Corrosion Behavior of Waste Package and Drip Shield Materials

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Abstract—*The susceptibility to various forms of corrosion that could be experienced by the alloys considered by the U. S. Department of Energy for the waste package and drip shield for the proposed repository at Yucca Mountain is evaluated on the basis of experimental studies conducted at the Center for Nuclear Regulatory Analyses. Environmental, metallurgical, and mechanical conditions for the occurrence of uniform corrosion, localized corrosion, and environmentally assisted cracking of Alloy 22 (58Ni-22Cr-13Mo-3W-4Fe), the preferred material for the outer container, and Ti-Grade 7 (Ti-0.15 Pd), the alloy proposed for the drip shield, are reported.*

I. INTRODUCTION

The purpose of this paper is to provide a summary of the most recent work conducted at the Center for Nuclear Waste Regulatory Analyses in evaluating the corrosion behavior of the materials selected by the U.S. Department of Energy (DOE) for the design of the waste package and the drip shield considered in the site recommendation for the proposed high-level radioactive waste repository at Yucca Mountain, Nevada. The waste package and the drip shield are the principal components of the engineered barrier system. The work is being conducted to provide technical assistance to the U.S. Nuclear Regulatory Commission as it prepares to review a potential licence application for the proposed repository.

The reference waste package design in the DOE site recommendation consists of an outer container made of Alloy 22 (58Ni-22Cr-13Mo-3W-4Fe) surrounding an inner container made of Type 316 nuclear grade stainless steel (SS). The drip shield, in the form of an inverted U extending along the emplacement drifts, would be made of Titanium Grade 7 (Ti-0.15 Pd). For undisturbed repository conditions, corrosion is anticipated to be the primary degradation process limiting the life of these engineered barriers. We have studied uniform corrosion, which in these corrosion-resistant alloys is a very slow dissolution process through a protective oxide film, localized corrosion in the form of crevice corrosion, and

environmentally assisted cracking as the three dominant corrosion modes for such materials. The studies were conducted in chloride-containing solutions simulating the aqueous environments expected to contact the waste package and the drip shield.[1]

II. EXPERIMENTAL

Chemical compositions of the two heats (A and B) of hot rolled and mill-annealed plate of Alloy 22 used in these studies, as well as the composition of the Alloy 622 filler rod (C) used for welded specimens, are provided in Table 1. The geometry, dimensions, and preparation of the specimens used in the various tests were reported elsewhere.[1-4] Smooth cylindrical specimens (A: Heat 2277-8-3175) were used in potentiostatic tests to measure the passive dissolution current density. Flat specimens (A: Heat 2277-8-3175), fitted with two polytetrafluoroethylene (PTFE) crevice forming washers, were used in cyclic potentiodynamic polarization (CPP) or similar tests to measure the repassivation potential for crevice corrosion (E_{rcrev}). Some of these flat specimens were thermally treated at 870°C over times ranging from 5 to 30 min to determine the effect of thermal aging on localized corrosion. Welded specimens were machined from a plate (B: Heat 2277-8-3235) which

Table 1. Chemical Composition (In Weight Percent) of the Heats of Alloys 22 and 622 Filler Metal

Heat	Ni	Cr	Mo	W	Fe	Co	Si	Mn	V	P	S	C
Alloy 22 - A 2277-8-3175	57.8	21.40	13.60	3.00	3.80	0.09	0.030	0.12	0.15	0.008	0.002	0.004
Alloy 22 - B 2277-8-3235	56.5	21.40	13.47	2.87	3.94	1.31	0.023	0.24	0.17	0.008	0.001	0.003
622 Filler- C XX1045BG11	58.5	20.73	14.13	3.15	3.05	0.09	0.060	0.24	0.01	0.007	0.001	0.006

was welded using the gas tungsten arc welding (GTAW) procedure with argon as the shielding gas and Alloy 622 (C: Heat XX1045BG11) as the filler rod. The crevice forming washers were placed on top of the specimen weld. Alloy 22 compact tension (CT) fracture mechanics specimens were machined from heat A plate in the long transverse-longitudinal (T-L), orientation in which the crack plane is perpendicular to the width direction (T direction), and the crack propagation is in the longitudinal rolling direction (L direction). The specimens were fatigue precracked using a servo hydraulic test machine and loaded at a constant value (dead-weight loaded) in mechanical load frames at an initial stress intensity of 47 MPa m$^{1/2}$.[3,4]

The chemical composition of the Ti-Grade 7 plate is shown in Table 2, together with those of Ti-Grade 2 and Ti-Grade 5 used for comparison in the environmentally assisted cracking tests. As in the case of Alloy 22, smooth cylindrical specimens of Ti-Grade 7 were used for measuring the anodic

effect on localized corrosion. Specific tests were conducted in other solution compositions containing the same anions. The susceptibility to environmentally assisted cracking was evaluated in concentrated LiCl solutions (9.1 molal chloride) at 95°C [203°F] and in saturated concentrated water[1] at 73 to 95°C. These tests were conducted under potentiostatic conditions. Applied potentials are expressed in the saturated calomel electrode scale (SCE).

Most of the localized corrosion tests on Ti-Grade 7 were conducted at temperatures ranging from 95 to 165°C in deaerated, pure NaCl solutions and at 95 °C in deaerated 1M NaCl solutions containing various concentrations of F$^-$, with or without the presence of the other groundwater anions. The slow strain rate tests were performed at 95°C in both deaerated 1.0 M NaCl and 1.0 M NaCl + 1.0 M NaF solutions under open circuit conditions. Additional experimental details and procedures have been reported elsewhere.[1-5]

Table 2. Chemical Composition of the Titanium Alloys Used in This Study (wt%)

Material	Ti	C	N	Fe	O	H	Al	V	Pd
Ti-Grade 2	Balance	0.011	0.016	0.111	0.141	0.001	—	—	—
Ti-Grade 5	Balance	0.030	0.007	0.140	0.186	0.012	6.180	4.050	—
Ti-Grade 7	Balance	0.009	0.007	0.115	0.140	0.005	—	—	0.155

current density in potentiodynamic and potentiostatic tests, and flat creviced specimens were used to evaluate the susceptibility to localized corrosion.[1,5] The susceptibility to environmentally assisted cracking was evaluated using circumferentially notched round tensile specimens, machined either in the longitudinal or perpendicular direction with respect to the rolling direction, which were tested in slow strain rate tests.[4] An extension rate of 1.8 × 10^{-5} mm/s [7.1 × 10^{-7} in/s] was used in these tests .

Electrochemical corrosion tests on Alloy 22 were performed at temperatures ranging from 25 to 150°C in nitrogen-deaerated solutions containing 0.1 mM to 4.0 M Cl$^-$, 0.16 mM NO$_3^-$, 1.24 mM HCO$_3^-$, 0.20 mM SO$_4^{2-}$, and 0.1 mM F$^-$, with Na$^+$ as the single cation. These anions are the predominant groundwater anionic species in the vicinity of the proposed repository site.[1] The NO$_3^-$ concentration was increased up to 2.0 M in some tests to study its inhibiting

III. RESULTS AND DISCUSSION

III.A. Uniform Corrosion

Alloy 22 in the mill-annealed condition corrodes at a very slow rate under a wide range of environmental conditions as a result of the protection offered by a Cr$_2$O$_3$-rich film. The passive current density of mill-annealed Alloy 22 was measured over the potential range that extends from the corrosion potential in fully deaerated solutions (−600 mV$_{SCE}$) to the potential for transpassive dissolution.[1] As shown in Figure 1, anodic current densities, measured potentiostatically at 95°C in tests lasting 48 hours, were found to be consistently lower than 10^{-7} A/cm^2 and practically independent of Cl$^-$ concentration (0.028 to 4.0 M), pH (0.7 to 8.0), and potential The current density
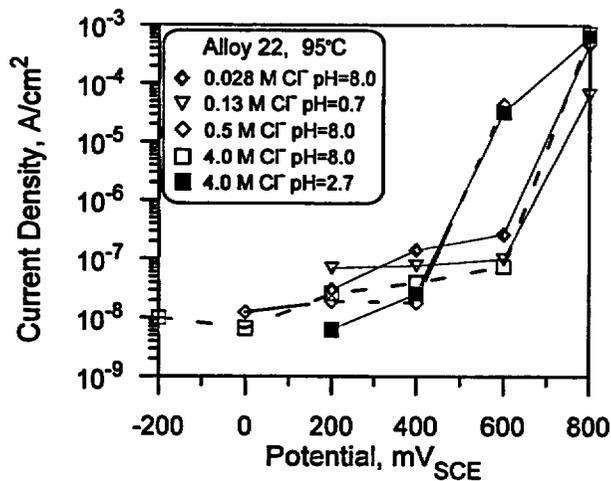
Figure 1. Steady-state anodic current densities for Alloy 22 in Cl⁻ solutions at 95°C

Figure 2. Effect of temperature on the passive current density of Alloy 22 in deaerated 0.028 M NaCl at 100 mV$_{SCE}$

increased only at potentials above 400 mV$_{SCE}$, as a result of transpassive dissolution presumably due to the dissolution of Mo as MoO_4^{2-}, followed at higher potentials by the dissolution of Cr(III) in the film to Cr(VI) species in solution and the concurrent evolution of oxygen. These high potentials are not anticipated under the mild oxidizing conditions expected in the repository. Corrosion rates lower than 1 µm/yr [0.039 mpy] were estimated from the current density measurements in the passive range using Faraday's law. As shown in Figure 2, the current density at 100 mV$_{SCE}$, a potential in the passive range, increases with increasing temperature. An activation energy of 44.7 ± 5.5 kJ/mol [10.7 ± 1.3 kcal/mol] was calculated in the temperature range of 25 to 95°C from median values of the passive current density. A reasonable upper bound for the uniform corrosion rate of 5 × 10⁻⁴ mm/yr [2 × 10⁻⁵ in/yr] was determined at 95°C.[6] However, potentiostatic tests conducted at the same temperature for times longer than 200 hours revealed that the current density in 0.028 M NaCl, 0.028 M NaCl + 0.052 M NaF, and 0.028 M NaCl + 0.021 M Na$_2$SO$_4$ solutions continuously decayed to values lower than 10⁻⁸ A/cm².[6]

In order to provide an explanation for such evolution of the anodic current density and evaluate the long-term stability of the protective oxide film, a model for the passive dissolution of Ni-Cr-Mo alloys (of which Alloy 22 is a particular example) was developed [1, 6] based on the Point Defect Model. The Point Defect Model was originally developed by Macdonald[7] to attain a mechanistic understanding of passivity and passivity breakdown of metals in low temperature aqueous systems and later extended to binary alloys.[8] From the model and thermodynamic data, it is assumed that the predominant charge carriers through the Cr$_2$O$_3$-rich film are Cr, Ni and Mo as cation interstitials. Dissolution of the alloy in the form of interstitials creates metal vacancies in the alloy. Vacancy creation resulting from metal oxidation has been observed in high-temperature Ni-Cr alloy systems. The model predicts that if vacancies are created in the alloy and accumulate at the metal-film interface, the passive current density should decrease as a
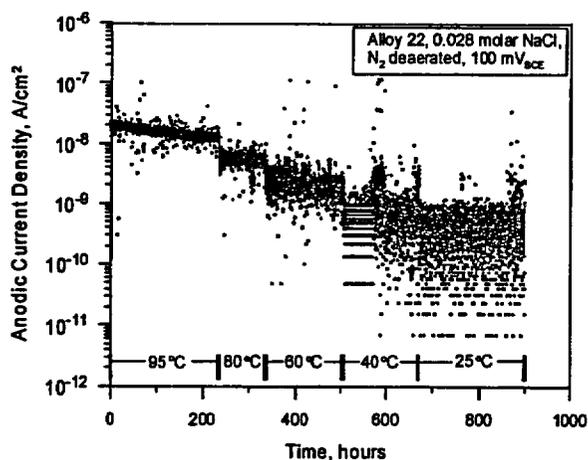
function of time, until a steady state is reached. This is indeed observed in the potentiostatic tests. A detailed discussion of the assumptions and values of the parameters used for the kinetics expressions contained in the model has been recently presented.[6] Adequate goodness of fit was obtained between measured and calculated current densities for particular selections of rate constants and finite difference parameters, as shown in Figure 3. It was thus concluded that the experimental data are consistent with the hypotheses of predominant interstitial cation conduction and vacancy injection at the metal-film interface. It is proposed that steady state in the anodic current density occurs after reaching a critical value of the vacancy concentration at the metal-film interface, which is higher than the equilibrium value at the same temperature. In addition, in the absence of environmental conditions leading to localized corrosion, these modeling studies suggest that breakdown of passivity or enhanced dissolution are unlikely to occur, with the exception of periodic spalling of the passive oxide film. Such periodic spalling may provide bursts of higher corrosion rates and also cause surface roughening,[6] but it would not result in a significant increase in the long-term
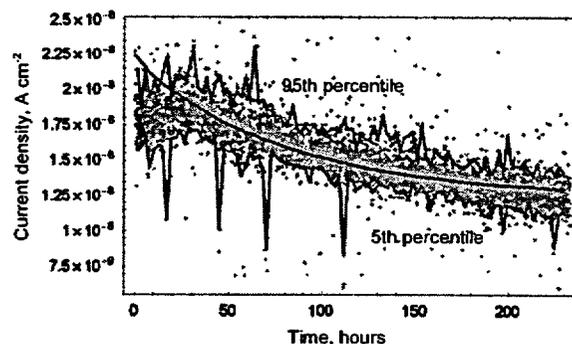

Figure 3. Comparison of experimental anodic current density (5th and 95th percentile) with model calculations for Alloy 22 in 0.028M NaCl at 95°C

steady state uniform corrosion rate.

Ti Grade 7 exhibits passive behavior over a wide range of environmental conditions including high Cl⁻ concentrations and elevated temperatures as a result of the formation of a protective TiO_2 film in aqueous solutions. Using potentiodynamic polarization tests, current densities lower than 10^{-5} A/cm², and almost independent of potential, were measured at 95°C over a wide potential range in solutions with Cl⁻ concentrations and pH ranging from 0.1 to 1.0 M and 2.1 to 10.7, respectively.[5] In more prolonged (~1,200 hours) potentiostatic tests, conducted in deaerated 1.0 M NaCl solution at the same temperature, steady state current densities lower than 1.0×10^{-7} A/cm² were measured by applying a potential of 0 V_{SCE}, which is in the passive range.[5] Such current density corresponds to a corrosion rate of 0.87 μm/yr [0.034 mpy], indicating that Ti Grade 7 exhibits very low corrosion rates in aqueous solutions. However, contrary to the case of Alloy 22, low F⁻ concentrations in the water increased the corrosion rate significantly, as can be inferred from the data in Figure 4. The anodic current density in 1M NaCl at 95°C at an applied potential of 0 V_{SCE} increased by several orders of magnitude with the addition of F⁻ at relatively low concentrations.[1] As shown in Figure 5, this detrimental effect of F⁻ is not attenuated by the presence of other anions prevailing in the groundwater such as NO_3^- or SO_4^{2-}.[1]

III.B. Localized Corrosion

Crevice corrosion of mill-annealed Alloy 22 in Cl⁻ containing solutions only occurs at potentials above the repassivation potential at Cl⁻ concentrations higher than 0.5 M and temperatures above 80°C.[1,9,10] The repassivation potential for crevice corrosion was measured in a series of electrochemical tests as a function of temperature (ranging from 80 to 150°C) at various Cl⁻ concentrations (varying

Figure 5. Effect of fluoride on the anodic current density in deaerated solutions containing various anions at 95°C and 0 mV$_{SCE}$

from 0.1 mM to 4M), after initiating crevice corrosion at higher potentials. Figure 6 shows a plot of the repassivation potential at various temperatures in which a linear dependence of the repassivation potential on the logarithm of Cl⁻ concentration is observed. The steady state corrosion potential (E_{corr}) in air-saturated solutions, measured in separate experiments, was found to be lower than the crevice corrosion repassivation potential (E_{rcrev}), even in relatively acidic solutions. Therefore, it is anticipated that crevice corrosion is unlikely to occur in the mill-annealed material under naturally corroding conditions. On the other hand, thermal aging for a short time at temperatures at which precipitation of intermetallic Mo-rich phases occurs (few minutes at 870°C) renders the alloy susceptible to crevice corrosion in the form of severe grain boundary attack even at lower Cl⁻ concentrations.[9-11] The result is a significant decrease in the repassivation potential, as shown in Figure 7 for tests conducted in 4M NaCl solution at 95°C. A similar behavior is observed in welded specimens in which the localized attack is interdentritic.[10] As a result, for both thermally aged and welded material the repassivation potential at a given Cl⁻ concentration decreases with respect to that measured in the mill annealed alloy, as summarized in Figure 8 for tests conducted at 95°C. In this case, as indicated in the same figure, the corrosion potential in air saturated solutions can reach the repassivation potential, and hence, crevice corrosion can occur. Nevertheless, the addition of NO_3^- to the Cl⁻ solutions, even at a low NO_3^- to Cl⁻ molar ratio (approximately 0.2), inhibits both the initiation and propagation of crevice corrosion resulting in a significant increase in the repassivation potential, as shown in Figure 9.[9,12]

Contrary to the case of Alloy 22, crevice corrosion of Ti Grade 7 was not observed in Cl⁻ solutions over a wide range of concentrations (0.1 to 5 M) and temperatures (95 to 165°C).[1,5] Breakdown of the TiO_2 passive film and localized
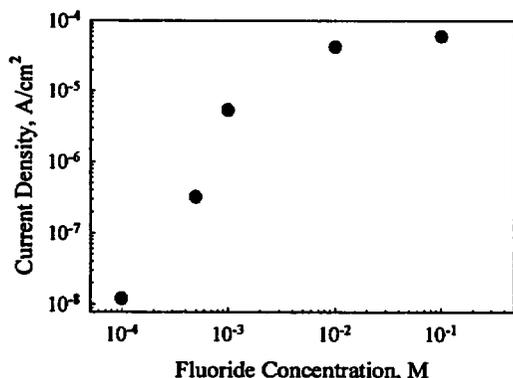
Figure 4. Effect of fluoride on the steady state passive current density for Ti Grade 7 in deaerated 1M NaCl solution at 95 °C and an applied potential of 0 V$_{SCE}$.
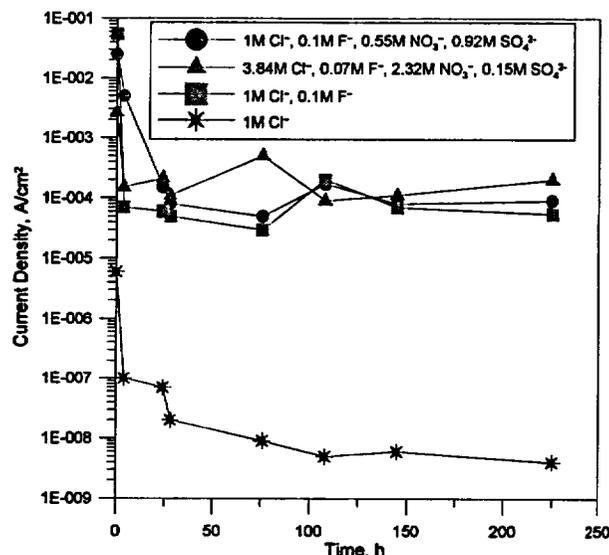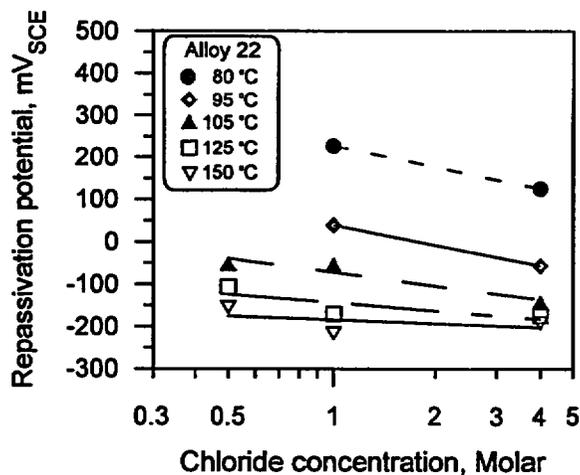
Figure 6. Repassivation potential for crevice corrosion of Alloy 22 as a function of Cl⁻ concentration at various temperatures
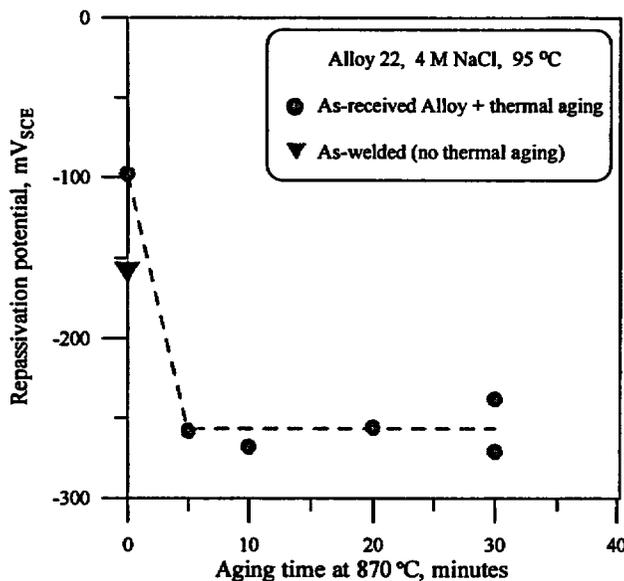

Figure 7. Effect of thermal aging at 870°C on the repassivation potential of Alloy 22

Figure 8. Crevice corrosion repassivation potential for mill annealed (MA), welded, and thermally aged (TA) Alloy 22 in NaCl solutions at 95°C.

Figure 9. Effect on nitrate on the crevice corrosion repassivation potential of welded Alloy 22 in 0.5 M NaCl at 95°C

corrosion of the bold specimen surface (not in the crevice areas) only occurred at potentials well above 1 V_{SCE}. Such high potentials are not attainable under naturally corroding conditions in the air saturated environments expected in the proposed repository, even in the presence of reducible cations such as Fe^{+3} or strong oxidants produced by radiolysis such as H_2O_2 or HNO_3. Under such testing conditions, both wrought and welded specimens exhibited practically the same breakdown and repassivation potentials. Therefore, crevice corrosion of the Ti Grade 7 drip shield should not occur under the environmental conditions expected to prevail in the emplacement drifts.
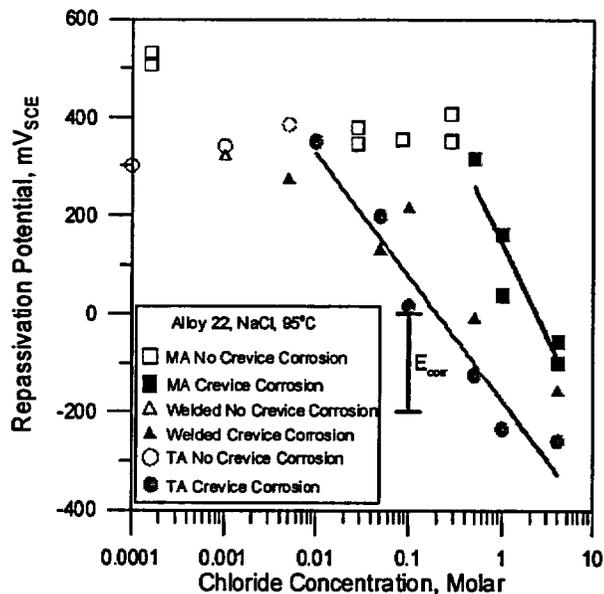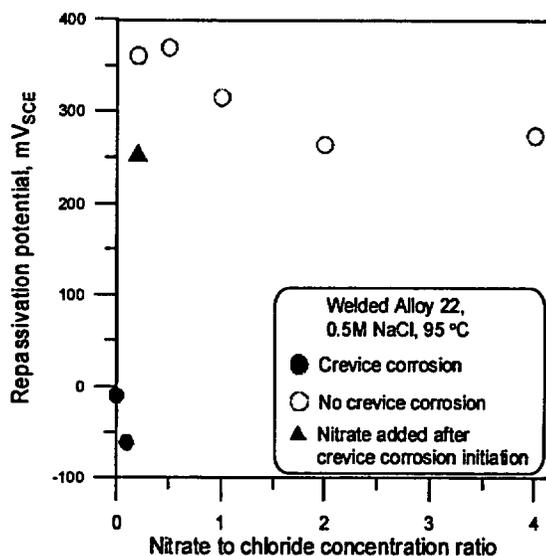
III.C. Environmentally Assisted Cracking

The environmentally assisted cracking susceptibility of Alloy 22 and Ti Grade 7 is being evaluated in relevant aqueous solutions using a variety of loading techniques that include fracture mechanics and slow strain rate tests and being compared with Type 316L SS as a reference.[3,4,13] Alloy 22 and Type 316L SS are being tested in hot, concentrated Cl⁻ solutions using double cantilever beam (DCB), wedge-opening-loaded (WOL), and compact tension (CT) specimens. As previously reported,[3] Type 316L SS exhibited crack growth rates ranging from 10^{-6} to 10^{-5} mm/s

[3.9 × 10⁻⁸ to 3.9 × 10⁻⁷in/s] in 9.1 M LiCl solution at 95°C and potentials above the repassivation potential when DCB and WOL specimens were tested at initial stress intensities of 22 to 33 MPa·m$^{1/2}$ [20 to 30 ksi·in$^{1/2}$]. The threshold stress intensity was found to be 13.1 MPa·m$^{1/2}$ [11.9 ksi·in$^{1/2}$], and no crack growth was detected after 116 days of continuous exposure to the solution at potentials below the repassivation potential. *In-situ* monitoring of crack growth was accomplished using CT specimens under a constant or cyclic applied load. Increases in crack opening displacement (COD), indicating crack growth, were measured as a function of potential and stress intensity. When the potential was decreased below the repassivation potential, under either constant or cyclic (R= 0.7 and 0.001Hz) loading, an almost constant value of COD was attained indicating that the crack growth rate decreased substantially. A higher sensitivity in the measurements of crack growth is needed, however, to confirm whether the crack was arrested or continued to grow at a very low rate at potentials below the repassivation potential. Similar tests were conducted using Alloy 22 DCB specimens. No crack growth was detected after 21 weeks of exposure even in 14.0 molal Cl⁻ as MgCl$_2$ at 110°C at an initial stress intensity of 32.7 MPa·m$^{1/2}$ (the detection limit was 3 × 10⁻¹⁰ mm/s [1.2 × 10⁻¹¹ in/s].[3] In tests using CT specimens in which an initial stress intensity of 47 MPa·m$^{1/2}$ was applied, no crack growth was observed over a 3,500-hour period in 9.1 M LiCl solution at 95°C and potentials below and above the repassivation potential (-250 mV$_{SCE}$). Even under cyclic loading (R = 0.7, 0.001 Hz, K$_{Imax}$ = 47 MPa·m$^{1/2}$), no crack growth was observed after 3,500 hours. Similar results were obtained when CT specimens were tested for 3,000 hours combining successive periods of constant and cyclic loadings in simulated concentrated water at 73–95°C and an applied potential of 380 mV$_{SCE}$.[13]

Preliminary slow strain rate tests of Ti Grade 7 (including specimens of Ti Grades 2 and 5 for comparison), were conducted under open circuit conditions in deaerated 1.0 M NaCl solution at 95°C.[4] Ductile failure was observed in all these tests. When 0.1 M NaF was added, however, signs of environmentally assisted cracking were detected in the longitudinal specimens through a slight decrease in the reduction in area and the occurrence of specific brittle fracture features on the fracture surface of the three Ti alloys. These limited results need to be confirmed and extended to other test conditions to verify if environmentally assisted cracking of Ti Grade 7 is possible in the presence of F⁻ anions in solution.

IV. CONCLUSIONS

Fabrication and closure processes such as welding and post welding operations may render Alloy 22 susceptible to localized corrosion in Cl⁻ containing solutions in the form of interdendritic or intergranular attack in crevice locations at potentials above the repassivation potential. However, nitrate can act as an effective inhibitor at relatively low molar concentrations ratios. The beneficial effect of nitrate should be studied over a wide range of chloride concentrations and temperatures. Slow corrosion rates can be expected for Alloy

22 containers over many thousands of years, as inferred from experimental and modeling studies. Alloy 22 was not found susceptible to environmentally assisted cracking in hot, concentrated Cl⁻ solutions, including simulated concentrated water.

The most detrimental process affecting the life of Ti Grade 7 drip shield appears to be enhanced dissolution in the presence of F⁻ in the water. Further evaluation will attempt to clarify the effect of F⁻ on environmentally assisted cracking.

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