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Effects of Test Methods on Crevice Corrosion Repassivation Potential Measurements of Alloy 22

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ABSTRACT

The U.S. Department of Energy (DOE) is considering Alloy 22 for the waste package outer container material for the disposal of high-level waste at the potential repository at Yucca Mountain, Nevada. Crevice corrosion is one of the corrosion processes that may affect the performance of the waste package outer container. The relative susceptibility of Alloy 22 to crevice corrosion is evaluated through the measurement of crevice corrosion repassivation potential (E_{rcrev}) using electrochemical test methods. The Center for Nuclear Waste Regulatory Analyses (CNWRA) observed that the fabrication process, particularly welding and postwelding solution annealing, increased the localized corrosion susceptibility based on the measurement of E_{rcrev} using an electrochemical method developed at CNWRA. DOE measured E_{rcrev} using the ASTM G61–86 standard test method, and the effects of welding on Alloy 22 localized corrosion susceptibility were not observed. The main purpose of this work is to verify some E_{rcrev} values in the DOE localized corrosion model and investigate the effects of different electrochemical test methods on the measurement of E_{rcrev} to provide risk insights and reduce the measurement uncertainties associated with the evaluation of the effects of the fabrication process of the waste package outer container on localized corrosion susceptibility. In this work, E_{rcrev} was measured in various chloride solutions at 90 °C [194 °F] using three methods, including (i) the DOE method adopted from ASTM G61–86, (ii) the CNWRA method, and (iii) the Tsujikawa–Hisamatsu Electrochemical method. The results indicate that at lower chloride concentrations (1 M NaCl and 1.25 M CaCl₂), the E_{rcrev} values CNWRA measured using the DOE method were higher compared to the data DOE used in developing the localized corrosion model. In addition, in these chloride concentrations, the E_{rcrev} values measured by using the CNWRA method were higher than those using the DOE method, whereas the E_{rcrev} values measured according to the DOE method were slightly higher than those measured by using the Tsujikawa–Hisamatsu Electrochemical method. At a high chloride concentration (5 M CaCl₂), the E_{rcrev} values DOE reported are reproducible and those measured by the three methods were found to be similar. DOE observed no effects of welding on localized corrosion susceptibility through the measurement of E_{rcrev} in 5 M CaCl₂ solution. This could be due to the aggressive solution composition combined with the fast electrochemical method used in measuring the E_{rcrev} values.

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INTRODUCTION

The possible waste package design for the disposal of high-level waste at the potential repository in Yucca Mountain, Nevada, consists of an outer container made of Alloy 22 (Ni–22Cr–13Mo–4Fe–3W) to resist various modes of corrosion and an inner container made of Type 316 nuclear grade stainless steel (low C–high N–Fe–18Cr–12Ni–2.5Mo) for structural support.¹ Localized corrosion is considered to be one of the corrosion processes that may affect the performance of the waste package outer container.² If localized corrosion occurs, it presumably would be in the form of crevice corrosion rather than pitting corrosion because of the high electrochemical potentials required to nucleate pits on an openly exposed surface in nickel-chromium-molybdenum alloys with high chromium and molybdenum (plus tungsten) contents such as Alloy 22.³ The chemistry of the water contacting the engineered barrier materials depends on the seepage water composition and the evolution of the water chemistry within the emplacement drifts. Retention of solutions such as concentrated chloride in occluded crevice areas could lead to crevice corrosion of the engineered barrier system materials in the evolving Yucca Mountain environments.

The U.S. Department of Energy (DOE) has included the process of localized corrosion of Alloy 22 outer container material in their performance assessment model.⁴ The model considers the effects of temperature, chloride concentration, and the inhibiting effects of nitrate. However, the model disregards the increased localized corrosion susceptibility of waste packages as a result of fabrication and closure processes. To support the U.S. Nuclear Regulatory Commission (NRC) prelicensing activities on topics of potential importance to the postclosure performance, the Center for Nuclear Waste Regulatory Analyses (CNWRA) is using a risk-informed approach to review the DOE localized corrosion model abstraction, focusing on the DOE technical basis for disregarding the effects of fabrication processes on localized corrosion susceptibility. Also, CNWRA is conducting an independent technical assessment of the effects of test methods on the measurement of electrochemical parameters used to evaluate the localized corrosion susceptibility. Results of the work will (i) support evaluation of the localized corrosion processes of waste package outer container materials including the effects of fabrication processes, (ii) provide risk insights and an independent corroborating assessment on the adequacy of the test method DOE used, and (iii) support the potential license application review.

The localized corrosion abstraction in CNWRA/NRC Total-system Performance Assessment (TPA) code is based on a critical potential model.⁵ 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}). E_{rcrev} is the lowest potential at which crevice corrosion can be initiated in the long term and is adopted in the TPA code as the critical potential used to define the occurrence of localized corrosion. In experiments conducted at CNWRA, Dunn^{6,7} observed that as-welded, thermally aged, and welded plus solution annealed Alloy 22 specimens have lower repassivation potentials for crevice corrosion, E_{rcrev} , than mill-annealed Alloy 22. If waste packages were directly contacted by seepage water of high temperatures {around 110 °C [230 °F]}, the probability of localized corrosion is estimated based on the localized corrosion model and the measured repassivation potential data. Welded areas were estimated to have a higher probability to exhibit localized corrosion than the mill-annealed surface.⁷

The DOE localized corrosion initiation model uses a similar approach.⁴ Localized corrosion of Alloy 22 is assumed to initiate when the corrosion potential (E_{corr}) is greater than the critical potential (E_{crit}). In the current DOE model, E_{crit} is defined as the repassivation potential for crevice corrosion (E_{rcrev}). The values of E_{corr} and E_{crit} were measured in laboratory tests using standard test procedures. Welded U-bend specimens and rod specimens were used to evaluate E_{corr} of Alloy 22 as a function of immersion time in a wide range of waters expected in the potential Yucca Mountain repository at temperatures ranging from 25 to 120 °C [77 to 248 °F] for up to 3 years. Values of the E_{crit} were obtained using mill-annealed and as-welded crevice specimens following ASTM G61–86 as the standard procedure⁸ in a wide range of waters with and without the addition of $\text{Ca}(\text{NO}_3)_2$ at temperatures ranging from 60 to 130 °C [140 to 266 °F]. However, the measured E_{crit} for mill-annealed Alloy 22 in 5 M CaCl_2 was similar to that measured for as-welded Alloy 22. The effect of welding on Alloy 22 localized corrosion susceptibility was not observed in DOE work.

It is not clear what caused the different observations on the effects of welding on the localized corrosion susceptibility of Alloy 22 as evaluated using electrochemical parameters such as E_{rcrev} . One possible cause could be the difference in the ASTM G61–86 standard test method DOE adopted and the potentiodynamic scan with intermediate potentiostatic hold method CNWRA used to measure the E_{rcrev} or E_{crit} as described previously. There are several methods reported in the literature to measure E_{rcrev} , including the cyclic potentiodynamic polarization method detailed in ASTM G61–86,^{4,8–11} the Tsujikawa–Hisamatsu Electrochemical method (a combination of a forward potentiodynamic scan, galvanostatic holding, and potentiostatic back stepping) and its variations,^{9,11–13} and a method consisting of a forward potentiodynamic scan with an intermediate potentiostatic hold followed by a slow backward potential scan.^{6,7,14,15}

ASTM G61–86⁸ is a standard test method for conducting cyclic potentiodynamic polarization primarily to evaluate pitting corrosion susceptibility of iron-, nickel-, or cobalt-based alloys. It was later extended to evaluate crevice corrosion susceptibility.^{4,9,16} This method seems to be adequate for less corrosion-resistant alloys such as stainless steel. As described previously, DOE used this method to measure E_{crit} to develop the localized corrosion model. DOE claimed that in most cases, ASTM G61–86⁸ gives accurate and reproducible values of the repassivation potential. In the fringes of susceptibility when the environment is not highly aggressive, the values of repassivation potential using this method may not be highly reproducible, especially because the method is fast and because transpassive corrosion may affect and hinder the nucleation and propagation of crevice corrosion.

To circumvent the problem with ASTM G61–86,⁸ DOE used the Tsujikawa–Hisamatsu Electrochemical method to measure E_{rcrev} of Alloy 22 in less aggressive solutions to compare with the data measured using ASTM G61–86.⁸ The Tsujikawa–Hisamatsu Electrochemical method is an anodic polarization method that combines techniques such as potentiodynamic, galvanostatic, and potentiostatic polarization. In this method, a constant current is applied to the specimen to initiate and grow the crevice corrosion until a specified value of electrical charge is attained. DOE reported that this method may give more reproducible repassivation potential values, especially when the environment is not aggressive. However, this method is time consuming.

The combination of cyclic potentiodynamic polarization with a potentiostatic hold was used in CNWRA work. This method starts with a forward potentiodynamic scan with the same rate as in

ASTM G61–86⁸ until it reaches a potential close to but below the transpassive dissolution or until the current indicates active crevice corrosion. Afterwards, the potential is held for several hours to allow crevice corrosion to propagate to form deep penetration sites, followed by a slower backward potential scan to allow crevice corrosion to repassivate with sufficient time. This method avoids transpassive dissolution during the forward potentiodynamic scan. The measured repassivation potential is not a function of the hold potential. Because the crevice corrosion sites are allowed to propagate during the potentiostatic hold, it has been shown that the measured repassivation potential does not depend on the penetration depth, which provides a valid measurement of the repassivation potential.^{6,15}

This work verifies some E_{rcrev} data in the DOE localized corrosion model⁴ and investigates (i) the effects of various electrochemical test methods on the determination of E_{rcrev} and (ii) how fabrication processes, especially welding, may affect the E_{rcrev} values, which indicate localized corrosion susceptibility. The lower the E_{rcrev} values, the higher the localized corrosion susceptibility. In this work, three methods, including (i) the DOE method adopted from ASTM G61–86, (ii) the CNWRA method, and (iii) the Tsujikawa–Hisamatsu Electrochemical method, were used to measure the E_{rcrev} values of Alloy 22 in various chloride solutions at 90 °C [194 °F]. This work aims to enhance the understanding of different electrochemical test methods and how the scanning mode, scanning rate, and the current and potential from the electrochemical process affect the measurement of E_{rcrev} of Alloy 22.

EXPERIMENTAL METHODS

E_{rcrev} measurements were conducted in a three-electrode glass test cell, consisting of the crevice assembly shown in Figure 1(a) as the working electrode, a platinum foil as the counter electrode, and a saturated calomel reference electrode. 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. The majority of the tests were performed using the mill-annealed Alloy 22 crevice specimen shown in Figure 1(b). The chemical composition of the Heat 2277-3-3266 used in these tests is provided in Table 1. Several tests were performed using an as-welded Alloy 22 specimen. Welded specimens were produced from a plate using gas tungsten arc welding with a U-groove joint geometry {25.4-mm [1-in]-thick Alloy 22 Heat 2277-3-3292 and Alloy 622 filler metal Heat WN813 in Table 1}. The location of the weld is shown in Figure 1(b). To further understand the effects of electrochemical test methods on E_{rcrev} measurement, limited tests were performed on 316L stainless steel crevice specimens. The chemical composition of the Heat 316L stainless steel used in this study is also shown in Table 1.

The E_{rcrev} measurement was performed using the three electrochemical methods schematically shown in Figure 2 including (i) the DOE method adopted from ASTM G61–86,⁸ (ii) the CNWRA method, and (iii) the Tsujikawa–Hisamatsu Electrochemical method:

- (i) In ASTM G61–86,⁸ the potential forward scan started from the corrosion potential (E_{corr}) 1 hour after specimen immersion, and the potential was scanned in the anodic direction at a scan rate of 0.167 mV/second, as shown in Figure 2(a). Then the scan was reversed when the current density reached 5 mA/cm² [4.6 A/ft²]. Typically, the cross-over potential is chosen as the repassivation potential, E_{rcrev} . The crevice was formed by sandwiching the crevice specimen between two ceramic formers wrapped with polytetrafluoroethylene tape with an applied torque of 7.8 N·m [70 in·lb].

- (ii) The CNWRA method as shown in Figure 2(b) was conducted using cyclic potentiodynamic polarization with an intermediate potentiostatic hold.^{6,7,14,15} 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 several hours (e.g., 8 hours), and then scanned down to $-700 \text{ mV}_{\text{SCE}}$ with a scan rate of 0.0167 mV/s until the current dropped below a specified value. The hold potential is limited to potentials below the onset of transpassive dissolution of Alloy 22. The E_{rcrev} is defined as the potential at which the current density decreases below $2 \times 10^{-6} \text{ A/cm}^2$ [$1.9 \times 10^{-3} \text{ A/ft}^2$] on the reverse scan of the polarization curve. The crevice was formed by sandwiching the crevice specimen between two polytetrafluoroethylene formers with an applied torque of 0.35 N·m [3.1 in·lb].
- (iii) The Tsujikawa–Hisamatsu Electrochemical method as shown in Figure 2(c) has three steps. In step 1, the potential was scanned in the anodic direction at a rate of 0.167 mV/s starting at 50 mV below E_{corr} . When the current reached a predetermined value corresponding to a current density of $20 \mu\text{A/cm}^2$ [$1.9 \times 10^{-2} \text{ A/ft}^2$], the control mode was switched from potentiodynamic to galvanostatic and the current was maintained for 6 hours. This second step of the experiment allows localized corrosion to propagate while the potential is recorded. After the constant current step, the control mode was switched to potentiostatic in step 3. Starting from the potential recorded at the end of step 2, the potential decreased discontinuously by 10 mV steps lasting 2 hours. The E_{rcrev} is defined as the potential at which the current density does not increase with time, as shown in Figure 2(c). The crevice was formed the same way as in (i).

All the repassivation potential measurements were performed in N_2 -deaerated chloride-containing solutions. The Alloy 22 and 316L stainless steel crevice specimens were polished to a 600-grit finish, rinsed in deionized water, ultrasonically cleaned in acetone, and dried. Tests were performed in duplicate to evaluate the reproducibility of the measurements.

RESULTS

Repassivation Potentials of Alloy 22 in Chloride Solutions at 90 °C [194 °F]

Table 2 lists the measured E_{rcrev} values of mill-annealed Alloy 22 in 0.01 M NaCl, 1 M NaCl, 1.25 M CaCl_2 , and 5 M CaCl_2 solutions at 90 °C [194 °F], using the three test methods. The E_{rcrev} values reported by DOE,⁴ are also included in the table for comparison. The E_{rcrev} values in Table 2 are plotted in Figure 3 to facilitate the comparison. The lines in Figure 3 are the trend lines of the measured E_{rcrev} values as a function of chloride concentration. Figure 4 shows the optical photomicrographs of the corroded specimens from some tests in Table 2. There are several features to note from the comparison of the test results in Table 2 and Figures 3 and 4.

- Figure 4(a) shows that a gold film indicating transpassive dissolution outside of the crevice region was often observed in the tests conducted using ASTM G61–86,⁸ especially at chloride concentrations of 1 M and 2.5 M. In ASTM G61–86,⁸ the potentiodynamic scan is reversed when the current density reaches 5 mA/cm^2 [4.6 A/ft^2], which often results in a potential close to 1 V_{SCE} , as shown in the potentiodynamic scans in Figure 5 (Tests 6 and 13 in Table 2). This potential is in the transpassive dissolution region of Alloy 22, as evident from the pronounced increase of current density with

increasing potential above $0.5 V_{SCE}$ and the lack of noticeable hysteresis in the backward scan within the same potential range in Figure 5.

2. Inconsistent initiation of crevice corrosion was often observed in the tests conducted using the CNWRA method, especially at chloride concentrations of 1 M and 2.5 M in which corrosion was limited to only 1 or 2 out of the 24 crevice sites as shown in Figure 4(b). In Tests 3, 4, 10, and 11 in Table 2, the hold potential was $550 mV_{SCE}$ and the hold time was 8 hours in the intermediate potentiostatic stage. For these tests, no E_{rcrev} value is reported because of the lack of crevice corrosion initiation. Crevice corrosion may be initiated with increasing hold potential and hold time. One attempt was made in Test 5 in Table 2 to increase the hold potential to $600 mV_{SCE}$ compared to Test 4 in Table 2 as shown in Figure 6. Crevice corrosion was initiated, although the current density recorded in Test 5 was lower than that in Test 4. However, the E_{rcrev} value was significantly higher than that measured using ASTM G61–86.⁸ This is entirely possible due to the random nature of localized corrosion initiation particularly noticeable in highly corrosion-resistant alloys such as Alloy 22. On the contrary, the E_{rcrev} values obtained by using the Tsujikawa–Hisamatsu Electrochemical method were highly reproducible and the specimens were uniformly corroded across the crevice region especially at chloride concentrations of 1 M and 2.5 M as shown in Figure 4(c). No transpassive dissolution was observed on any of the test specimens. Figure 7 shows the current and potential curves from Test 9 in Table 2 using the Tsujikawa–Hisamatsu Electrochemical method. When the established or adopted current density of $20 \mu A/cm^2$ [$1.9 \times 10^{-2} A/ft^2$] was reached, the potential was below $550 mV_{SCE}$, which avoids the onset of transpassive dissolution.
3. In 1 M NaCl and 1.25 M $CaCl_2$ solutions, the E_{rcrev} values measured using the CNWRA method were higher than those in ASTM G61–86,⁸ and such values were higher than those measured by the Tsujikawa–Hisamatsu Electrochemical method. In 0.01 M NaCl solution, the measured E_{rcrev} values using the Tsujikawa–Hisamatsu Electrochemical method were much lower than the high E_{rcrev} value of $550 mV_{SCE}$ reported by Dunn⁷ in the same chloride concentration at $95^\circ C$ [$203^\circ F$], and the crevice specimens were corroded in the crevice region. These results suggest that the Tsujikawa–Hisamatsu Electrochemical method may be a more appropriate method to generate reproducible and reliable E_{rcrev} values especially in less aggressive environments.
4. At a high chloride concentration (5 M $CaCl_2$), the E_{rcrev} values measured by the three methods were very close, ranging from -239 to $-158 mV_{SCE}$. The specimens in Figure 4 based on the tests using CNWRA and ASTM G61–86⁸ methods show that corrosion occurred extensively inside and outside of the crevice region (Tests 17 and 19, respectively); however, the corroded specimens using the Tsujikawa–Hisamatsu Electrochemical method showed corrosion in the crevice area only, although the corrosion sites were very shallow. Higher current density [$30 \mu A/cm^2$ [$2.8 \times 10^{-2} A/ft^2$]] than $20 \mu A/cm^2$ [$1.9 \times 10^{-2} A/ft^2$] was used in Test 23 during the galvanostatic step, but it resulted in very similar corrosion sites and E_{rcrev} value.
5. In 1 M NaCl and 1.25 M $CaCl_2$ solutions, the E_{rcrev} values measured in this study using ASTM G61–86⁸ (the method DOE adopted) were slightly higher than those DOE used in its localized corrosion model,⁴ whereas the values measured using the Tsujikawa–Hisamatsu Electrochemical method were close to what DOE used in the

model. In 5 M CaCl_2 solutions, the measured E_{rcrev} values were similar to those DOE used in its localized corrosion model.

Repassivation Potentials of As-welded Alloy 22 in Chloride Solutions at 90 °C [194 °F]

A limited number of tests were performed on as-welded Alloy 22 to investigate the difference in E_{rcrev} values measured using the different methods. The test results are summarized in Table 3. In 1 M NaCl and 1.25 M CaCl_2 solutions, the E_{rcrev} values of the as-welded Alloy 22 were found to be lower than those of the mill-annealed Alloy 22 under the same test conditions (Test 5 in Table 2 compared to Test 25 in Table 3 and Test 12 in Table 2 compared to Test 26 in Table 3); however, there are insufficient data to draw a trend and compare to what DOE reported. Figure 8 plots the current and potential curves of Test 12 in Table 2 and Test 26 in Table 3 for comparison. Under the same hold potential, the current density from the as-welded specimen was higher than what was measured from the mill-annealed specimen.

Tests 27–30 in Table 3 showed that the E_{rcrev} values measured by the ASTM G61–86⁸ and CNWRA methods for the as-welded Alloy 22 were close. They were also similar to the E_{crev} values of the mill-annealed Alloy 22 in Tests 17–20 in Table 2. Figure 9 shows the corroded crevice specimen from Tests 28 and 30 in Table 3. Specimens from both methods show that significant corrosion occurred in the area outside of the crevice region in addition to corrosion inside the crevice area. Corrosion does not appear to be limited to the welded region only. Severe corrosion occurred at the lower part of the crevice specimen, which could be primarily due to gravity effect. The E_{rcrev} values for the mill-annealed and as-welded Alloy 22 lay within a relatively narrow range (–239 to –158 mV_{SCE}) and are close to what was reported by DOE.⁴ In 5 M CaCl_2 solution, DOE⁴ also did not observe any difference between the repassivation potential values of mill-annealed and as-welded Alloy 22. The lack of difference observed between mill-annealed and as-welded Alloy 22 and the E_{crev} values measured by different electrochemical methods could be due to the aggressive nature of the 5 M CaCl_2 solution, which masks the difference between the different microstructural features.

Repassivation Potentials of 316L Stainless Steel at 90 °C [194 °F]

Table 4 lists the measured crevice corrosion repassivation potential values of 316L stainless steel in 1 M NaCl and 1.25 M CaCl_2 solutions at 90 °C [194 °F]. Except for the values measured using the ASTM G61–86,⁸ the E_{rcrev} values decreased with increasing chloride concentration from 1 to 2.5 M. This observation suggests that the localized corrosion susceptibility of 316L stainless steel increased with the increasing chloride concentration. The values measured using the CNWRA and Tsujikawa–Hisamatsu Electrochemical methods were similar, lying within a range of 0–44 mV. However, the E_{rcrev} values measured according to ASTM G61–86⁸ were more than 100 mV lower than those measured using the other two methods. This suggests that the E_{rcrev} values measured using the DOE method may be inappropriately low. Figure 10 shows the corroded 316L stainless steel specimens. For the tests using ASTM G61–86⁸ and the CNWRA method, in addition to crevice corrosion, pitting corrosion was also observed on the specimen surface external to the crevice region. This may contribute to the exceptionally low E_{rcrev} values measured using ASTM G61–86.⁸

DISCUSSION

The waste package outer container is proposed to be fabricated from Alloy 22 plates. After welding, the waste package outer container may be solution annealed to eliminate residual stresses created during fabrication. Fabrication processes such as welding, postweld heat treatments, and short-term exposures to temperatures in the range of 600 to 900 °C [1,112 to 1,652 °F] are reported to increase the localized corrosion susceptibility of Alloy 22 waste package outer container materials.^{17,18}

The localized corrosion abstraction of the waste package outer container in both the NRC/CNWRA TPA code and DOE Total System Performance Assessment code is based on a critical potential model.^{4,5} Crevice corrosion is considered possible if the E_{corr} of a metal in a given environment exceeds the E_{rcrev} . E_{corr} is measured under natural corroding conditions in air-saturated solutions simulating the emplacement drift environments after the heat pulse and is mainly dependent on the solution pH, temperature, and oxygen reduction kinetics. It is widely reported that the E_{rcrev} depends on temperature, chloride concentration, and the relative concentration of inhibiting anions to the chloride concentration. Dunn^{6,7,14,15} reported that the E_{rcrev} also depends on the metallurgical conditions of Alloy 22 as shown in Figure 11. As-welded, welded plus solution annealed, and thermally aged Alloy 22 had lower E_{rcrev} values than mill-annealed Alloy 22. The E_{rcrev} values of the as-welded and welded plus solution annealed materials were similar at chloride concentrations above 0.5 M. The welded plus solution annealed material had a lower E_{rcrev} value in chloride concentrations less than 0.5 M. The thermally aged material is reported to have the lowest E_{rcrev} values.

In DOE⁴ the effects of welding on the localized corrosion susceptibility of Alloy 22 were evaluated by comparing the E_{rcrev} values for mill-annealed and as-welded Alloy 22 in 5 M CaCl₂ solution at 90 °C [194 °F] and 120 °C [248 °F]. Based on the similar values of the E_{rcrev} for the mill-annealed and the as-welded materials, it was determined that welding had no effect on the crevice corrosion susceptibility of Alloy 22. The E_{rcrev} values for the mill-annealed material were assumed to be applicable to welded Alloy 22. Recent measurements of E_{rcrev} of Alloy 22 by Rebak¹⁹ with different metallurgical conditions (mill-annealed, as welded, and as-welded plus accelerated aging at higher temperatures) in simulated concentrated groundwaters at various temperatures up to 105 °C [221 °F] showed no effect of such metallurgical conditions. Ilevbare¹⁶ conducted tests of Alloy 22 in 5 M CaCl₂ solution, and the weld metal was found to be less susceptible to localized corrosion under the conditions tested. However, this observation could be diminished by the aggressive solution used in the test.

Obtained by Dunn,⁷ the regression lines by fitting to data at 95 °C [203 °F] for various metallurgical conditions are plotted in Figure 11. The E_{rcrev} values of mill-annealed and as-welded Alloy 22 measured in chloride solutions at 90 °C [194 °F] reported by DOE⁴ were included in Figure 11 for comparison along with several data points reported by Evans⁹ for as-welded Alloy 22 measured at 90 °C [194 °F]. Although the temperature difference is 5 °C [41 °F], this small difference should not affect the comparison. At the higher end of the chloride concentration range, the E_{rcrev} values Dunn⁷ reported are very similar those DOE⁴ reported except for the thermally aged material. The E_{rcrev} values for thermally aged Alloy 22 were significantly lower than all other values over almost all of the range of chloride concentrations plotted in Figure 11. At lower chloride concentrations, the E_{rcrev} values Evans⁹ reported were significantly lower than those Dunn⁶ reported. This is consistent with what is shown in Figure 3. At a lower chloride concentration, the E_{rcrev} values measured by the CNWRA method were higher than those measured by using ASTM G61–86.⁸ Except for the E_{rcrev} values of thermally

aged material, the difference in E_{rcrev} values at the lower end of the chloride concentration range appears to be mainly caused by different methods used to obtain the data. The lack of a deleterious effect of welding on localized corrosion susceptibility reported by DOE⁴ could be due to the aggressive solution combined with the fast electrochemical method used in obtaining the E_{rcrev} values.

SUMMARY AND CONCLUSIONS

Measurements of the crevice corrosion repassivation potential, E_{rcrev} , were performed with three electrochemical methods, including (i) the DOE method adopted from ASTM G61–86,⁸ (ii) the CNWRA method, and (iii) the Tsujikawa–Hisamatsu Electrochemical method in various chloride solutions at 90 °C [194 °F].

In 1 M NaCl and 1.25 M CaCl₂ solutions, the E_{rcrev} values measured by using the CNWRA method were higher than those by ASTM G61–86, whereas the E_{rcrev} values measured according to ASTM G61–86⁸ were higher than those measured by using the Tsujikawa–Hisamatsu Electrochemical method. At a high chloride concentration (5 M CaCl₂), the E_{rcrev} values measured by the three methods were very close. In 1 M NaCl and 1.25 M CaCl₂ solutions, the E_{rcrev} values measured using the DOE method (ASTM G61–86⁸) were slightly higher compared to those DOE used in the localized corrosion model. However, the values measured using the Tsujikawa–Hisamatsu Electrochemical method were similar to what DOE used in the model. Due to the high potential attained during the potentiodynamic scan used in ASTM G61–86,⁸ the crevice specimen often suffered transpassive dissolution in areas external to the crevice region, in addition to crevice corrosion in the crevice, which may contribute to the lower values of the crevice corrosion repassivation potential. Inconsistent initiation was often observed in the tests conducted using the CNWRA method especially at chloride concentrations of 1 M and 2.5 M, resulting in data exhibiting large scatter. However, this could be mitigated by increasing the hold potential and hold time during the intermediate potentiostatic step. On the contrary, the E_{rcrev} values obtained by using the Tsujikawa–Hisamatsu Electrochemical method were highly reproducible and the specimens were uniformly corroded across the crevice region, especially at chloride concentrations of 1 M and 2.5 M. In addition, no transpassive dissolution was observed on any of the test specimens. The Tsujikawa–Hisamatsu Electrochemical method appears to be a more appropriate method to produce reproducible and reliable E_{rcrev} values, especially in less aggressive environments. DOE observed no effects of welding on localized corrosion susceptibility through the measurement of E_{rcrev} in 5 M CaCl₂ solution. This could be due to the aggressive solution composition combined with the fast electrochemical method used in measuring the E_{rcrev} values.

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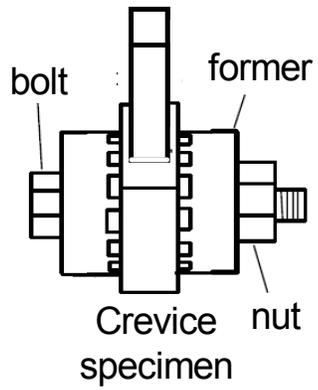
This paper describes work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC–02–02–012. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste

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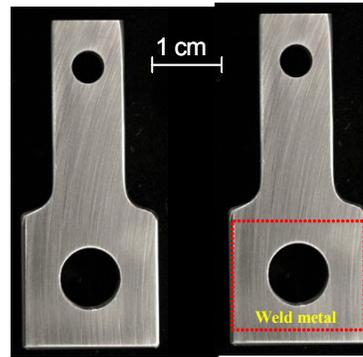
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a. Crevice assembly including crevice specimen, crevice formers, bolt, and nut



b. Alloy 22 crevice specimen including mill-annealed and as-welded

Figure 1. (a) Illustration of the crevice assembly as the working electrode and (b) optical photos of Alloy 22 crevice specimens.

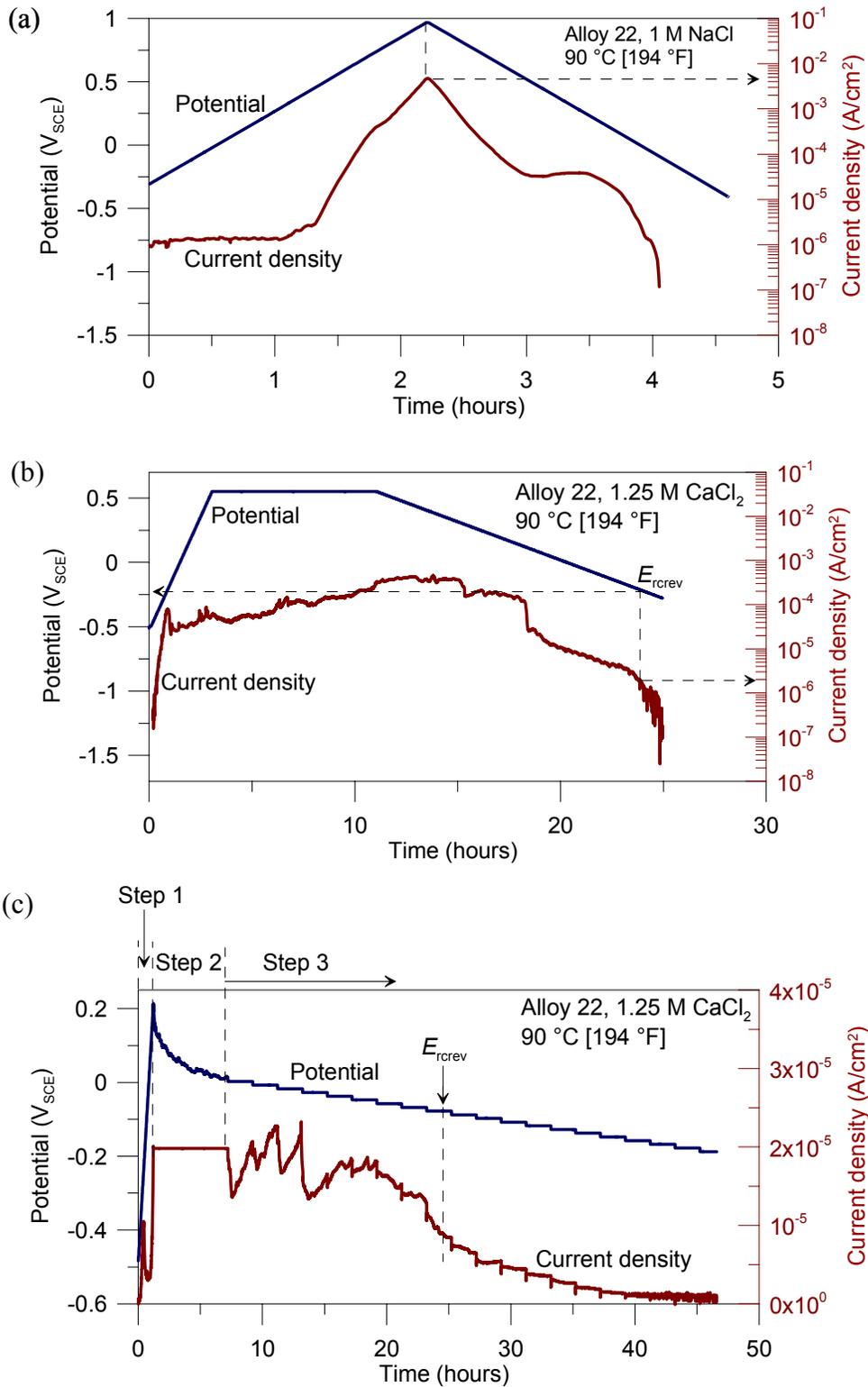


Figure 2. Examples of different test methods (a) ASTM G61–86 used by DOE,⁴ (b) method used by CNWRA, and (c) Tsujikawa–Hisamatsu Electrochemical method.

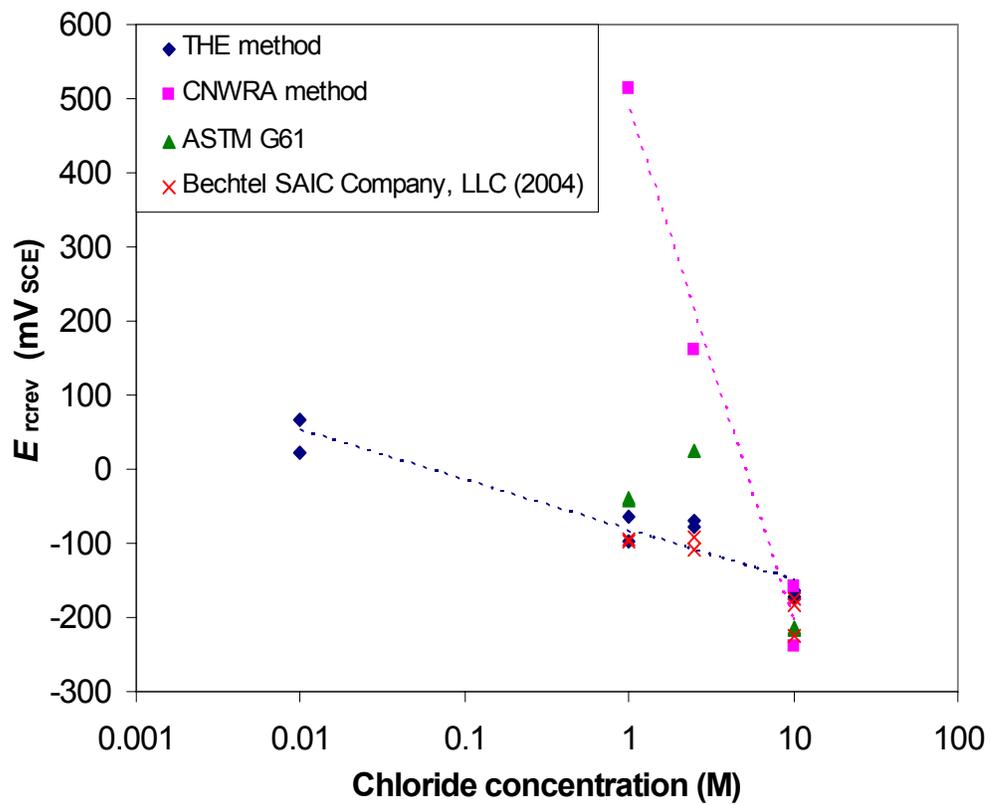
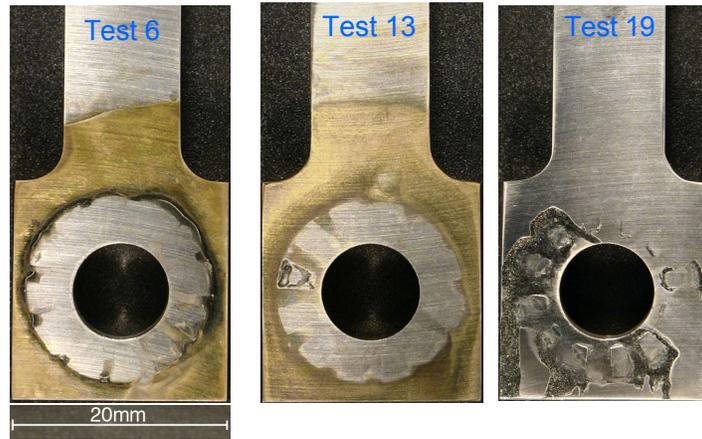
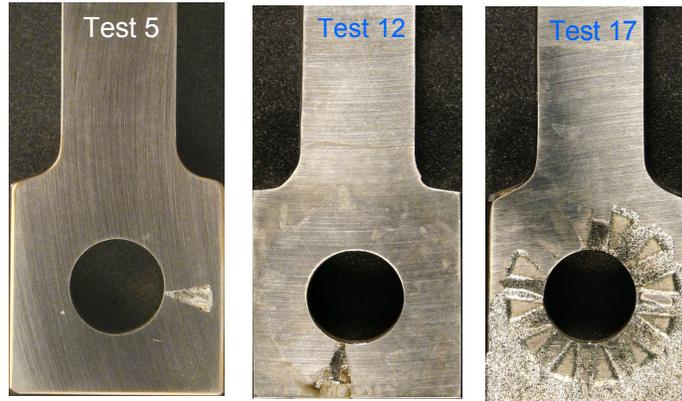


Figure 3. Measured crevice corrosion repassivation potential values of Alloy 22 using different methods in various chloride concentrations at 90 °C [194 °F]. Note: THE = Tsujikawa–Hisamatsu Electrochemical.

(a) ASTM G61–86 method



(b) CNWRA method



(c) Tsujikawa–Hisamatsu Electrochemical method

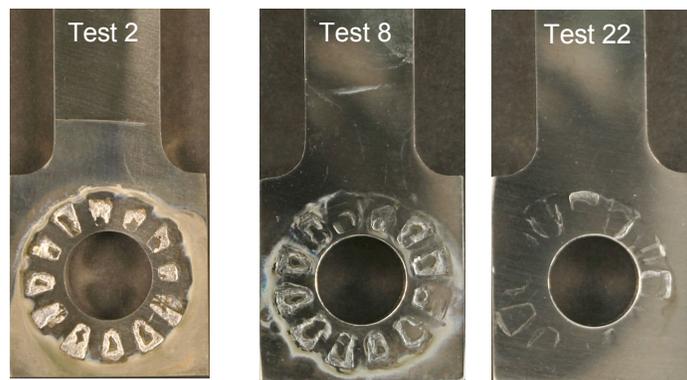


Figure 4. Optical photos of corroded Alloy 22 crevice specimens from some tests in Table 2 in chloride solutions at 90 °C [194 °F] using different methods: (a) ASTM G61–86, (b) CNWRA, and (c) Tsujikawa–Hisamatsu Electrochemical method.

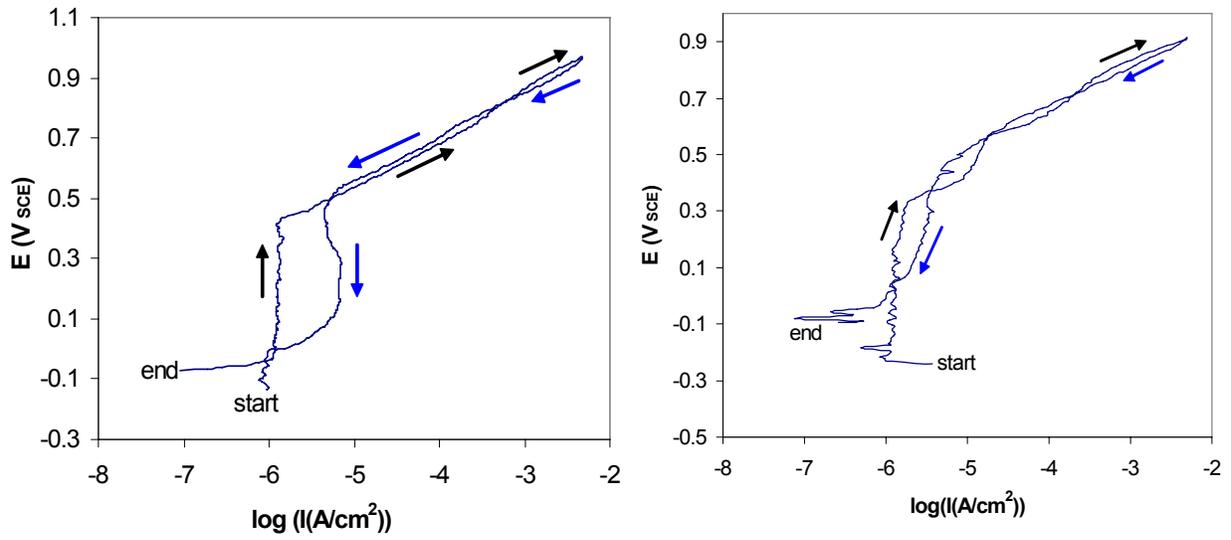


Figure 5. Cyclic potentiodynamic polarization curves of Alloy 22 at 90 °C [194 °F] following ASTM G61–86.⁸ (a) in 1 M NaCl solution (Test 6 in Table 2) and (b) in 1.25 M CaCl₂ solution (Test 13 in Table 2).

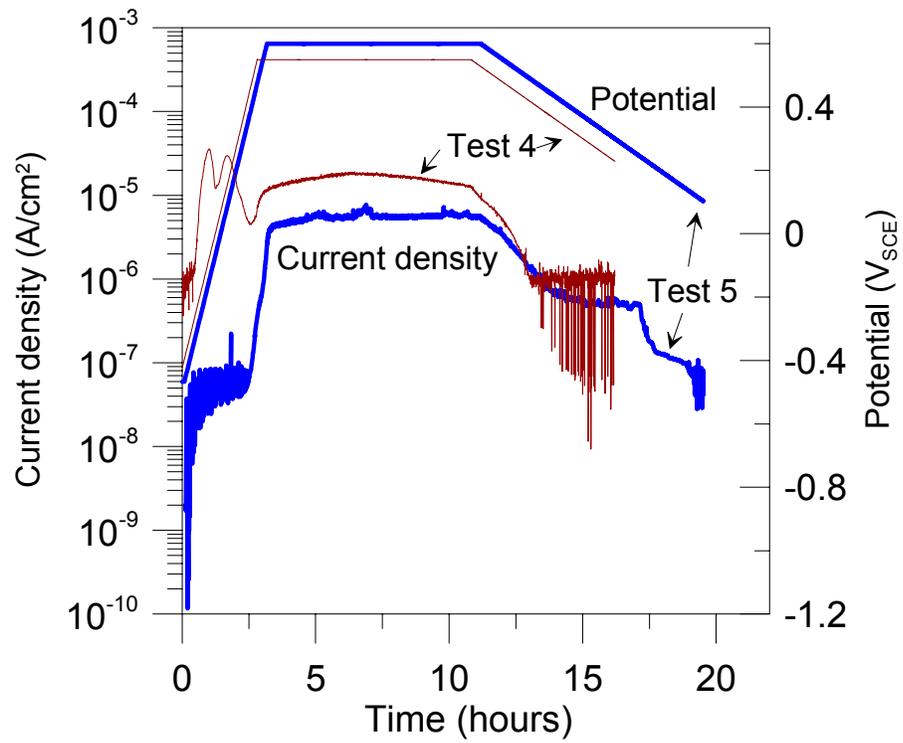


Figure 6. Current and potential curves of Alloy 22 following the CNWRA method for Tests 4 and 5 in Table 2 with hold potential of 550 mV_{SCE} and 600 mV_{SCE}, respectively, in N₂ deaerated 1 M NaCl solution at 95 °C [203 °F].

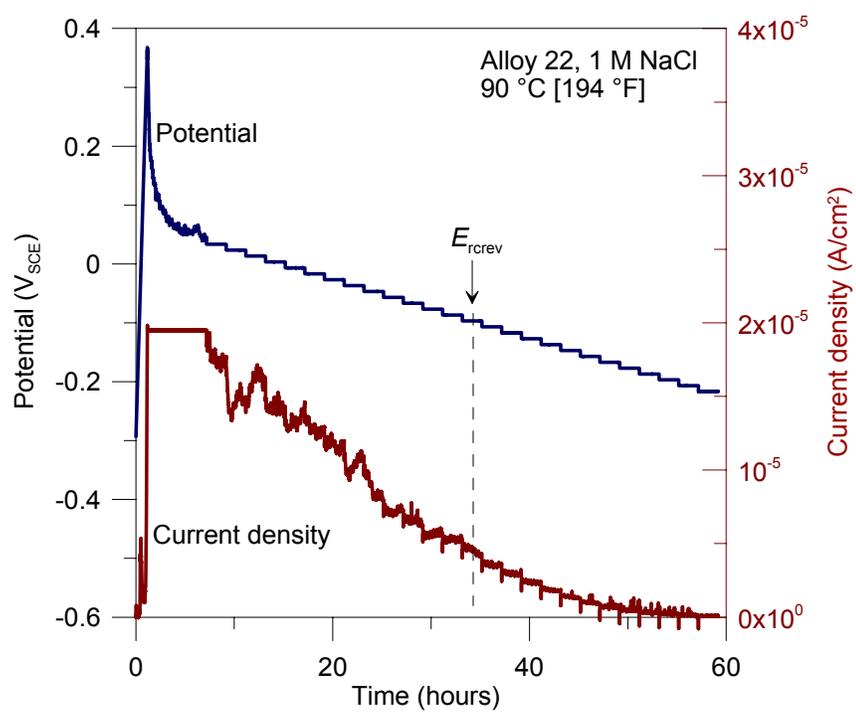


Figure 7. A Tsujikawa–Hisamatsu Electrochemical test of Alloy 22 at 90 °C [194 °F] in 1 M NaCl solution (Test 9 in Table 2).

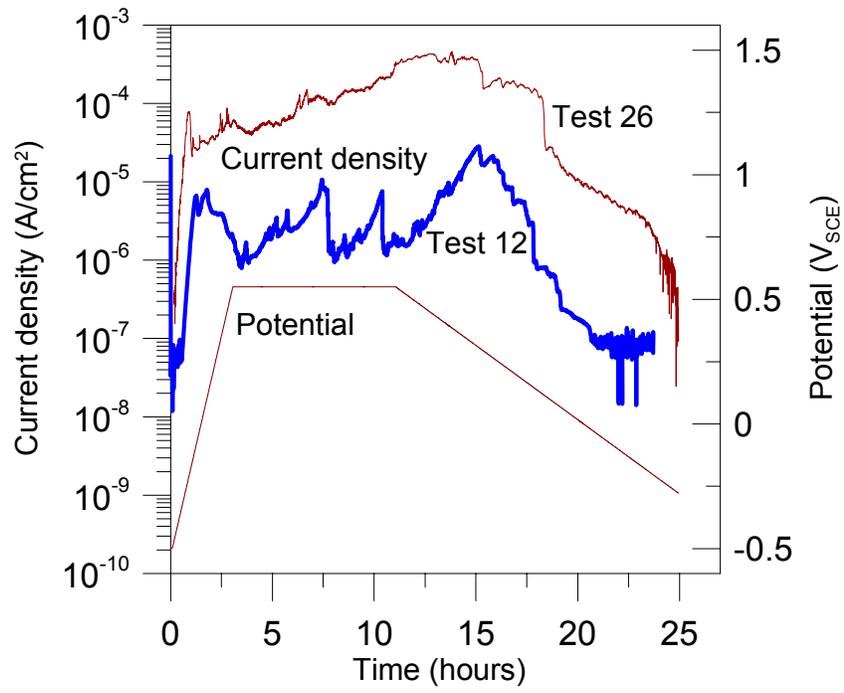


Figure 8. Current and potential curves of mill-annealed Alloy 22 (Test 12 in Table 2) and as-welded Alloy 22 (Test 26 in Table 3) following the CNWRA method in N₂ deaerated 1.25 M CaCl₂ solution at 90 °C [194 °F].

(a) CNWRA method



(b) ASTM G61–86 method



Figure 9. Optical photos of corroded as-welded Alloy 22 crevice specimens from Tests 28 and 30 in Table 3 in 5 M CaCl_2 solutions at 90 °C [194 °F] using different methods: (a) CNWRA method and (b) ASTM G61–86.⁸

(a) ASTM G61–86 method



(b) CNWRA method



(c) Tsujikawa–Hisamatsu Electrochemical method



Figure 10. Optical photos of corroded 316L stainless steel crevice specimens from some tests in Table 4 in chloride solutions at 90 °C [194 °F] using different methods: (a) ASTM G61–86, (b) CNWRA method, and (c) Tsujikawa–Hisamatsu Electrochemical method.

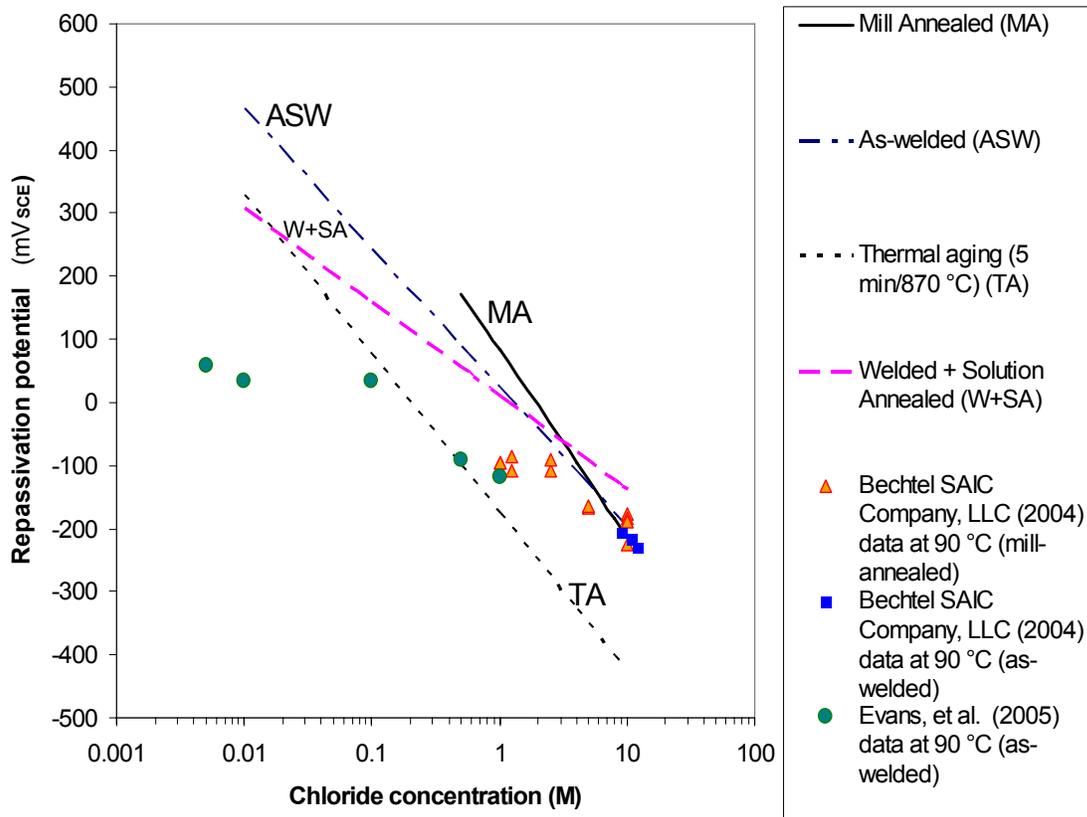


Figure 11. Comparison of crevice corrosion repassivation potential values of Alloy 22 reported in Dunn⁷ at 95 °C [203 °F], Bechtel SAIC Company, LLC,⁴ and Evans⁹ at 90 °C [194 °F].

Table 1. Chemical Composition of Alloy 22 and 316L Stainless Steel (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 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

*Ni—nickel, Cr—chromium, Mo—molybdenum, W—tungsten, Fe—iron, Co—cobalt, Si—silicon, Mn—manganese, V—vanadium, P—phosphorus, S—sulfur, C—carbon

Table 2. Measured Repassivation Potentials of Mill-Annealed Alloy 22 at 90 °C [194 °F]				
Test Number	Solution	Method	Repassivation Potential (mV_{SCE})	Corroded Sites Out of 24 Sites
1 2	0.01 M NaCl	THE*	23 66	24 24
3 4 5	1 M NaCl	CNWRA	Not Available Not Available 515‡	0 0 2
6 7		ASTM G61–86	–42 –38	11 21
8 9		THE*	–64 –96	24 24
		Reported†	–95 –96	Not Available Not Available
10 11 12		1.25 M CaCl ₂	CNWRA	Not Available Not Available 162
13 14	ASTM G61–86		24 Not Available	1 0
15 16	THE*		–70 –77	24 23
	Reported†		–107 –91	Not Available Not Available
17 18	5 M CaCl ₂		CNWRA	–239 –158
19 20		ASTM G61–86	–215 –216	22 19
21 22 23		THE*	–163 –173 –175	1 19 10
		Reported†	–226, –176, –183, 190	Not Available

*THE = Tsujikawa–Hisamatsu Electrochemical
† Reported in Bechtel SAIC Company, LLC⁴
‡The hold potential at the intermediate potentiostatic step is 600 mV_{SCE}

Table 3. Measured Repassivation Potentials of As-Welded Alloy 22 at 90 °C [194 °F]				
Test Number	Solution	Method	Repassivation Potential (mV_{SCE})	Corroded Sites Out of 24 Sites
24 25	1 M NaCl	CNWRA	Not Available 114	0 1
		DOE Reported*	-117	Not Available
26	1.25 M CaCl ₂	CNWRA	-209	2
27 28	5 M CaCl ₂	CNWRA	-183 -261	21 24
29 30		ASTM G61-86	-209 -224	22 18
		DOE Reported*	-231 -205 -217	Not Available
*Reported in Bechtel SAIC Company, LLC ⁴				

Table 4. Measured Repassivation Potentials of 316L Stainless Steel at 90 °C [194 °F]

Solution	Method	Repassivation Potential From Duplicate Tests (mV_{SCE})
1 M NaCl	CNWRA	-213, -226
	ASTM G61-86	-400, -406
	THE*	-262, -254
1.25 M CaCl ₂	CNWRA	-314, -324
	ASTM G61-86	-372, -384
	THE*	-296, -280

*THE = Tsujikawa-Hisamatsu Electrochemical