that Tests 19 and 22 were assembled with unused and freshly polished Titanium Grade 7 crevice washer, bolt, and nut, whereas Tests 20, 21, 23, and 24 were assembled with previously used crevice washers, bolts, and nuts. Only the plateaued surface of the crevice washer that contacts the crevice specimen was freshly polished. No such peak was observed after the Titanium Grade 7 washers, bolts, and nuts were descaled with hydrofluoric acid solution following the recommended procedure (Tests 21, 24, 33, and 38 in Table 2) (American Society for Testing and Materials International, 2005b).

The measured E_{corr} and E_{rcrev} values for welded plus solution annealed Alloy 22 coupled to Titanium Grade 7 (Tests 29–38 in Table 2) were similar to those of mill-annealed Alloy 22 to Titanium Grade 7 couples. Except in one case (Test 31 in Table 2) where fresh hardware was

used to assemble the crevice, no crevice corrosion was observed after potentiodynamic polarization. The E_{rcrev} values were significantly higher than the E_{corr} of the crevice couple.

2. E_{corr} and E_{rcrev} Measurements in 0.5 M NaCl and 4 M MgCl₂ Solutions at 95 °C [203 °F]

The tests conducted in 4 M NaCl solution at 95 °C [203 °F] have shown that no significant effects of crevice tightness and area ratio of crevice specimen to crevice washer were observed. Except for stainless steel and several tests on Alloy 22 (Tests 7, 19, 22, and 31 in Table 2), the crevice specimens remained passive during polarization. In the potential repository, the chloride concentration in waters contacting the waste package could range from very dilute water to very concentrated brines due to evaporation (Dunn, et al., 2005a). Additional tests to measure E_{corr} and E_{rcrev} of mill-annealed Alloy 22 to Titanium Grade 7 and welded plus solution annealed Alloy 22-to-Titanium Grade 7 were performed in 0.5 M NaCl and 4 M MgCl₂ solution at 95 °C [203 °F]. All the Titanium Grade 7 washers, bolts, and nuts were descaled before use (American Society for Testing and Materials International, 2005b). In addition, the plateaued surface of the crevice washer was polished after descaling. The test results are summarized in Table 4. Tests 39–42 were performed in 0.5 M NaCl solution and Tests 43–50 were performed in 4 M MgCl₂ solution. Since no significant effect of area ratio was observed in 4 M NaCl solution, only small crevice washers [Figure 1(b)] were used in these tests in Table 4.

In 0.5 M NaCl solution, the Alloy 22 and welded plus solution annealed Alloy 22 specimen remained passive even after polarization up to 550 mV_{SCE}. No crevice corrosion was observed on the crevice specimens and test fixtures. The measured E_{rcrev} values were 350 mV above the E_{corr} values.

Figure 7 shows the E_{rcrev} values measured in 4 M MgCl₂ solution in Table 4, along with the E_{rcrev} values measured previously in 3.5 M MgCl₂ and 5 M MgCl₂ solution at 95 °C [203 °F] from Alloy 22-to-polytetrafluoroethylene crevices (Dunn, et al., 2005a). In all cases represented in Figure 7, crevice corrosion was observed on crevice specimens. However, no crevice corrosion was observed on Titanium Grade 7 washers for tests listed in Table 4. Figure 7 shows that the E_{rcrev} values for metal-to-metal crevices were higher than those measured from the corresponding metal-to-polytetrafluoroethylene crevices in 3.5 M MgCl₂ and 5 M MgCl₂, indicating less susceptibility of metal-to-metal crevices to crevice corrosion. However, the E_{rcrev} values measured in 4 M MgCl₂ solution (Tests 43–50 in Table 4) were lower than those measured in 4 M NaCl solution when crevice corrosion was observed (Tests 7, 19, 22, and 31 in Table 2). This result is consistent with the increasing susceptibility of Alloy 22 to crevice corrosion with increasing chloride concentration. Another feature noticed from Table 4 is that the difference between E_{corr} and E_{rcrev} was within 100 mV, except for one test (Test 46 in Table 4). If we consider the uncertainty in the measurement of E_{corr} and E_{rcrev} (typically ± 100 mV), the small difference suggests that crevice corrosion might occur under such test conditions. In addition, it appears that the E_{rcrev} values were lower for welded plus solution annealed Alloy 22 than for mill-annealed Alloy 22.

3. Galvanic Coupling Tests in 5 M NaCl Solution at 95 °C [203 °F]

Galvanic coupling tests were conducted in CO₂-free air saturated 5 M NaCl solution at 95 °C [203 °F]. The crevice specimens were coupled to either an Alloy 22 or a Titanium Grade 7 plate using metal or polytetrafluoroethylene to form crevices. The area ratio of the crevice

specimen to the plate was 1:14. To simulate the possible tight metal-to-metal crevice present in the potential repository, only high torque, 8.4 N·m [75 in·lb], was applied to assemble the metal-to-metal crevice. A torque of 0.70 N·m [6.2 in·lb] was applied between metal-to-polytetrafluoroethylene to observe the effect of crevice washer material {0.70 N·m [6.2 in·lb] is the highest torque that can be applied to the assembly with polytetrafluoroethylene as the crevice washer}. The tests conducted and the results are summarized in Table 5. Three types of crevice specimens were evaluated: (i) Type 316L stainless steel (Tests G1–2 in Table 5), (ii) mill-annealed Alloy 22 (Tests G3–5 in Table 5), and (iii) welded plus solution annealed Alloy 22 (Tests G6–10 in Table 5).

3.1 Type 316L Stainless Steel Galvanically Coupled to Alloy 22

For tests on Type 316L stainless steel using Alloy 22 or polytetrafluoroethylene as the crevice forming material, crevice corrosion was initiated under an open-circuit condition. Figure 8 shows the galvanic coupling current density and potential as a function of time. (In the current setup, positive current corresponds to anodic current from crevice specimen.) After coupling, crevice corrosion initiated instantaneously, resulting in a current density peak. This was followed by current density decay and potential drop. After a period of crevice corrosion propagation, tests were terminated at 40 and 60 days, respectively. For these two tests, no repassivation was observed in the testing period.

Post-test examination revealed that crevice corrosion was limited to the Type 316L stainless steel specimen. This result is consistent with the more noble corrosion potential observed on Alloy 22 in 4 M NaCl solution (Figure 3). Figure 9 shows Type 316L stainless steel specimens with crevice corrosion. For the specimen with Alloy 22 as crevice forming material, crevice corrosion occurred in the creviced region on 22 out of 24 crevice sites with varying penetration depths, as listed in Table 5. For the Type 316L stainless steel specimen with polytetrafluoroethylene as the crevice washer, crevice corrosion led to penetration through the specimen with a thickness of 5 mm [0.2 in]. In addition to crevice corrosion, there was also pitting corrosion inside and outside of the crevice for the stainless steel specimen using polytetrafluoroethylene as the crevice washer.

3.2 Alloy 22 Galvanically Coupled to Alloy 22 or Titanium Grade 7

For other tests in Table 5, crevice corrosion was not initiated under the open-circuit condition with Alloy 22 or Titanium Grade 7 as galvanic coupling material in the air saturated chloride solution (Tests G3–G10 in Table 5). However, after the addition of CuCl_2 as an oxidant to raise the E_{corr} for all the tests using polytetrafluoroethylene as crevice washers (Tests G5 and G8 in Table 5), crevice corrosion was initiated. In contrast, crevice corrosion was not initiated for all the tests using Alloy 22 or Titanium Grade 7 metals as crevice washers (Tests G3–4, G6–7, and G9–10 in Table 5).

Figure 10 shows the galvanic coupling current density and potential obtained from Tests G6 and G8, which represent tests of a metal-to-metal crevice and a metal-to-polytetrafluoroethylene crevice. (In the current setup, positive current corresponds to anodic current from the crevice specimen.) For Test G6, where welded plus solution annealed Alloy 22 was galvanically coupled to Alloy 22, the corrosion potential remained at $\sim -200 \text{ mV}_{\text{SCE}}$ and the current density remained at values of $10^{-10} \text{ A}\cdot\text{cm}^{-2}$ [$9.5 \times 10^{-8} \text{ A}\cdot\text{ft}^{-2}$] after coupling, which indicates that no crevice corrosion was initiated. After the galvanic couple remained passive for ~ 10 days, a

small amount of CuCl_2 solution was added into the solution as an oxidant. The addition of CuCl_2 raised the coupling potential by 600 mV and increased the current density to $10^{-7} \text{ A}\cdot\text{cm}^{-2}$ [$9.5 \times 10^{-5} \text{ A}\cdot\text{ft}^{-2}$]. However, no active metal dissolution current was observed after the initial current increase. Another equal amount of CuCl_2 was added to raise the corrosion potential further. The corrosion potential increased slightly; however, the current remained at the same values. The test was terminated at ~50 days. For the tests where crevice corrosion was initiated, large potential drops resulting from active dissolution in the occluded crevice washers were observed, as shown in Test G8 in Figure 10. Test G5 in Table 5 was terminated by power disruption. The other test (G8 in Table 5) arrested after crevice corrosion propagated for a period of 5 days.

Discussion

1. Uncertainty of the E_{rcrev} Values for Metal-to-Metal Crevices

There are several methods reported in the literature to measure E_{rcrev} , including cyclic potentiodynamic polarization detailed in ASTM G61 (American Society for Testing and Materials International, 2005c; Bechtel SAIC Company, LLC, 2004; Evans, et al., 2005; Ilevbare, et al., 2005; Jain, et al., 2003), the Tsujikawa-Hisamatsu Electrochemical method and its variations (Evans, et al., 2005; Jain, et al., 2003; Tsujikawa and Hisamatsu, 1984; Tsujikawa and Kojima, 1991), and a combination of potentiostatic and cyclic potentiodynamic polarization methods (Dunn, et al., 2005a,b,c, 2006). Typically, the crevice is formed by sandwiching metals between washers made from a polymer. Because the objective of this work is to evaluate if the metal-to-metal contact is detrimental to metals in the potential engineered barrier system, the same method (a combination of potentiostatic and cyclic potentiodynamic polarization) as previously used in evaluating the Alloy 22 corrosion performance in contact with polytetrafluoroethylene as a crevice former material (Dunn, et al., 2005a,b,c, 2006) was used in this work; however, the crevice washer was machined from Alloy 22 or Titanium Grade 7. Except for the E_{rcrev} values measured from stainless steel (Tests 1–4 in Table 2), other E_{rcrev} values shown in Table 2 span a potential range from 550 mV_{SCE} to -39 mV_{SCE}—a large data scatter. In addition to large data scatter at a chloride concentration of 4 M, the initiation of crevice corrosion was not consistently observed (Table 2). In contrast, at chloride concentration of 0.5 M (Table 4) no initiation of crevice corrosion was consistently observed, and at chloride concentration of 8 M (4 M MgCl_2 in Table 4), the initiation of crevice corrosion was consistently observed. For most tests in Table 2 and Table 4 where crevice corrosion did not occur, the E_{rcrev} had no physical meaning. Only the E_{rcrev} values from tests where crevice corrosion occurred were used in the localized corrosion model abstraction for performance assessment calculations (Dunn, et al., 2005a,b) and in comparison to evaluate the relative crevice corrosion resistance. The E_{rcrev} values were a strong function of chloride concentration. The spread in the E_{rcrev} values was typically less than 100 mV in replicate experiments at chloride concentrations above 1 M for the Alloy 22-to-polytetrafluoroethylene crevice, but it increased with decreasing chloride concentration (Dunn, et al., 2005a,b). At marginally low chloride concentrations, inconsistent results of crevice corrosion initiation were also observed (Dunn, et al., 2005a,b).

2. Evaluation of Corrosion of Similar and Dissimilar Metal Crevices in the Potential Engineered Barrier System

In the potential repository, metal-to-metal crevices may be formed between Alloy 22 to Titanium Grade 7, Alloy 22 to Type 316L stainless steel, and Alloy 22 to Alloy 22. During the fabrication

processes the waste package may be solution annealed to eliminate residual stresses created during fabrication. Therefore, both mill-annealed and welded plus solution annealed metallurgical conditions may be present in the Alloy 22 waste package outer container. Retention of aggressive waters in occluded crevice areas could lead to crevice corrosion of the engineered barrier materials. Initiation and propagation of crevice corrosion is considered to be possible in the NRC/CNWRA Total-system Performance Assessment code (Mohanty, et al., 2002) when the E_{corr} is greater than the E_{rcrev} . The E_{corr} of Alloy 22 depends on temperature, pH, and oxygen reduction kinetics, and the E_{rcrev} is dependent on the metallurgical condition of the alloy, temperature, chloride concentration, and the relative concentration of inhibiting anions (NO_3^- , CO_3^{2-} , HCO_3^- , and SO_4^{2-}) to the chloride concentration. The E_{rcrev} model was constructed using data from Alloy 22 crevice corrosion repassivation tests in pure chloride solutions and solutions containing chloride and inhibiting anions. The test method is the same as that used in this study, but in all the tests polytetrafluoroethylene was used as the crevice washer with a torque of 0.35 N·m [3.1 in·lb] (Dunn, et al., 2005a,b).

Tests conducted in this study showed that, except for 316L stainless steel, all other realistic metal-to-metal crevices were less susceptible to crevice corrosion than the corresponding metal-to-polytetrafluoroethylene crevices. Figure 11 summarizes the E_{rcrev} values for mill-annealed Alloy 22 and welded plus solution annealed Alloy 22 obtained over a wide range of chloride solutions at 95 °C [203 °F] using polytetrafluoroethylene or metal (Alloy 22 or Titanium Grade 7) as the crevice-forming material. Results of tests where no crevice corrosion was initiated are indicated in Figure 11 as open symbols. Also included in Figure 11 are log-linear regression lines of the repassivation potential with chloride concentration. Despite the fact that crevice corrosion was not consistently observed in the 4 M NaCl solution, the regression lines for metal-to-metal crevices were above those of the metal-to-polytetrafluoroethylene crevices. This result suggests that the metal-to-metal crevices are less susceptible to localized corrosion than the metal-to-polytetrafluoroethylene crevices. The E_{rcrev} values of metal-to-metal crevices where crevice corrosion was initiated were higher than those for metal-to-polytetrafluoroethylene crevices, especially at chloride concentrations of 4 M. This observation is consistent with a large difference between E_{corr} and E_{rcrev} (Table 2) and far less corrosion observed on crevice specimens after potentiodynamic polarization. The difference in crevice corrosion susceptibility is a result of a difference in crevice washers. Upon torque, polytetrafluoroethylene washers may deform and fill the small voids created by the surface roughness of the specimen, which results in a better occluded region on the specimen. Conversely, in Alloy 22 to other metal contact, due to the rigidity of the crevice forming metals (Alloy 22 and Titanium Grade 7) used in this study, the crevice is not as tight as the Alloy 22-to-polytetrafluoroethylene crevices, resulting in less crevice corrosion susceptibility. Consistently, no crevice corrosion initiation of Alloy 22 by galvanic coupling was observed when metal was used as a crevice washer to form metal-to-metal crevices in 5 M NaCl solution, even with the addition of CuCl_2 as an oxidant. This result suggests that the Alloy 22 crevice corrosion resistance is not degraded by coupling to metals in the potential engineered barrier system.

The E_{corr} of mill-annealed Alloy 22 and welded plus solution annealed Alloy 22 was not affected by coupling to Titanium Grade 7 as shown in Table 2 and Figure 5. In all tests, no crevice corrosion of the Titanium Grade 7 crevice washers was observed. Ikeda and Quinn (2003) reported that the corrosion potential of Alloy 22 to Titanium Grade 7 or Alloy 22 to Titanium Grade 16 tight crevice was $-500 \text{ mV}_{\text{SCE}}$ in simulated concentrated water at 90 °C [194 °F], which was more negative than that of each uncreviced Alloy 22, uncreviced Titanium Grade 7, or uncreviced Titanium Grade 16. Ikeda and Quinn (2003) attributed this potential

drop to enhanced corrosion in the metal-to-metal crevice, specifically on Titanium Grades 7 and 16. The significant potential drop observed by Ikeda and Quinn (2003) was not observed in this work by coupling Alloy 22 to Titanium Grade 7 in 4 M NaCl solution. On the contrary, the corrosion potential of the Alloy 22 to Titanium Grade 7 crevice shifted in noble direction after immersion. No difference in corrosion potential was observed between uncreviced Alloy 22, Titanium Grade 7, and Alloy 22 to Titanium Grade 7 crevice couples. The discrepancy could be mainly due to the difference of solution used in the tests. Simulated concentrated water contains significant amount of fluoride, which typically attacks titanium oxide film and induces corrosion (Nakagawa, et al., 2001; Pulvirenti, et al., 2002; Schutz and Grauman, 1986). In addition, in the tests conducted by Ikeda and Quinn (2003), the solution was not aerated, which may also lead to lower corrosion potential than that observed in this work.

The susceptibility of Alloy 22 to localized corrosion is strongly related to the quantity and chemistry of water that contacts the waste package. In the NaCl solution, localized corrosion is not likely to occur since the E_{corr} under air saturated conditions is well below the E_{rcrev} . If localized corrosion occurs, the penetration is likely to be limited due to the repassivation tendency of localized corrosion. The limited penetration was previously reported when Alloy 22 was coupled to Alloy 22 using polytetrafluoroethylene as the crevice washer in a 5 M NaCl solution at 95 °C [203 °F]² (He and Dunn, 2005). Crevice corrosion propagation was quite limited under such test conditions. More aggressive water chemistries (high chloride concentration and low pH) would be necessary to initiate localized corrosion of Alloy 22.

Type 316L stainless steel is the potential material for the waste package inner container and for rock bolts. The tests in this work showed that, when stainless steel contacted Alloy 22 in concentrated chloride solutions and temperatures near boiling, stainless steel was corroded at a fast rate, but Alloy 22 was protected. Stifling and arrest of crevice corrosion of Type 316L stainless steel has not been evaluated. It appears, however, that crevice corrosion of Type 316L stainless steel is not likely to be initiated in dilute chloride solutions at temperatures below 95 °C [203 °F].

Conclusions

Crevice corrosion is considered possible if the corrosion potential (E_{corr}) exceeds the repassivation potential for crevice corrosion (E_{rcrev}). In this study, potentiodynamic polarization and potentiostatic hold were used to determine the E_{rcrev} values of the metal-to-metal crevices in 0.5 M NaCl, 4 M NaCl, and 4 M MgCl₂ solutions at 95 °C [203 °F]. The E_{rcrev} values were compared with previously obtained data on crevices between Alloy 22 and polytetrafluoroethylene. Five types of crevices were evaluated: (i) Type 316L stainless steel to mill-annealed Alloy 22, (ii) mill-annealed Alloy 22 to mill-annealed Alloy 22, (iii) welded plus solution annealed Alloy 22 to mill-annealed Alloy 22, (iv) mill-annealed Alloy 22 to Titanium Grade 7, and (v) welded plus solution annealed Alloy 22 to Titanium Grade 7. It was observed that, except for Type 316L stainless steel, all other metal-to-metal crevices were less susceptible to crevice corrosion than the corresponding metal-to-polytetrafluoroethylene crevices. The Alloy 22 corrosion resistance appears not to be degraded by galvanic coupling to Titanium Grade 7.

²He, X. and D.S. Dunn. "Alloy 22 Localized Corrosion Propagation in Chloride-Containing Waters." *Corrosion*. Accepted for Publication. 2006.

Galvanically coupled specimens were used to measure crevice corrosion propagation in 5 M NaCl at 95 °C [203 °F]. The crevice specimens were coupled to either an Alloy 22 or a Titanium Grade 7 plate using metal or polytetrafluoroethylene to form crevices. For all the tests that used polytetrafluoroethylene as crevice washers, crevice corrosion was initiated at open-circuit potential by the addition of CuCl_2 as an oxidant, whereas crevice corrosion was not initiated for all the tests that used Alloy 22 or Titanium Grade 7 metals as crevice washers to form metal-to-metal crevices. However, crevice corrosion propagation was very limited under the test conditions due to repassivation of crevice corrosion. The metal-to-metal crevices examined were found not to enhance localized corrosion propagation. The E_{crev} model constructed using data obtained from metal-to-polytetrafluoroethylene crevices conservatively bound crevice corrosion resistance for susceptibility and propagation.

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REFERENCES

American Society for Testing and Materials International. "Metals Test Methods and Analytical Procedures." *ASTM G78-01 (2004): Standard Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-containing Aqueous Environments. Vol. 3.02: Wear and Erosion—Metal Corrosion*. Published on CD-ROM. West Conshohocken, Pennsylvania: American Society for Testing and Materials International. 2005a.

American Society for Testing and Materials International. "Reactive and Refractory Metals and Alloys." *ASTM B600-91 (2005): Standard Guide for Descaling and Cleaning Titanium and Titanium Alloy Surfaces. Vol. 2.04: Titanium*. Published on CD-ROM. West Conshohocken, Pennsylvania: ASTM International. 2005b.

American Society for Testing and Materials International. "Metals Test Methods and Analytical Procedures." *ASTM G61-86 (2005): Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys. Vol. 3.02: Wear and Erosion—Metal Corrosion*. Published on CD-ROM. West Conshohocken, Pennsylvania: American Society for Testing and Materials International. 2005c.

ASM International. *Corrosion*. Volume 13: Metals Handbook. 9th Edition. Metals Park, Ohio: ASM International. 1987.

Bechtel SAIC Company, LLC. "General Corrosion and Localized Corrosion of Waste Package Outer Barrier." Rev. 2. Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2004.

Bechtel SAIC Company, LLC. "Technical Basis Document No. 6: Waste Package and Drip Shield Corrosion." Rev. 1. Las Vegas, Nevada: Bechtel SAIC Company, LLC. 2003.

Dunn, D.S., Y.-M. Pan, L. Yang, G.A. Cragnolino. "Localized Corrosion Susceptibility of Alloy 22 in Chloride Solutions: Part 2—Effect of Fabrication Processes." *Corrosion*. Vol. 62. pp. 3–12. 2006.

Dunn, D.S., O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chaing. "Passive and Localized Corrosion of Alloy 22—Modeling and Experiments." CNWRA 2005-002. San Antonio, Texas: CNWRA. 2005a.

Dunn, D.S., O. Pensado, Y.-M. Pan, L. Yang, and X. He. "Modeling Corrosion Processes for Alloy 22 Waste Packages." Scientific Basis for Nuclear Waste Management XXIX, Ghent, Belgium, September 12–16, 2005. Symposium Proceedings 932. P. Van Iseghem, ed. Pittsburgh, Pennsylvania: Materials Research Society. 2005b.

Dunn, D.S., Y.-M. Pan, L. Yang, G.A. Cragnolino. "Localized Corrosion Susceptibility of Alloy 22 in Chloride Solutions: Part 1—Mill-Annealed Condition." *Corrosion*. Vol. 61. pp. 1,078–1,085. 2005c.

Evans, K.J., A. Yilmaz, S.D. Day, L.L. Wong, J.C. Estill, and R.B. Rebak. "Using Electrochemical Methods to Determine Alloy 22's Crevice Corrosion Repassivation Potential." *Journal of Metals*. Vol. 57. pp. 56-61. 2005.

He, X. and D.S. Dunn. "Alloy 22 Localized Corrosion Propagation in Chloride-Containing Waters." CNWRA 2006-001. San Antonio, Texas: CNWRA. 2005.

Ikeda, B.M. and M.J. Quinn. "Corrosion of Dissimilar Metal Crevices in Simulated Concentrated Ground Water Solutions at Elevated Temperature." AECL-12167. Rev. 00. Pinawa, Manitoba, Canada: Atomic Energy of Canada Limited. 2003.

Ilevbare, G.O., K.J. King, S.R. Gordon, H.A. Elayat, G.E. Gdowski, and T.S.E Gdowski. "Effect of Nitrate on the Repassivation Potential of Alloy 22 in Chloride-Containing Environments." *Journal of the Electrochemical Society*. Vol. 152. pp. B547–B554. 2005.

Jain, V., D.S. Dunn, N. Sridhar, and L. Yang. "Effect of Measurement Methods and Solution Chemistry on the Evaluation of the Localized Corrosion of Candidate High-Level Waste Container Materials." Proceedings of the CORROSION 2003 Conference. Paper No. 690. Houston, Texas: NACE International. 2003.

Mohanty, S., T.J. McCartin, and D. Esh (coordinators). "Total-system Performance Assessment (TPA) Version 4.0 Code: Module Descriptions and User's Guide." San Antonio, Texas: CNWRA. 2002.

Nakagawa, M., S. Matsuya, and K. Udoh. "Corrosion Behavior of Pure Titanium and Titanium Alloys in Fluoride-Containing Solutions." *Dental Materials Journal*. Vol. 20, No. 4. pp. 305–314. 2001.

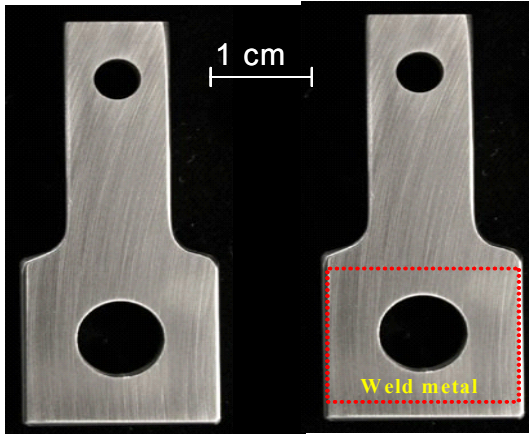
Payer, J.H., U. Landau, X. Shan, and A.S. Agarwal. "Effect of Crevice Former on Corrosion Damage Propagation." Annual Report. Washington, DC: U.S. Department of Energy, Office of Science and Technology and International. 2005.

Pulvirenti, A.L., K.M. Needham, M.A. Adel-Hadadi, and A. Barkatt. "Corrosion of Titanium Grade-7 in Solutions Containing Fluoride and Chloride Salts." Proceedings of the CORROSION 2002 Conference. Paper No. 552. Houston, Texas: NACE International. 2002.

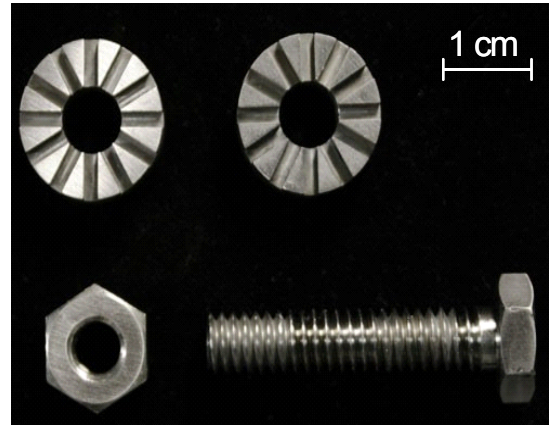
Schutz, R.W. and J.S. Grauman. "Corrosion Behavior of Titanium and other Alloys in Laboratory FGD Scrubber Environments." *Materials Performance*. Vol. 25, No. 4. pp. 35–42. 1986.

Tsujikawa, S. and Y. Hisamatsu. "Repassivation Potential as a Crevice Corrosion Characteristics for Austenitic and Ferritic Stainless Steels." *Improvement of Corrosion Resistance of Structural Materials in Aggressive Media*. Ya. M. Koloyrkin, ed. Moscow, Russia: Nauka Publishers. 1984.

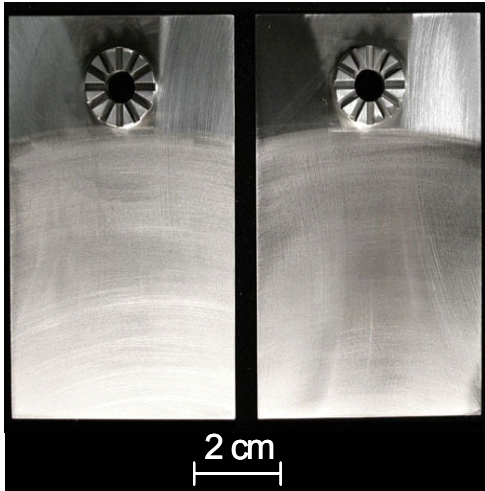
Tsujikawa, S. and Y. Kojima. "Repassivation Method to Predict Long-Term Integrity of Low-Alloy Titanium for Nuclear Waste Package." Proceedings of the Scientific Basis for Nuclear Waste Management XIV. Symposium Proceedings 212. T. Abrajano and L.H. Johnson, eds. Pittsburgh, Pennsylvania: Materials Research Society. pp. 261–268. 1991.



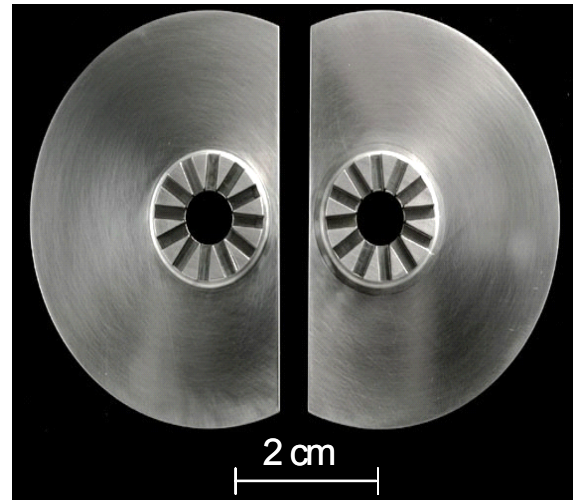
(a) Alloy 22 crevice specimen, mill-annealed and welded plus solution annealed. Surface area = 11.6 cm^2 [1.80 in^2].



(b) Titanium Grade 7 washers, bolt, and nut. Combined surface area = 39.3 cm^2 [6.09 in^2].



(c) Large Titanium Grade 7 washers. Surface area = 186 cm^2 [28.8 in^2].



(d) Large Alloy 22 washers. Surface area = 87.2 cm^2 [13.5 in^2].

Figure 1. Optical photographs of crevice specimen and test fixtures (crevice washers, bolts, and nuts) used to assemble crevices

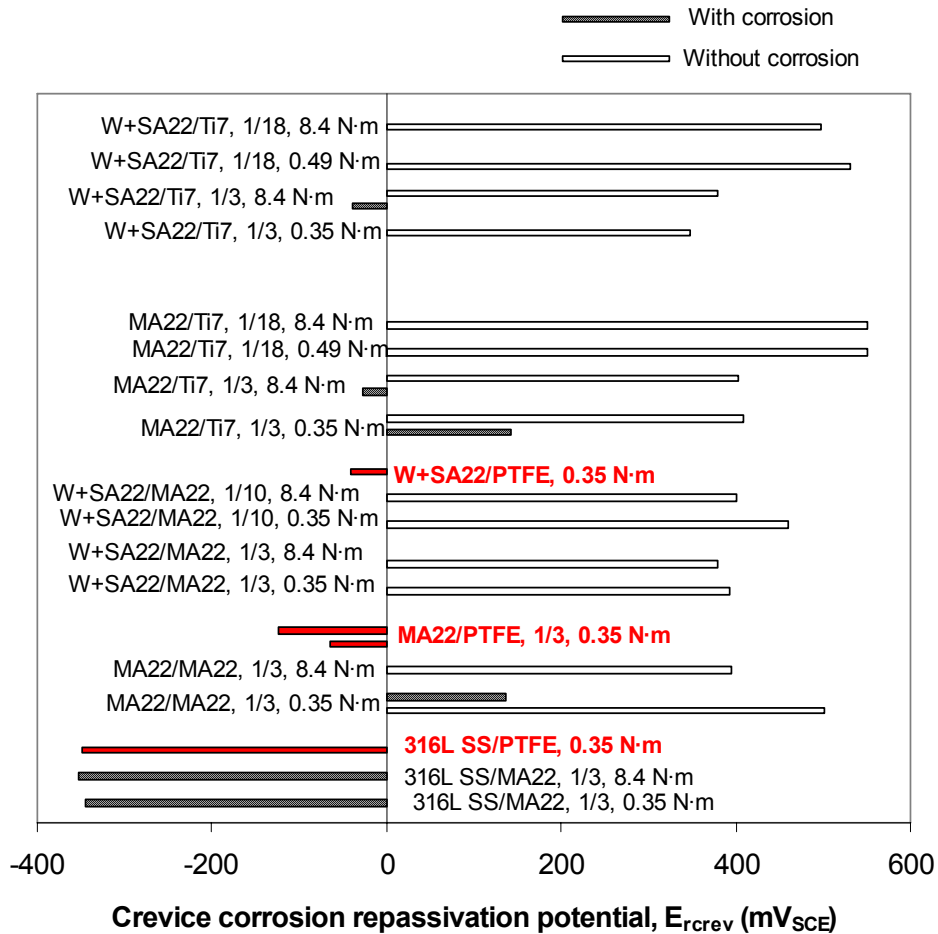


Figure 2. Measured repassivation potentials for crevice corrosion in 4 M NaCl solution at 95 °C [203 °F] for different specimens with different torque levels (Tables 2 and 3). (Note: SS—stainless steel, MA 22—mill-annealed Alloy 22, W+SA 22—welded plus solution annealed Alloy 22, Ti7—Titanium Grade 7, PTFE—polytetrafluoroethylene, 1 N·m = 8.93 in·lb)

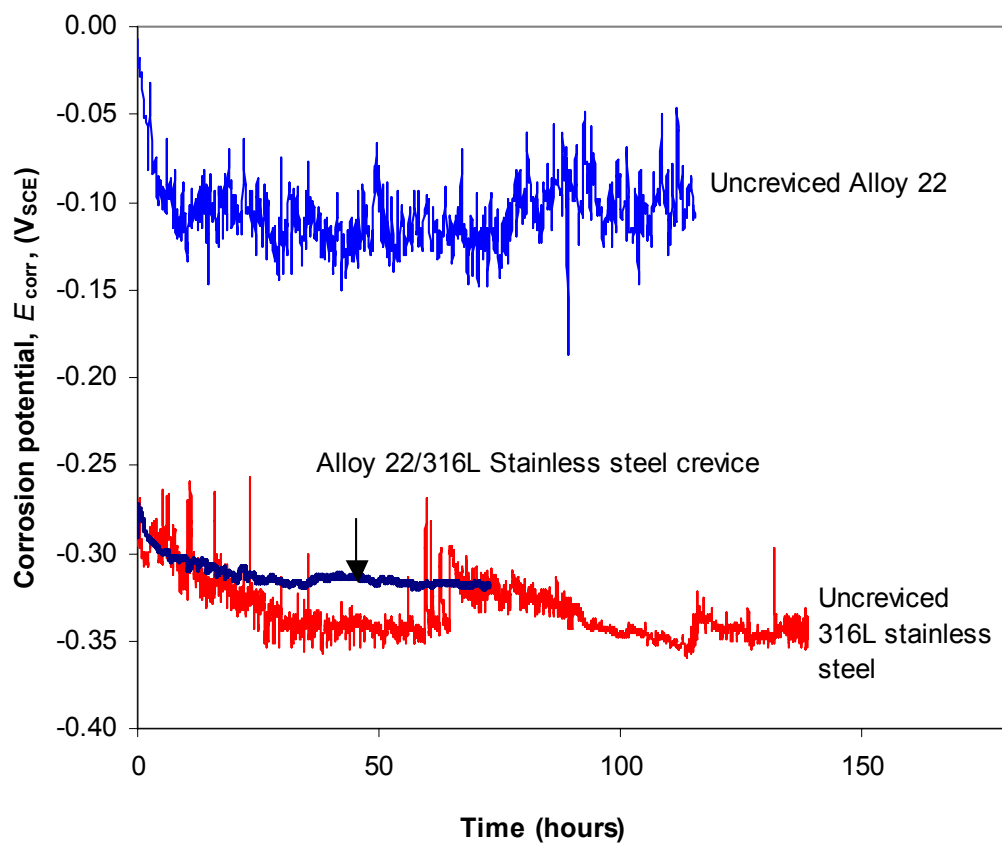


Figure 3. Open circuit potential of uncreviced Alloy 22, 316L stainless steel, and Alloy 22-to-316L stainless steel crevice assembly measured in 4 M NaCl solution at 95 °C [203 °F]

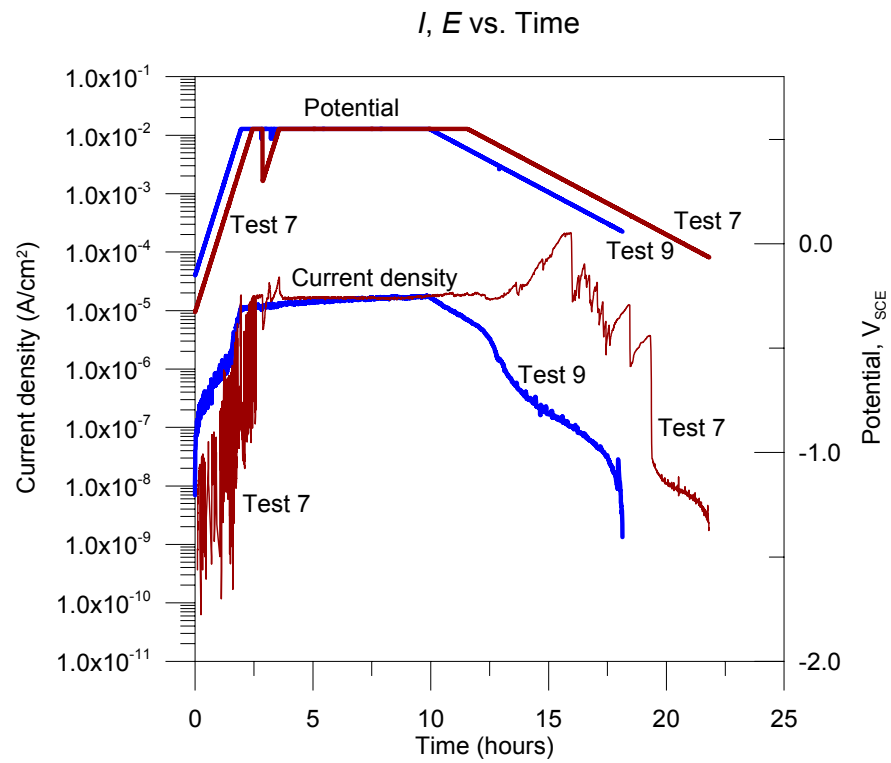


Figure 4. Potentiodynamic polarization and potentiostatic hold curves of Alloy 22 to Alloy 22 crevices (Tests 7 and 9 in Table 2) in N₂ deaerated 4 M NaCl solution at 95 °C [203 °F]

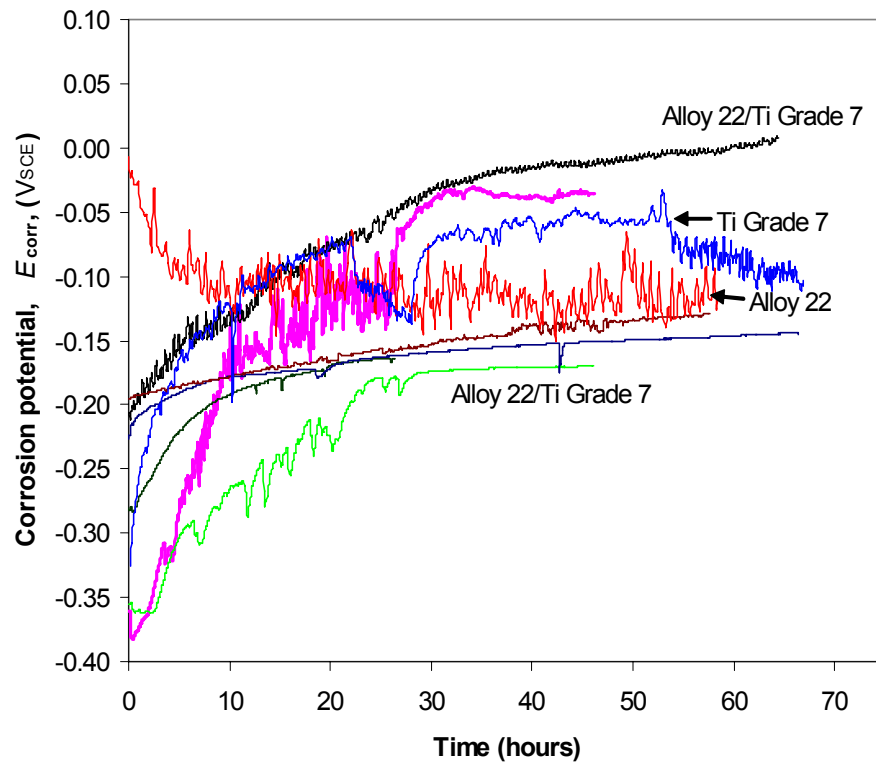


Figure 5. Open circuit potential of uncreviced Alloy 22 and Titanium Grade 7 specimens, and Alloy 22 to Titanium Grade 7 crevice couples (Tests 20, 21, 22, 23, 25, and 27 in Table 2) measured in 4 M NaCl solution at 95 °C [203 °F]. For clarity, only one set of data for uncreviced Alloy 22 and Titanium Grade 7 are shown. Other data are shown for Alloy 22 to Titanium Grade 7 crevice couples.

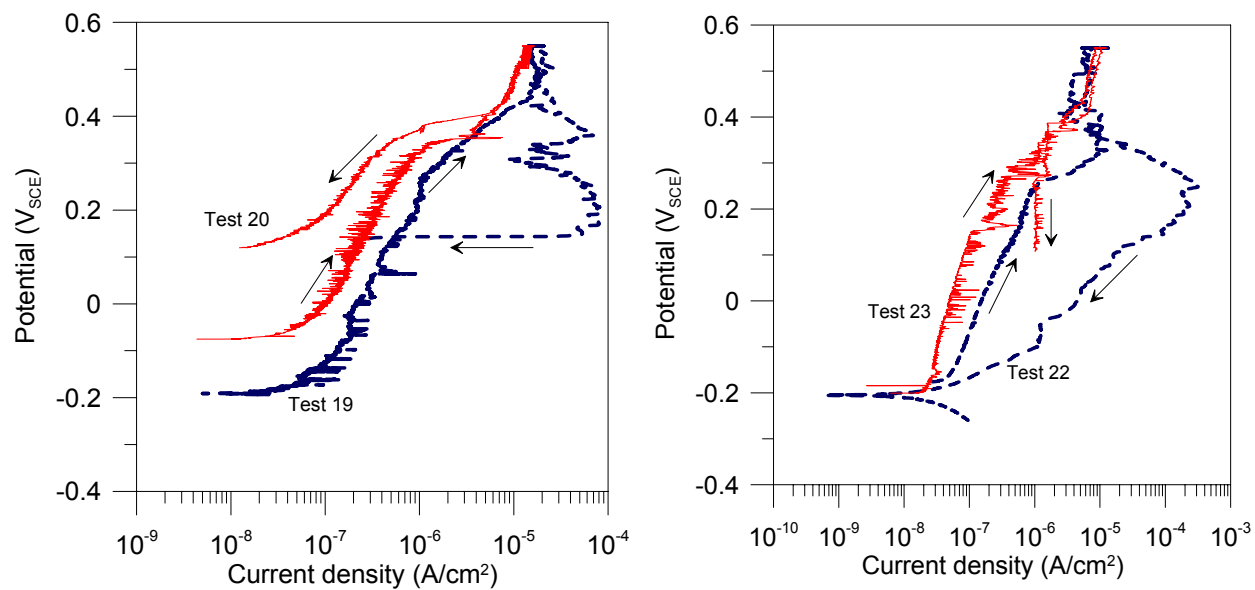


Figure 6. Potentiodynamic polarization curves of Alloy 22 to Titanium Grade 7 crevices (Tests 19, 20, 22, and 23 in Table 2) in N₂ deaerated 4 M NaCl solution at 95 °C [203 °F]

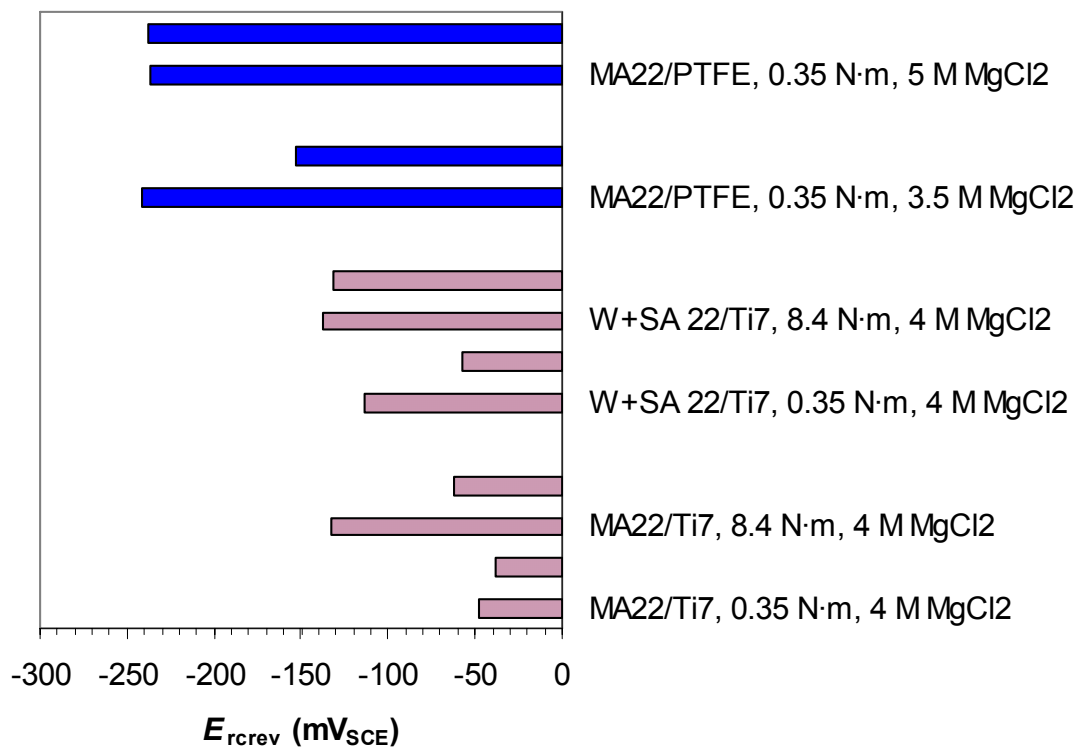


Figure 7. Comparison of crevice corrosion repassivation potential, E_{rcrev} , for mill-annealed Alloy 22 and welded plus solution annealed Alloy 22 to Titanium Grade 7 crevices measured in 4 M MgCl₂ solution with Alloy 22 to polytetrafluoroethylene crevices measured in 3.5 M and 5 M solutions (Dunn, et al., 2005a) at 95 °C [203 °F]. Duplicate tests were performed at all test conditions. Crevice corrosion was observed in all cases using Titanium Grade 7 or polytetrafluoroethylene as crevice-forming material. (Note: MA22—mill-annealed alloy 22, Ti7—Titanium Grade 7, W+SA 22—welded plus solution annealed Alloy 22, PTFE—polytetrafluoroethylene, MgCl₂—MgCl₂)

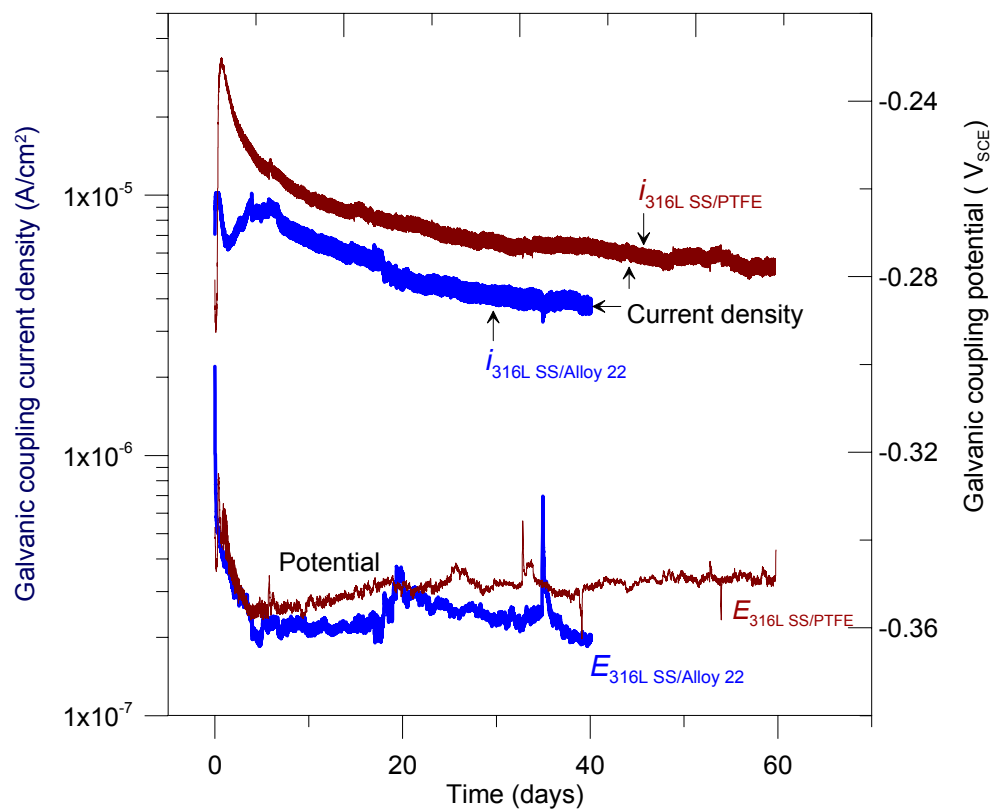
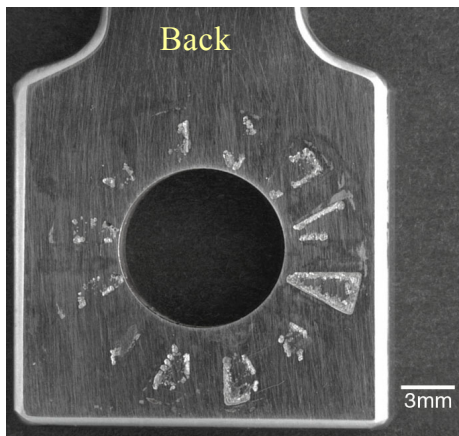
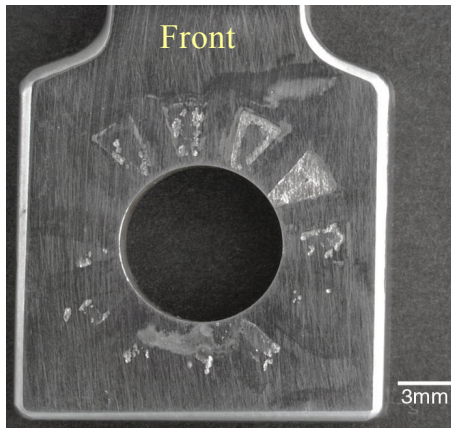
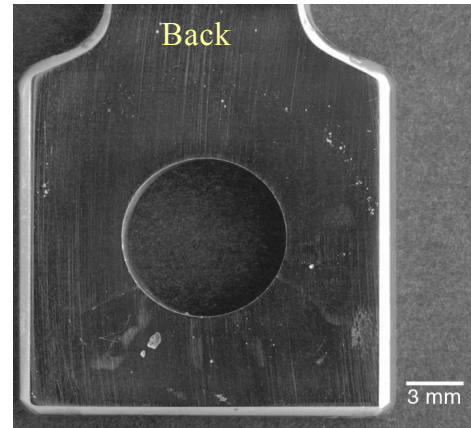
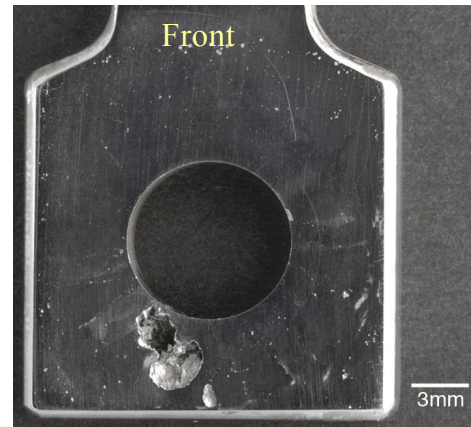


Figure 8. Measured galvanic coupling current density and potential for 316L stainless steel crevice specimen galvanically coupled to Alloy 22 using Alloy 22 or polytetrafluoroethylene as crevice-forming material in 5 M NaCl solution at 95 °C [203 °F] (Tests G1 and G2 in Table 5)



(a)



(b)

Figure 9. Crevice corroded 316L stainless steel after being coupled to Alloy 22 in 5 M NaCl solution at 95 °C [203 °F] (a) using Alloy 22 as crevice washer (Test G1 in Table 5) and (b) using polytetrafluoroethylene as crevice washer (Test G2 in Table 5)

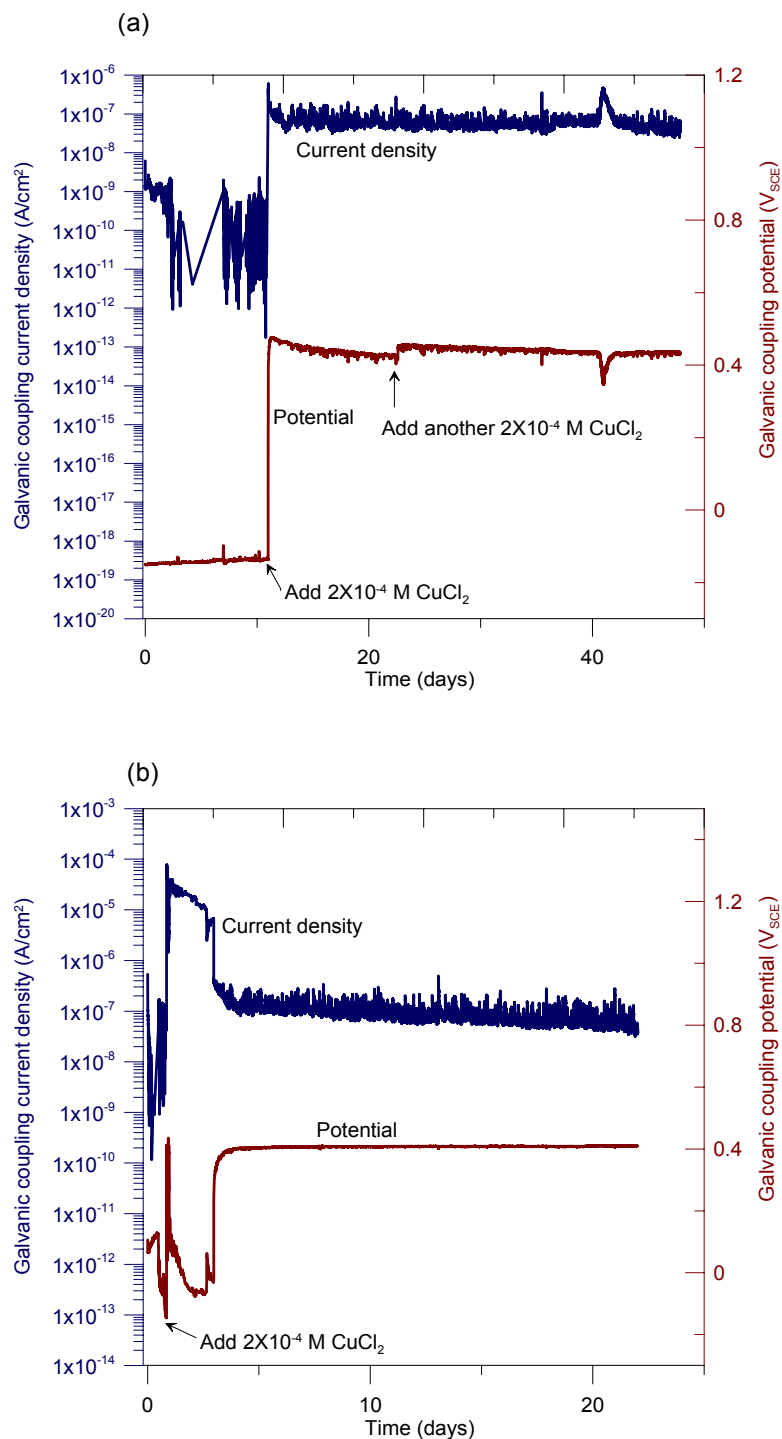


Figure 10. Measured galvanic coupling current density and potential for welded plus solution annealed Alloy 22 crevice specimen galvanically coupled to Alloy 22 using (a) Alloy 22 as crevice forming material (Test G6 in Table 5) or (b) polytetrafluoroethylene as crevice forming material (Test G8 in Table 5) in 5 M NaCl at 95 °C [203 °F]

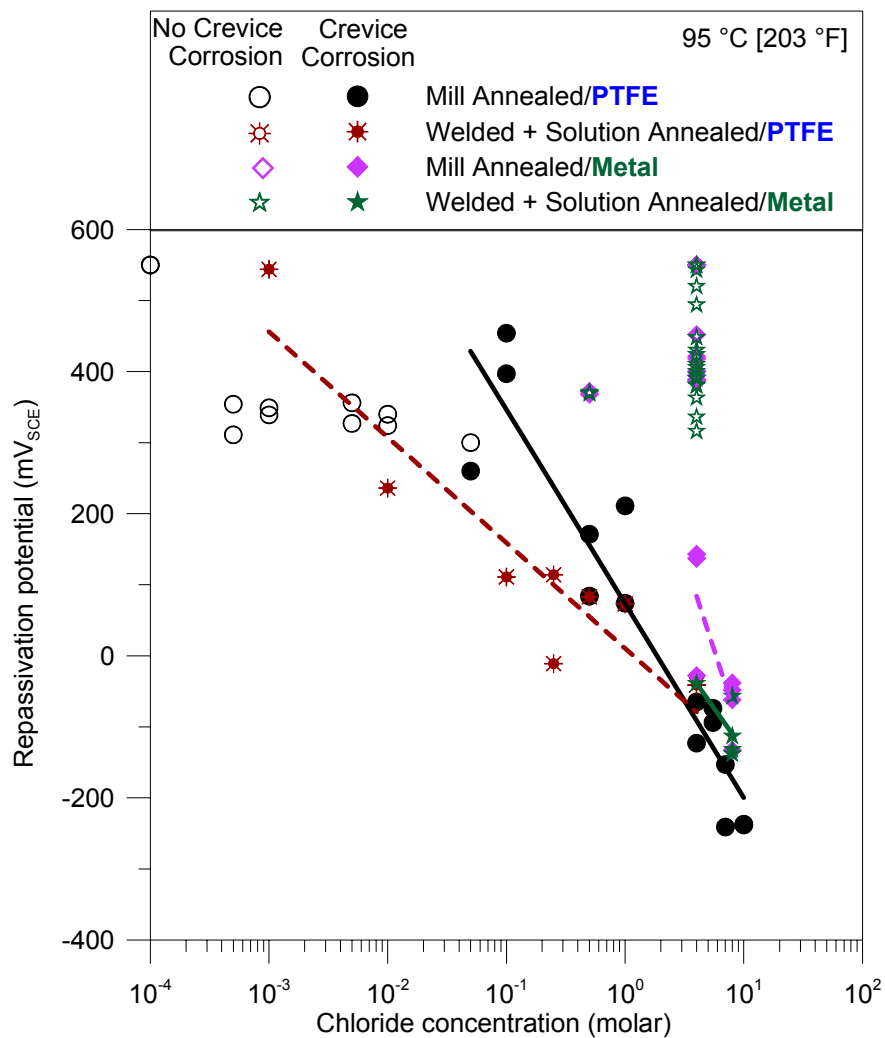


Figure 11. Crevice corrosion repassivation potentials for mill-annealed, welded plus solution annealed Alloy 22 in chloride solutions at 95 °C [203 °F] using polytetrafluoroethylene or metal (Alloy 22 or Titanium Grade 7) as crevice forming material. The lines are log linear regression lines of the repassivation potential with chloride concentration.

Table 1. Composition of Potential Engineered Barrier Materials (in Weight Percent)												
Material	Ni*	Cr*	Mo*	W*	Fe*	Co*	Si*	Mn*	V*	P*	S*	C*
Alloy 22 Heat # 2277-3-3266	Bal†	21.40	13.30	2.81	3.75	1.19	0.03	0.23	0.14	0.008	0.004	0.005
Alloy 22 Heat # 2277-3-3292	Bal†	21.22	13.64	2.96	3.69	1.32	0.02	0.23	0.13	0.005	0.003	0.005
Alloy 622 Weld Filler Wire Heat # WN813	Bal†	22.24	13.7	3.13	2.37	0.41	0.02	0.34	0.01	0.003	0.001	0.003
316L Stainless Steel Heat # P80746	10.04	16.35	2.07	NA‡	Bal†	NA‡	0.49	1.58	NA‡	0.026	0.018	0.014
	Ti*	Pd*	Fe*	C*	N*	O*	H*					
Titanium Grade 7 Heat # CN 2775	Bal†	0.16	0.08	0.01	0.01	0.13	0.001					
*Ni—nickel, Cr—chromium, Mo—molybdenum, W—tungsten, Fe—iron, Co—cobalt, Si—silicon, Mn—manganese, V—vanadium, P—phosphorus, S—sulfur, C—carbon, Ti—titanium, Pd—palladium, N—nitrogen, O—oxygen, H—hydrogen †Bal—Balance ‡NA—Not Available												

Table 2. Corrosion Potential, E_{corr} , and Crevice Corrosion Repassivation Potential, E_{rcrev} , of Metal-to-Metal Crevices in Air Saturated (for E_{corr}) and Deaerated (for E_{rcrev}) 4 M NaCl Solution at 95 °C [203 °F]							
Test Number	Crevice Specimen	Crevice Washer	$\frac{\text{Area}_{\text{crevice specimen}}}{\text{Area}_{\text{crevice washer}}}$	Torque (N·m*)	E_{corr} (mV _{SCE})	E_{rcrev} (mV _{SCE})	Number of Corrosion Sites on Crevice Specimen
1 2	316L SS†	MA 22‡	1/3	0.35	-320 -321	-345 -346	21/24 18/24
3 4	316L SS	MA 22	1/3	8.4	-320 -342	-349 -355	24/24 24/24
5 6	MA 22	MA 22	1/3	0.35	-190 -192	452 550	0/24 0/24
7 8 9	MA 22	MA 22	1/3	8.4	-180 -143 Not Measured	137 401 389	1/24 0/24 0/24
10 11	W + SA 22§	MA 22	1/3	0.35	-70 -163	380 406	0/24 0/24
12 13	W + SA 22	MA 22	1/3	8.4	-123 -115	363 395	0/24 0/24
14 15 16	W + SA 22	MA 22	1/10	0.35	-105 -23 -197	550 400 430	0/24 0/24 0/24
17 18	W + SA 22	MA 22	1/10	8.4	-161 -0.4	410 390	0/24 0/24
19 20 21	MA 22	Ti Gr 7	1/3	0.35	-143 -35 -7	143 395 421	5/24 0/24 0/24
22 23 24	MA 22	Ti Gr 7	1/3	8.4	-166 -170 Not Measured	-27.9 387 418	11/24 0/24 0/24
25 26	MA 22	Ti Gr 7	1/18	0.49	-195 -134	550 550	0/24 0/24
27 28	MA 22	Ti Gr 7	1/18	8.4	-145 -116	550 550	0/24 0/24
29 30	W + SA 22	Ti Gr 7	1/3	0.35	-116 -120	316 381	0/24 0/24
31 32 33	W + SA 22	Ti Gr 7	1/3	8.4	-160 -137 Not Measured	-39 336 424	12/24 0/24 0/24

Table 2. Corrosion Potential, E_{corr} , and Crevice Corrosion Repassivation Potential, E_{rcrev} , of Metal-to-Metal Crevices in Air Saturated (for E_{corr}) and Deaerated (for E_{rcrev}) 4 M NaCl Solution at 95 °C [203 °F] (continued)

Test Number	Crevice Specimen	Crevice Washer	$\frac{\text{Area}_{\text{crevice specimen}}}{\text{Area}_{\text{crevice washer}}}$	Torque (N·m*)	E_{corr} (mV _{SCE})	E_{rcrev} (mV _{SCE})	Number of Corrosion Sites on Crevice Specimen
34 35	W + SA 22	Ti Gr 7	1/18	0.49	-84 -82	520 543	0/24 0/24
36 37 38	W + SA 22	Ti Gr 7	1/18	8.4	-155 -56 Not Measured	550 494 448	0/24 0/24 0/24

Notes:

The spread in the E_{corr} values is typically 200 mV.

For tests where crevice corrosion did not occur, the E_{rcrev} had no physical meaning. Only the E_{rcrev} values from tests where crevice corrosion occurred were used to evaluate the relative crevice corrosion resistance. The spread in the E_{rcrev} values was typically less than 100 mV in replicate experiments at chloride concentrations above 1 M for Alloy 22-to-polytetrafluoroethylene crevice, but it increases with decreasing chloride concentration (Dunn, et al., 2005a,b).

* N·m = 8.93 in·lb

†SS—Stainless steel

‡MA 22—Mill-annealed Alloy 22

§W + SA 22—Welded plus solution annealed Alloy 22

||Ti Gr 7—Titanium Grade 7

Table 3. Corrosion Potential, E_{corr} , of Uncreviced Alloy 22 [Dunn, et al., 2005a], Titanium Grade 7, and Type 316L Stainless Steel, and Crevice Corrosion Repassivation Potential, E_{rcrev} , of Metal-to-Polytetrafluoroethylene Crevices in Air Saturated (for E_{corr}) and Deaerated (for E_{rcrev}) 4 M NaCl Solution at 95 °C [203 °F]

Specimen		Crevice Washer	Torque (N·m*)	E_{corr} (mV _{SCE})	E_{rcrev} (mV _{SCE})	Number of Corrosion Sites on Crevice Specimen
Uncreviced	MA 22†	None	—	-127 -81 -100	—	—
	Ti Gr 7‡	None	—	-60 -71	—	—
	316L SS§	None	—	-320	—	—
Creviced	MA 22	PTFE	0.35	—	-65 -123	7/24 20/24
	W + SA 22¶	PTFE	0.35	—	-41	23/24
	316L SS	PTFE	0.35	—	-348	Not Reported

*1 N·m = 8.93 in·lb

†MA 22—Mill-annealed Alloy 22

‡Ti Gr 7—Titanium Grade 7

§SS—Stainless steel

||PTFE—Polytetrafluoroethylene

¶W + SA 22—Welded plus solution annealed Alloy 22

Table 4. Corrosion Potential, E_{corr} , and Crevice Corrosion Repassivation Potential, E_{rcrev} , of Alloy 22-to-Titanium Grade 7 Crevices With Area Ratio of 1/3 in 0.5 M NaCl and 4 M MgCl₂ Solutions at 95 °C [203 °F] (Aerated for E_{corr} and Deaerated for E_{rcrev})

Solution	Test Number	Crevice Specimen	Crevice Washer	Torque* (N·m)	E_{corr} (mV _{SCE})	E_{rcrev} (mV _{SCE})	Number of Corrosion Sites on Crevice Specimen
0.5 M NaCl	39 40	MA 22†	Ti Gr 7‡	0.35	-13 109	372 368	0/24 0/24
	41 42	W + SA 22§	Ti Gr 7	0.35	100 127	369 371	0/24 0/24
4 M MgCl ₂	43 44	MA 22†	Ti Gr 7	0.35	-81 46	-48 -38	3/24 3/24
	45 46	MA 22	Ti Gr 7	8.4	-165 -181	-133 -62	22/24 3/24
	47 48	W + SA 22	Ti Gr 7	0.35	-28 -9	-113 -57	10/24 4/24
	49 50	W + SA 22	Ti Gr 7	8.4	-148 -160	-138 -132	22/24 12/24

*1 N·m = 8.93 in·lb

†MA 22—Mill-annealed Alloy 22

‡Ti Gr 7—Titanium Grade 7

§W + SA 22—Welded plus solution annealed Alloy 22

Table 5. Tests Performed to Evaluate Crevice Corrosion Initiation and Measure Crevice Corrosion Penetration Depths in 5 M NaCl Solution at 95 °C [203 °F]

Test ID	Crevice Assembly			Coupling Large Plate	Torque (N·m*)	Did Crevice Corrosion Initiate Under Coupling?	Did Crevice Corrosion Initiate with the Addition of CuCl ₂ as Oxidant?	Penetration Depths (μm)†
	Crevice Specimen	Crevice Washer	Bolt and Nut					
G1	316LSS‡	MA 22§	MA 22	MA 22	8.4	Yes	Not added	258, 101, 76, 70, 68, 66, 57, 47, 44, 44, 40, 38, 36, 31, 30, 24, 22, 20, 18, 18, 16, 15
G2	316LSS	PTFE	C276	MA 22	0.70	Yes	Not added	Penetrate through the specimen with thickness of 5 mm [0.2 in]
G3 G4	MA 22	Ti Gr 7¶	Ti Gr 7	Ti Gr 7	8.4	No No	No No	—
G5	MA22	PTFE	C276	Ti Gr 7	0.70	No	Yes	181, 164
G6 G7	W + SA 22#	MA 22	MA 22	MA 22	8.4	No No	No No	—
G8	W + SA 22	PTFE	C276	MA 22	0.70	No	Yes, but it arrested in < 5 days	284, 265
G9 G10	W + SA 22	Ti Gr 7	Ti Gr 7	Ti Gr 7	8.4	No No	No No	—

*1 N·m = 8.93 in·lb

†1 μm = 0.04 mils

‡SS—Stainless steel

§MA 22—Mill-annealed Alloy 22

|| PTFE—Polytetrafluoroethylene

¶Ti Gr 7—Titanium Grade 7

#W + SA 22—Welded plus solution annealed Alloy 22