Effect of chloride concentration on the corrosion-fatigue crack behavior of an age-hardenable martensitic stainless steel

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Abstract

Crack growth rate and S-N fatigue testing of Custom 465-H950 was performed in 0.0006-3M NaCl with different levels of pre-exposure. Custom 465-H950 exhibited a strong corrosion resistance to various NaCl-based exposures. Concurrent exposure and loading did not result in corrosion damage sufficiently severe to drive crack formation away from microstructure features (TiC particles). The total fatigue life of precorroded specimens (pit depth $\approx 40\ \mu\text{m}$, surface diameter $\approx 175\ \mu\text{m}$) increased 4-9 fold as $[\text{Cl}^-]$ decreased from 3.0M to 0.0006M. Detailed analysis demonstrated that the varying $[\text{Cl}^-]$ most strongly influenced the initiation life, with secondary contributions from the long- and short-crack propagation regimes.

1. Introduction

Ensuring structural integrity of highly stressed engineering components operating in corrosive environments requires an engineering approach grounded in precise understanding of electrochemical and mechanical driving forces governing damage evolution. Of particular interest are high strength steels which contribute 7-20% of commercial and military aircraft weight [1-3]. Such components can be exposed to aqueous chloride environments where ambient salt aerosol contaminants (with NaCl as a major component [4]) result in a wetted surface under ambient humidity [5, 6]. A critical aspect of next generation structural integrity efforts is incorporation of loading environment effects into either empirical (stress/strain life) or fracture mechanics-based life prediction models used in the design and management of structural components [7-12].

Modern Ni/Co rich steels, most prominently AF1410 and AerMet100, meet the strength and toughness requirements for aerospace structural components and are more resistant to environmentally-induced degradation than legacy 4340 or 300M [13]. However, they are expensive due to their alloying elements and are still susceptible to broad surface corrosion. As such, hazardous coatings and platings containing cadmium, nickel, and/or chromium are used to effectively counter environmental damage [14, 15]. The cost, environmental impact, inherent inspection challenges, and handling hazards associated with such coatings motivate the use of ultra-high strength stainless steels (UHSSS) that are intrinsically resistant to general corrosion (but still susceptible to localized corrosion such as pitting) in the operational environment. Modern UHSSS offer mechanical properties that meet the demanding requirements of aerospace applications and the addition of Cr/Mo stabilizes the native protective passive film [16, 17] to preclude general corrosion and eliminate the need for protective plating/coatings. There are several UHSSS currently in service throughout the aviation industry, including 17-4PH, 15-5PH, Custom 450, 13-8Mo, Custom 455 and Custom 465 [13, 18]. Of particular interest is Custom 465 due to its engineering relevance and use in a wide-range of applications (aircraft landing gear, torque tubes, arresting hooks, engine attachments, etc.) [19, 20]. Critically, Custom 465 shows environmental cracking susceptibility (stress corrosion cracking due to H-embrittlement) in aqueous chloride environments in the H900/H950 tempers necessary to obtain the mechanical properties for the most demanding applications [21, 22]. The corrosion fatigue behavior for these conditions in such environments have not been rigorously established.

For atmospheric exposure conditions, the thickness and composition (e.g. chloride concentration ($[Cl^-]$)) of a deliquesced electrolyte film will be dependent on the salt loading density and relative humidity [23]. A broad literature has identified the phenomenological distinctions (and to a lesser extent the mechanistic distinctions [24-27]) between full immersion and thin-film atmospheric corrosion behavior [4, 24, 28]. For a constant chloride concentration and pH, the environment assisted fatigue crack propagation (EFCP) behavior in a thin-film electrolyte may deviate from full immersion due to differences in the pertinent mass transport

distances and/or local ionic resistance influencing the cathodic/anodic reaction kinetics that the control crack tip H production [29]. The EFCP behavior under thin-film conditions has not been studied outside of limited testing of an Al-Cu-Li alloy that suggested a secondary influence on crack growth kinetics [30]. While the electrochemical subtleties of cracking in thin film conditions are not fully established, as a first step it is reasonable to use varying $[Cl^-]$ in full immersion solutions as a proxy for the varying thin film chloride concentrations that arise from different salt-loading densities and humidities [6].

Aqueous chloride environments have a highly deleterious effect on the fatigue life of precipitation-hardened UHSSS despite their stainless nature [31-38]; specifically, Ebara reports an order of magnitude decrease in the fatigue limit as $[Cl^-]$ increases from 0.0006M to 3.0M. This behavior is generally attributed to the evolution of pitting damage and an aggressive environment at the base of the pit that results in an enhanced mechanical and chemical driving force for crack formation [32, 39-41]. However, to inform rigorous modeling of the effect of $[Cl^-]$ on the total fatigue life, it is critical to identify the relative impact of the $[Cl^-]$ on the different stages of corrosion- and environment-enhanced fatigue damage. First, if present, corrosion pits have been found to preferentially nucleate fatigue cracking [39, 42, 43]. As such, if the pitting is concurrent with fatigue loading, then it is critical to understand the kinetics of pit formation as a function of $[Cl^-]$ [44, 45] and loading level [46, 47] relative to the loading frequency and duration of cyclic loading. Second, once a pit has formed it is necessary to quantify the pit-to-crack transition life as a function of the bulk $[Cl^-]$. The third stage is chemically short crack growth and the fourth stage is long crack growth [45, 48-50]; the distinction is defined below in the context of the H-embrittlement mechanism.

A broad literature establishes that $[Cl^-]$ containing environments lead to accelerated crack growth rates for a wide range of steels [21, 29, 34, 51-55]; such behavior is widely attributed to the H-embrittlement mechanism [56]. In aqueous environments, the crack tip electrochemical conditions (pH and electrochemical potential) govern the overpotential for H production thus the growth rate enhancement [57]. For a wide range of high strengths in aqueous environments, researchers have demonstrated that the occluded crack tip environment deviates substantially from the bulk and is conducive to H-production; specifically resulting in low pH (as low as 1 for stainless steels), high $[Cl^-]$ concentrations, and an IR drop from the mouth to the tip of the crack [58-63]. Even extremely low bulk anion concentrations can support the crack tip acidification process; as demonstrated for chloride concentrations below 10^{-6} M and distilled water due to trace impurities or dissolved alloy constituents [64, 65]. Due to the relevant mass transport path and distances, crack size and geometry are critically important to the development of an occluded environment [50, 55, 66, 67]. As such, chemically short cracks where there is significant interaction with the bulk solution are distinguished from long cracks where a consistent-aggressive crack tip environment develops. The subtleties associated with crack size effects on local chemistry are further detailed in the Discussion.

Fatigue life modeling efforts require (1) quantification of pit formation kinetics and morphology, (2) an understanding and empirically based modeling of the cycles required to form a crack from a pit (note that linear elastic fracture mechanics (LEFM) models do not predict crack formation life), (3) an accurate prediction of crack propagation life based on crack growth kinetics specific to the operational environment. The overarching objective of this study is to quantitatively evaluate the effect of bulk $[Cl^-]$ on each of the stages of crack growth to more rigorously understand the mechanisms that govern the dependence of fatigue life on $[Cl^-]$. Once the controlling regime is established, modeling efforts can be targeted to the appropriate stage of the corrosion-fatigue process to enable more accurate engineering scale modeling of this behavior. The detailed goals of the current work on Custom 465-H950 are: (1) characterize the fatigue crack formation feature for pristine specimens exposed to aggressive $[Cl^-]$ environments; investigate the links between the corrosion morphology evolved during loading, the crack nucleating feature, and the fatigue life. (2) Quantitatively assess the effect of various $[Cl^-]$ on the overall fatigue life of specimens with a fixed level of pre-corrosion damage. (3) Quantify the effect of bulk $[Cl^-]$ on the crack formation, small crack growth, and long crack growth behavior to identify the regime that is most deleteriously influenced by increasing $[Cl^-]$.

2. Experimental Methods

2.1 Material

Specimens were machined from a $\frac{3}{4}$ " (19.05mm) diameter bar of Custom 465 and heat treated in the H950 condition (510°C aging temperature). The bulk and trace element compositions (Table 1) were measured via inductively coupled plasma optical emission spectroscopy (ICP-OES) or infrared combustion (IC), and glow discharge mass spectroscopy (GDMS), respectively. Duplicate compression tests were used to establish the yield strength (σ_{ys} = 1827 MPa) and Ramberg-Osgood hardening parameters (α = 0.13-0.15 and n =23-35); a plain strain fracture toughness (K_{IC}) of 95 MPa $\sqrt{m}$ is reported by the manufacturer [19]. This double vacuum melted alloy consists of a predominantly tempered martensitic microstructure with an unrecovered dislocation structure where the retained austenite is often minimized by a sub-zero chill following solution treatment. Low- and high-magnification (250 nm and 12 nm step size, respectively) electron backscatter diffraction orientation maps are presented in Figure 1. Spheroidal to cube shaped TiC carbides ($\approx$ 1-5 μ m) are present and serve to pin the grain boundaries. While not explicitly observed, limited literature suggests the presence of MoC precipitates [68]. Aging strengthens the material by precipitation of a rod-shaped, nano-scale (10-50 nm) hexagonal phase (Ni_3Ti ; η -phase) [13, 19, 69-71], but also can cause a small fraction of austenite reversion along all grain and lath boundaries [72, 73]. However, EBSD confirms less than 1% reverted austenite for H900 condition of the current lot of material [22].

2.2 Testing Conditions

Two experimental paradigms are used to investigate the effect of $[Cl^-]$ on the fatigue behavior of Custom 465-H950. First, fracture mechanics testing single edge notched (SEN) specimens establish the long crack growth behavior. Second, constant amplitude loading (with marker sequences included) of pristine and pre-corroded smooth bar specimens are used to characterize the crack formation life, microstructurally small crack growth regime, and total fatigue life behavior (S-N data).

2.2.1 Environmental Conditions

Both S-N and long crack growth rate data were generated in various environments; specifically in high humidity (RH>90%) nitrogen, in distilled water, and in unbuffered 3.0, 1.5, 0.6, 0.06, 0.006, 0.0006 M NaCl solutions at 23°C. The environments/solutions are maintained in a Plexiglas chamber (360-500 mL volume) that is anchored to the specimen via an O-ring compression mechanism. Electrolyte solutions were prepared using high purity deionized (DI) water (Resistivity = 18.2 MΩ-cm) and reagent-grade crystalline NaCl. For long crack growth rate testing, aerated solution was pumped using a peristaltic pump from a 1 liter reservoir at a rate of 20mL/min into a Plexiglas cell with a volume of 360mL. Pre-test solution pH averaged 5.8 (standard deviation (SD) of 0.3), and post-test solution pH averaged 5.7 (SD of 0.3). For S-N testing no peristaltic pump or solution reservoir was employed so as not to disturb any local chemistry changes associated with pitting. Pre-test solution pH averaged 5.6 (SD of 0.2) and post-test solution pH averaged 5.4 (SD of 0.2). Electrochemical parameters are monitored/controlled through a potentiostat operating in floating ground mode; the specimen is grounded through the testing frame via the grips. A standard calomel reference electrode (SCE) is inserted into the environmental cell and the specimen is surrounded by a platinum mesh ring that serves as a counter electrode.

Crack tip hydrogen production is proposed to be controlled by pH and local potential, as such to maintain consistency between different solutions and to eliminate the effect of time dependent OCP changes, all testing is conducted at a fixed potential ($-200mV_{SCE}$) near the OCP for 0.6M NaCl solution (measured as $-220 mV_{SCE}$). Such consistency is necessary to decouple the effect of chloride concentration from the influence of potential. However, the OCP is found to vary with $[Cl^-]$; specifically, Schaller et al. reported OCP measurements of -150, -220, and -300mV_{SCE} after 1 hour for 0.05, 0.9, and 5.3 M NaCl solutions, respectively [74]. As such the constant $-200mV_{SCE}$ value results in an anodic polarization (relative to OCP) at high $[Cl^-]$ and cathodic polarizations at low $[Cl^-]$. While cathodic polarizations can influence the crack tip chemistry, current values are likely insufficient to prohibit acidification of the crack tip in a 12% Cr alloy [59, 75]. However, even for an acidified crack tip, a substantial cathodic polarization could potentially create a sufficient concentration of OH⁻ at the bulk surface, leading to a strong gradient of pH from low at the tip to high at the mouth. This behavior would likely result in the precipitation of corrosion products near the crack mouth due to changes in solubility with pH; such corrosion products were not observed suggesting little effect of chloride-dependent OCP values.

2.2.2 Mechanical Testing Conditions

2.2.2.1 Long Crack Growth Rate Testing

SEN specimens (600 grit surface finish) with threaded ends were machined with the rectangular reduced gauge section of width 10.16 ± 0.13 mm, and thickness of 2.67 ± 0.05 mm, and a length of 35.00 ± 0.50 mm. A slow-grind final machining process was used to impart an initial notch 0.51 ± 0.03 mm deep and 0.51 ± 0.03 mm in height at the center of the reduced gauge to avoid residual stresses and surface layer melting which could influence localized corrosion behavior [37, 76-78]. Useful information on the interaction of pitting and crack formation at the notch was compromised by variable machining quality and a near-square notch geometry that resulted in crack formation at the corners. Regardless, such complications did not influence subsequent growth rate data that is only reported for crack lengths above ≈ 1 mm where an influence of the initiating notch is not expected.

Cyclic loading (sinusoidal waveform) was applied at a maximum stress of 300 MPa, a stress ratio ($R = \sigma_{\min}/\sigma_{\max}$) of 0.5, and a frequency (f) of 2Hz. After crack formation, the ΔK increased with crack extension (at constant $\Delta\sigma$) up to $27.5 \text{ MPa}\sqrt{\text{m}}$ (thus a $K_{\max}$ of $55 \text{ MPa}\sqrt{\text{m}}$). Crack length was continuously monitored via direct current potential difference (dcPD) [79, 80] using a 4 A current. Alumel wires (0.13 mm) were symmetrically welded 0.5 and 17.5 mm from the notch center to collect active and reference potential readings, respectively. Johnson's equation for single edge cracks converts the potential signal to a real-time measurement of crack length (a). Post-test visual linear corrections were made to account for the fatigue pre-crack and final crack depth (variation between dcPD and measured values did not exceed 5%), and da/dN is calculated via the secant method [81].

2.2.2.2 S-N Testing of Dog-bone Specimens

Testing pristine and corroded (either concurrent or pre-corroded) dog-bone specimens in various chloride concentrations is performed to provide high fidelity crack initiation life estimates, characterize initiation features, and collect small crack growth rate data. Flat dog-bone specimens were machined from the cylindrical bar stock with fillets tangentially blended to the uniform gauge. The height, width, and thickness of the reduced gauge section are 22.0, 7.6, and 3.2 mm, respectively; all corners are blended to a radius of 0.4 mm. The specimen surface is polished to a 600 grit finish to achieve a surface area roughness (root mean square height, S_q) below $0.15 \text{ }\mu\text{m}$ measured via white light interferometry (WLI). Constant amplitude uniaxial fatigue testing was performed per ASTM E466-07 [82], specimens were centered in hydraulically actuated grips textured with 90° diamond serrated wedges. Cyclic loading (following a sinusoidal waveform) was applied at a maximum baseline stress ($\sigma_{\max}=1153 \text{ MPa}$, which is $\approx 70\% \sigma_{YS}$), $R=0.5$, and $f = 2\text{Hz}$.

A programmed loading sequence generated resolvable marker bands on the fracture surface; post-test fractography (via SEM) enables quantification of the crack initiation life and

tracking of the crack front in the microstructurally small crack regime [83]. There are 1000 baseline constant amplitude $R=0.5$ cycles applied at the beginning of each test. After the initial baseline fatigue segment, a loading sequence is applied to mark the crack front location; these marker sequences are then alternated with baseline loading cycles (typically 2000-3000 cycles). The exact details of the marker sequence evolved during the program to maximize marker band clarity. Generally, the $\sigma_{\max}$ for marker band sequences is 20-40% lower than baseline $\sigma_{\max}$. A single marker sequence consisted of 3 to 11 segments of 5-20 cycles at $R=0.1$ then 10-40 cycles at $R=0.5$. Ensuring that the maximum stress value was well below that of the baseline loading precluded plasticity-induced overload retardation. The marker band sequence loads comprised only 10-15% of the overall fatigue life; experimental results only report baseline cycles. Prior work suggests that such loading protocols do not cause da/dN transients or significantly influence the total fatigue life [84-89]. The number of marker sequences applied, the number of markers apparent on the fracture surface, and cycles between each sequence are known, as such the number of cycles to reach the first marker (typically $\approx 5\mu\text{m}$ from the initiating corrosion feature) can be calculated [42] and is defined as the crack initiation life. Additionally, microstructure scale growth rates can be calculated using the spacing of the fracture surface marks and are reported as a function of the crack depth [83].

Each dog-bone specimen was subject to one of four different pre-fatigue specimen preparations, summarized in Table 2. These conditions are based on a corrosion study reported elsewhere [90]. Condition 1 specimens were tested in a pristine as-polished condition in humid N_2 (>95% humidity) to serve as a control. For Condition 2, pristine specimens were masked with a rubber-butyl stop-off lacquer to expose a constant area of 200 mm^2 within the gauge section, then were installed into the hydraulic frame and environmental cell containing 0.6, 1.5 or 3.0M NaCl and held at $-200\text{ mV}_{\text{SCE}}$ for 24 h before initiating cyclic loading at $-200\text{ mV}_{\text{SCE}}$. Condition 3 is identical to Condition 2, except specimens are held at a more anodic potentials of 100 or $150\text{ mV}_{\text{SCE}}$ for 24 h prior to initiating cyclic loading at $-200\text{ mV}_{\text{SCE}}$. The prior two protocols aimed to induce the pitting then study concurrent pit evolution and crack formation from growing pits.

In Condition 4 specimens, two evenly spaced co-planar controlled pits were galvanostatically imparted to the center of the specimen gauge on both broad faces of the specimens (a total of four co-planar pits). The specimens were fully masked (using a rubber-butyl lacquer and electroplating tape) and a $50\text{ }\mu\text{m}$ hole was drilled through the masking tape. The specimen were then submerged in a room-temperature solution of 1.0M NaCl acidified with HCl to lower the pH to 3. A potentiostat supplied a constant current of 18 mA for 20 min. To ensure solution contact with the surface, a peristaltic pump circulated solution into the hole in the masking to remove the H_2 bubbles produced during the dissolution process. This process is repeated to induce each of the four pits. After this precorrosion process, specimens were ultrasonically bathed in a commercial oxide remover (containing citric acid, ethoxylated nonylphenol, and aqueous ammonia), DI water, acetone, and methanol for 20 min each to

remove surface oxides. Each pit was then characterized via SEM (Figure 2a) and WLI (Figure 2b). Note the highly smooth nature of the pit in the line-scan (Figure 2c) that shows cross-sectional profile. Once the pre-corrosion protocol was complete, specimens were loaded into a Plexigalss cell containing in humid N₂ or full immersion solutions of 0.0006, 0.006, 0.06, 0.6, 1.5, and 3 M NaCl. Following a 1 h OCP measurement, the specimens were polarized to -200 mV_{SCE} and cyclic loading began. All specimens were fatigued to final fracture, at which point the ultrasonic cleaning protocol was repeated and the specimen was then stored in a desiccator. Post-test SEM characterization was conducted on both the fracture and corroded surfaces.

3 Results

3.1 Long Crack Growth Rates

The da/dN vs. ΔK relationship generated at constant σ_{max} of 300 MPa and R of 0.5 for humid N₂ and full immersion in 0.0006, 0.006, 0.06, 0.6, and 1.5 M NaCl solutions polarized to -200 mV_{sce}, are reported in Figure 3. While testing was also completed in deionized (DI) water and 3M NaCl solutions, these data are not reported due to the onset of an time dependent intergranular (IG) fracture process, attributed to an SCC cracking mode exacerbated by cyclic loading [18, 90-94]. The onset of SCC for the DI water conditions is not fully understood and a full investigation is outside of the scope of the current effort, however, such behavior is not unprecedented [77] and an inhibiting effect of low [Cl⁻] concentrations in acid solutions has been reported [95]. The humid N₂ test serves as a baseline to which the [Cl⁻] containing electrolyte results are compared; however, it is recognized that humid gaseous environments are not fully inert and will enable crack growth rate enhancement above vacuum or inert/dry gaseous environments. Growth rates for all tests conducted in [Cl⁻]-containing electrolytes are tightly clustered (independent of [Cl⁻]) and are 2-3-fold faster than humid N₂ results for $\Delta K > 12.5$ MPa $\sqrt{m}$. As ΔK -decreases below 13 MPa $\sqrt{m}$, all full immersion data exhibit a change in slope tending toward lower da/dN , these data merge with the humid N₂ data at ≈ 10 MPa $\sqrt{m}$.

Fractography of the specimens at ΔK of roughly 20 MPa $\sqrt{m}$ reveals transgranular cleavage-like fracture mechanism for each of the environmental conditions reported in Figure 4 and is consistent for the full range of increasing ΔK . The scale and morphology of the features on the fracture surface suggest crack propagation through grains either along the martensite lath interfaces or through the laths. The clarity of these features is diminished as the [Cl⁻] increases; specifically, the features are well-defined in for the humid N₂ fracture surface (Figure 4a), but fracture surface degradation due to corrosion is observed on both the 0.006 (less severe) and 1.5 M (more severe) NaCl test condition in Figure 4b and 4c, respectively.

3.2 S-N Testing

The number of cycles to failure are reported in Figure 5 for each loading environment and pre-exposure condition. At a given [Cl⁻], Condition 4 is the most damaging pre-fatigue condition, though other exposures often demonstrate only slightly better fatigue life

performance. Condition 4 tests demonstrate an inverse relationship between fatigue life and $[Cl^-]$, where fatigue life decreases by as much as an order of magnitude as $[Cl^-]$ increased from 0.0006M to 3.0M. This is consistent with findings on other martensitic precipitation hardened stainless steel [31-34]. Also notable are distinct variations in the fracture surface morphologies between pre-fatigue conditions. The details of the crack formation feature, loading environment dependence, and fracture morphology are detailed in the ensuing sections for Condition 1 through 4.

3.2.1 Condition 1

The failure life of pristine specimens (5 replicates) cyclically loaded in a humid N_2 environment are plotted as white open circles in Figure 5, showing significant variation in the fatigue life despite identical testing conditions. This is reasonable and expected for S-N testing where (single or multiple) crack formation is expected at stochastically distributed microstructural “hot-spots” that intersect the free surface within the gauge. Furthermore, every test experienced nearly identical initiation characteristics; representative fractographs are included in Figure 6. SEM of the fracture surface shows that initiation occurs at some microstructure feature (more details in the Discussion) and exhibits a transgranular cleavage-like morphology for the first $\approx 50 \mu m$ (Figure 6e). Beyond this an intergranular morphology dominates (with interspersed transgranular behavior) out to a depth of 300-600 μm (Figure 6d), at which point transgranular morphology (similar that observed for long crack growth in Figure 4) is prevalent (Figure 6c). The environmental effects leading to IG based small crack growth in humid N_2 are poorly understood. While Custom 465 has been reported to show susceptibility to environment induced IG cracking [22], it is unclear why this IG fracture mode is more prevalent in for small crack in humid N_2 where lower levels of H-embrittlement would be expected compared to aqueous $[Cl^-]$ solutions. While this finding is interesting, mechanistic investigation and interpretation is outside the scope of this project.

3.2.2 Condition 2/3

Despite differences in the electrochemical severity of Condition 2 (near OCP polarization of $-200 mV_{SCE}$) and 3 (strongly anodic polarization of 100-150 mV_{SCE}), post-test analysis of the exposed surfaces show similar corrosion damage morphology and severity. WLI of the baseline polished pristine sample is shown in Figure 7a (orthogonal view) and 7b (tilted to show illustrate the profile). For both Condition 2 and 3 there is a high density of pits (example WLI image in Figure 7c) that have a surface diameter of $<3 \mu m$ and depth $<1 \mu m$; an SEM image of a representative pit is shown in Figure 7d. Typically these small pits are preferentially located at the base of the polishing grooves. Pit density is approximately 30,000 pits/ cm^2 , calculated by counting pits in several discrete $1 \times 10^{-4} mm^2$ surface images. For Condition 3, a very low density (3 per $1 mm^2$) of larger pits (WLI in Figure 7e-f) were observed that were on order 30 μm in surface diameter and 3 μm in depth. Despite the low density such features, they could reasonably influence fatigue due to the extreme value statistics nature of the damage formation process [86]. The micro-features within the corrosion damage have been shown to be critical to the crack

formation process [42], critically line scans of the pits (of both sizes) showed a smooth micro-morphology, consistent with prior observations of pitting in other low Cr stainless steels [43].

The fatigue life results (Figure 5) show that at both 0.6 and 3 M pre-exposure and testing conditions that Condition 3 specimens demonstrate longer lives than Condition 2, despite the more severe pre-test electrochemical exposure. Furthermore, Condition 3 samples tested in 3M environments show longer lives than the 0.6M. These seemingly counterintuitive results are understood by examination of the crack formation feature and location. Crack formation largely occurs at microstructure features and never occurs at corrosion damage for Condition 2 or 3, such behavior makes the pre-test electrochemical protocol largely irrelevant besides a potential contribution of H-charging. Additionally, the two long life Condition 3 specimens tested at 3M initiated from microstructure features that were within the gauge section but were beneath the lacquer thus not exposed to the electrolyte. These findings are clarified in Figure 8 where the Condition 2/3 results are represented with an X and a description of the initiation feature is included.

The dominant crack initiation features (75%) present in Condition 2/3 specimens were Ti-rich intermetallic inclusions (likely TiC) sized from 6-20 μm . Figure 9a-c shows the morphology and composition of these particles gathered via backscatter electron imaging and electron dispersive spectroscopy (EDS) (inset in Figure 9a and 9c). Traditional blocky TiC morphology (Figure 9a) as well as a blunt-rounded morphology (Figure 9b) are observed. The particle is present at the initiation site on both sides of the fracture surface likely indicative of brittle rupture of the inclusion. Similar sized TiC inclusions are not uncommon, as demonstrated by the many particles that intersect the transgranular fracture path as the crack grows. Other initiation sites include Si-based particle (Figure 9c), an MnS-based particle, and an intergranular feature (Figure 9d). The pure intergranular fracture morphology was observed for a single Condition 2 test at 0.6 M, the IG initiation site extends 200 μm into the material then transitions to a transgranular morphology. This may be associated with intergranular attack during the corrosion process that then served as a severe site for crack formation during fatigue loading, the IG attack at this moderate environmental exposure is not expected but could reflect a grain cluster with an unusually high level of trace element segregation.

In toto, these results clearly demonstrate that the corrosion damage produced during Condition 2/3 is secondary to microstructural features that dominate the crack nucleation process. Specifically, initiation feature analysis for Condition 2/3 show that neither (1) the size and smooth geometry of the pits, nor (2) the local material embrittlement proximate to the pit perimeter due to possible H charging during the dissolution process, were sufficiently severe to overcome the dominant role of inclusion particles on the crack formation process.

3.2.3 Condition 4

The high pitting resistance of Custom 465 in $[\text{Cl}^-]$ environments leads to small/smooth pitting for Conditions 2/3 (Figure 7) that do not produce initiation conditions as severe as native microstructural features. As such, artificially induced larger pits are produced by pre-exposure Condition 4 (4 pits on each specimen) to investigate the pit-to-crack transition in various chloride-containing electrolytes (0.0006-3.0M) and humid N_2 . This pre-pitting procedure decouples any effects of the aggressive local environment within a growing pit from the effects of initiation feature geometry. WLI analysis prior to cycling show consistency in the size and surface morphology of the pits; specifically, the pits have a mean pit depth of 41 μm (standard deviation of 10 μm) and surface diameter of 177 μm (standard deviation of 22 μm). The size and smooth micro-morphology of the pits are consistent with literature expectations [96-100]; such similarities suggest that the high current densities used during galvanostatic pitting are not unrealistically skewing this critical morphology. EDS analysis of the corrosion products show predominantly chromium-oxides with some nickel- and iron-based oxides [90].

The total fatigue life results in Figure 5, demonstrate that there is a trend of increasing life with decreasing $[\text{Cl}^-]$. Additionally, for 0.6, 1.5 and 3M $[\text{Cl}^-]$ test environments the Condition 4 specimens have a lower fatigue life than the Condition 2/3 specimens. The relative influence of the initiation feature severity/depth and the multi-site nature of the artificially induced pits will be investigated in the Discussion. Also of note is the overlapping fatigue life behavior for Condition 1 and Condition 4 specimens tested in humid N_2 . In all but one specimen, corrosion pits are the only features that lead to crack formation (the lone exception was a humid N_2 test which produced initiation and fracture characteristics identical to those observed in Condition 1 specimens). For $[\text{Cl}^-]$ below 1.5 M the fracture morphology is purely transgranular (Figure 10a) whereas some 3 M tests transitioned from transgranular to intergranular for crack depths between $\approx 250 \mu\text{m}$ and $600 \mu\text{m}$, followed by a transition back to transgranular (Figures 10b).

These results demonstrate that the corrosion morphology produced by Condition 4 is sufficiently severe to drive crack formation to these pits rather than the microstructural features. However, of the 56 total pits only 45% initiated a crack suggesting that even though these relatively large smooth pits shift crack formation away from microstructural features, in some instance they are benign enough to require a significant number of cycles prior to crack formation. Subtle differences in the pit depth do not govern the lack of crack formation at 55% of the pits as evidenced by (1) the largest of the four pits on a single specimen was the first to initiate a crack in only 29% of specimens, and (2) there is no statistical correlation between the corrosion depth (or fracture surface area) and the cycles to failure. However, the data do suggest increasing the $[\text{Cl}^-]$ increases the probability of crack initiation. For example, at 0.006M $[\text{Cl}^-]$ and above, the proportion of pits transitioning into cracks (22 of 40 or 55%) is significantly greater than that in 0.0006M and humid N_2 (3 of 16 or 19%).

4. Discussion

4.1 Pitting Behavior

Three aspects of the pitting process will play a critical role in the pit-to-crack transition process: (1) the geometry of the damage serving as a local stress/strain concentrator [42], (2) the aggressive local chemistry (high $[\text{Cl}^-]$ and low pH [101]) that will develop at the base of the pit [97], and (3) embrittlement due to the local absorption of H produced during the pitting process [102, 103]. In the context of this work, Condition 2/3 testing will potentially be influenced by each of these while Condition 4 will be subject to only (1) and (3). While the precise testing protocol for the current study is different, similar prior studies [32-34, 39, 53, 104] demonstrate a strong role of pit evolution during loading for materials and corrosion conditions similar to Condition 2/3 (where pitting was not found to be governing crack formation). As such it is useful to discuss the origins of the pitting process in Custom 465 to interpret the lack of corrosion induced failure in Condition 2/3. Pitting corrosion behavior has been extensively studied in stainless steels [45, 78, 101, 105-109], as well as work specifically focused on low chromium martensitic stainless steels exposed to chloride environments [33, 110]. In general, pitting proceeds by the stochastic environment-induced rupture of the stable passive film [111, 112] that initiates an autocatalytic process (metal dissolution, hydrolysis, and anion ingress to the pit for charge neutrality) that creates the local aggressive chemistry necessary for continued dissolution [105-107]. This process often occurs proximate to second phase particles, such as magnesium sulfide (MnS) inclusions [76, 113-117], other sulphides [113], metallic carbides (typically large non-strengthening carbides) [53, 71, 108], and/or in chromium-depleted zones that are often adjacent to the second phase particles [101]. While the process and causal microstructural features are common to many stainless steels, the tempering process for precipitation hardened UHSS can exacerbate the formation of such corrosion inducing features [53, 71]. A rigorous investigation of the microstructural origins of the pitting behavior observed in Condition 2/3 is outside the scope of this study. However, the size and distribution of the pitting damage in the current study reasonably correlates to that of impurity inclusions (As, P, or S-based), and NiAl-based precipitates that were observed during a detailed microstructural analysis of this alloy [22].

To understand the effect of $[\text{Cl}^-]$ on the fatigue behavior, it is necessary to identify how varying $[\text{Cl}^-]$ and applied load will influence these pitting processes. The deleterious effect of increasing $[\text{Cl}^-]$ on the passive film stability, thus the susceptibility of electrochemical degradation of stainless steels, is well known [44, 45, 118-120]. This is of critical importance to thin film atmospheric exposure conditions [24, 121]. Some researchers suggest that pit growth kinetics are not strongly dependent on the bulk $[\text{Cl}^-]$ [45, 105, 122], possibly due to the development of the local, aggressive, high $[\text{Cl}^-]$ environment at the base of the pit. However, $[\text{Cl}^-]$ can drastically influence the corrosion mechanism/morphology [119, 120] and the pit formation behavior, as quantified by changes in the critical potential [32, 47, 123] and the frequency of metastable pitting [44]. Furthermore, experimental findings [47, 124-126] and modeling [127] suggest that an applied stress/strain will potentially enhance the pitting process [40, 41, 128, 129], though this opinion is not unanimous [130]. The current Condition 2/3 results show no

change in pitting behavior between (1) different levels of $[Cl^-]$, and (2) loaded samples and identical exposures on unloaded samples [90]. This deviation from expectations is not fully understood but potentially due to either insufficient time for damage evolution, subtleties of the repassivation kinetics, a low size/density of inclusion particles, and/or environmental severity that is below the threshold necessary to induce/sustain significant damage.

Consistent with the current results, prior researchers have demonstrated high levels of pitting resistance for Custom 465 in 3.5% NaCl salt spray [19, 20] as well as in atmospheric NaCl exposures [74, 131]. Furthermore, a companion corrosion study on this lot of material showed high levels of resistance for a wide range of NaCl electrolytes and polarizations [90]; notably, no pitting was observed for a 1.5 M NaCl exposure at OCP after 5500 h. The high pitting resistance is interesting due to the relatively low chromium (and general low alloy) content of Custom 465 for a stainless steel. The pitting resistance equivalent number ($PREN = wt\% Cr + 3.3 wt\% Mo + 16 wt\% N$) correlates pitting corrosion resistance of stainless steels in $[Cl^-]$ environments to their chemical compositions [132, 133]. Anecdotal industry practices recommend PREN values >32 for seawater applications [134] or >24 for aggressive atmospheric exposures [118]. Despite the low PREN number for Custom 465 (max of 16.3 for nominal composition; 14.1 using values in Table 1), the pitting resistance is on par (or better) with other alloys in this materials class with higher PREN values (max nominal PREN for 17-4PH, 15-5PH, PH 13-8Mo, Alloy 355, Custom 450 are 17.5, 15.5, 20.9, 27.8, and 19, respectively [135]). Several microstructural features may contribute to this behavior. First, the PREN metric does not account for other alloying elements (such as Ni [136] and Ti [118]) that some researchers suggest could beneficially influence pitting resistance. Second, the vacuum induction melted-vacuum arc remelted (VIM-VAR) processing technique results in very low concentrations of deleterious inclusion forming impurities such as manganese, sulfur, and phosphorus. Finally, as shown in Table 1 there is a lack of gettering elements (e.g. La, Ce) which are designed to reduced grain boundary segregation of S by forming stable sulphides. While the baseline S contents are low and the La/Ce contents of other materials are not rigorously investigated in this study, the lack of gettering elements (thus pit forming La/Ce-based sulphides) in Custom 465 is a potential means of improved pitting resistance.

4.2 Effect of Crack Formation Feature

4.2.1 Condition 2/3

While crack formation did not occur from corrosion-induced damage for Condition 2/3, the effect of $[Cl^-]$ concentration and initiating feature on the crack formation behavior can still be investigated. The current data enables a unique correlation between particle size (both depth (Figure 11a) and cross-sectional area (Figure 11b) were analyzed) and the formation and total fatigue life. To enable consistent and direct comparisons this analysis focuses on only the Ti-based carbide particles that were the primary formation feature. Figure 11 demonstrates that increasing pit depth (measured from the fracture surface) or cross-sectional area of the carbides

does not show a statistical correlation with decreasing total fatigue life; similar trends were observed for comparisons with initiation life. The $[Cl^-]$ associated with each data point were analyzed and do not show any relevant trend. However, the morphology of the carbides is critical, the low life specimens contained blocky particles (Figure 9a) that generally have a corner protruding directly into the sample, whereas long lives tend to be associated with more blunt/rounded particle (Figure 9b) morphologies. Such behavior is consistent with the expected higher local stress/strain concentrations associated with a sharper particle morphology and supports prior findings that suggest a strong role of micro-scale shape on the evolution of local plastic damage accumulation [42]. While this qualitative correlation is reasonable and consistent with literature, evaluation of the 3D nature of the initiation features coupled with modeling of the local stress/strain state associated with such features (akin to that done in Ref. [42, 137, 138]) is necessary to rigorously establish the role of particle morphology/orientation on the crack formation behavior.

4.2.2 Condition 4

4.2.2.1 Crack Formation Location Within the Macro-Pit

Exact initiation locations and associated geometric features were collected via SEM imaging of both the corroded and fracture surfaces post-fatigue. Comparing the fracture (Figure 12a) and corroded surfaces (Figure 12b) allowed for the identification of the exact initiation location within the pit (Figure 12c). These data can then be coupled with the 3D WLI representations of the corrosion (Figure 12d). Due to the symmetry of the pits the initiation locations can be plotted on an idealized quadrant of a corrosion pit (Figure 13). Each pit is slightly different so this representation is not fully rigorous but does serve as a useful comparative tool. The effect of bulk environmental $[Cl^-]$ on the crack formation location within the pit is included, but a clear trend is not observed. Critically the crack formation location does not typically correspond with a prominent micro-feature within the macro-pit. This finding is distinct from prior work on Al alloys where corrosion damage morphology was highly tortuous and crack formation was dominated by the local features on the pit surface rather than the global stress concentration field [42]. This variation between precipitation hardened Al and stainless steels is expected due to relatively smooth pitting morphology typically associated with stainless steels; for similarly smooth pits in a 12% Cr steel Turnbull et al. observed that the pit to (stress corrosion) crack transition was more prominently influenced by the macro-pit stress concentration field [99]. Results in Figure 13 support this view, specifically crack initiation tends to occur close to the latitudinal center of the pit perpendicular to the loading axis; specifically, 89% initiate within 40 μ m of the center (box in Figure 13). This is expected as the highest macro-pit induced stresses have been found to occur at this centerline for a variety of geometries [99, 139]. Regarding the longitudinal location of crack formation, 72% of cracks initiated on the walls of the pit closer to the mouth than the base, consistent with modeling by Turnbull et al. of

hemispherical pit geometries that show an increase in stress concentration moving from the base of the pit to the mouth [99].

The clustering of crack formation near the mouth of the pits also suggests that the influence of variations in H-uptake about the pit surface is secondary. Specifically during the pre-pitting process the pit chemistry and dissolution rates (thus H production rates) are the most severe at the pit base. Since no preferential crack formation occurred at the base of the pit, it suggests that such potential variations in the H concentration profile proximate the corrosion damage are of secondary importance for the loading environments used in the current study. Two considerations preclude a more general conclusion on the effect of H charged due to the dissolution process. First, the H-produced at the crack tip or formation site during loading may overwhelm the effects of the pre-charged H for the aggressive conditions probed in this study; a more pronounced influence may be observed for more inert loading environments. Second, local hydrostatic stresses are known to concentrate interstitial H, as such it is possible that the loading frequency is sufficiently slow to allow the redistribution of the original H concentration profiles (from the precorrosion process) to align with the local stress fields [140]. Regardless, the current results support a primary role of macro-pit based stress concentration in determining the crack formation location within the pit, this is consistent with prior literature findings and the smooth pit morphology.

In three instances crack formation occurred unusually far from the regions of highest macro-pit induced stress (circled in Figure 13); in each case an inclusion particle was observed at the crack formation site. These inclusions increase the local stress/strain condition above that associated with the macro-pit. Of note, is that the overall fatigue behavior for these instances align with general trends observed for other Condition 4 data. This suggests that the increased local severity associated with these particles intersecting the surface of the pit may be balanced by the lower macro-scale stress location, yielding similar fatigue lives. Whether this interaction manifests itself in the crack formation regime or in the small crack growth regime is unknown and outside the scope of this work. Regardless, preferential crack formation from severe micro-features is consistent with previous work on aluminum alloys that shows the crack nucleation is strongly dependent on such micro-features on the surface of a macro-pit.

4.2.2.2 Macro-Pit Dimensions

Several fracture mechanics-based approaches to predicting crack formation assume that the geometry of the initiating feature can be used as the crack size input for stress intensity calculation [86, 139, 141, 142] (the inherent inaccuracies of such an approach have been detailed elsewhere [85]). Furthermore, the preceding discussion established the critical role of the macro-pit induced stress field on the crack formation behavior. These considerations motivate analysis of the subtle changes in macro-pit geometry for Condition 4; specifically, (1) the deepest point of the initiative feature relative to the uncorroded surface, and (2) the 2D area of the initiating

feature observed on the fracture surface. For Condition 4 specimens (in each environment), plotting the maximum pit depth versus the fatigue life (Figure 14) reveals no statistical correlation; similar results were observed when the cross-sectional area was examined. It is well known that the stress concentration associated with a macro-pit will be dependent on the shape of the pit rather than the size [143], however, larger flaws produce a larger region of increased stress which would increase the probability that a severe microstructural (or other) feature falls within this region. The lack of correlation between fatigue life and pit dimensions is attributed to the fact that the pits do not greatly differ in size, geometry, or area. While the Figure 14 show a distribution of pit depths, the fine depth/area scales on the y-axes serve to highlight only minor differences in pit dimensions that exert minimal influence on fatigue life.

It is also useful to compare fatigue life data between pits (Condition 4) and inclusions (Condition 2/3) as shown in Figure 8. Despite the pits being approximately an order of magnitude larger in depth (over two orders larger in area) than the inclusion features, the detrimental effects of the initiation feature is much less pronounced. In 0.6M NaCl environments, data show that Condition 4 fatigue life is 2-3-fold less than that demonstrated by specimens initiating on a blunt inclusion. In the same environment, fatigue lives associated with sharp inclusions can be similar to those of Condition 4 pits. The similarities in final fatigue life are particularly striking considering that (1) cracks initiated from an inclusion particles on the scale of 5-10 μm will need to have a significant amount of small crack propagation to reach the size of the pit nucleated crack (40-60 μm) and (2) the concentrated stress gradient associated with the inclusion will be over a smaller scale than that for the larger pit. This suggests that the smooth nature of the pit strongly limits its severity as a crack formation feature.

4.3 Relative Influence of $[\text{Cl}^-]$ on the Different Fatigue Stages

Four important stages of the corrosion initiated fatigue process were defined as (1) the formation of the corrosion damage, (2) the corrosion-to-crack transition process, (3) chemically small crack growth, and (4) long crack growth behavior. In the context of the current study of Custom 465, the lack of corrosion nucleated fatigue for the Condition 2/3 specimens suggests that corrosion damage occurring concurrent with loading is not controlling for the NaCl electrolytes, electrochemical conditions, and time-scales examined in this study. As such, the relative influence of stages (1)-(3) on the $[\text{Cl}^-]$ dependent behavior observed in Figure 5 (and literature) in will be evaluated for the Condition 4 specimens that were pre-corroded then tested in various NaCl environments. The systematic long crack growth rate testing and detailed marker-band based quantification of the crack initiation and small crack behavior enables the decoupling of these effects to understand the relative influence of each stage on the observed overall fatigue life trends.

4.3.1 Crack Propagation

4.3.1.1 Crack Chemistry Considerations

For a wide-range of stainless steels, it is well known that saltwater, marine and hydrogen-containing environments lead to crack growth rates that are faster and cracking below threshold ΔK values established for less aggressive environments (i.e. vacuum, inert gas, or humid air) [29, 34, 51-53]. In precipitation hardened martensitic stainless steels, this deleterious influence is enhanced for high strength tempers, elevated temperatures, and cathodic polarizations [34, 36, 53, 144, 145]. Current results in Figure 3, are consistent with the literature in that the NaCl electrolytes of various concentrations show accelerated crack growth kinetics relative to testing in humid N_2 . The hydrogen environment embrittlement (HEE) mechanism proposes that the enhanced fatigue crack advance in these aqueous $[Cl^-]$ environments is governed by the interaction of localized cyclic plasticity, tensile stress, and absorbed atomic H in the fracture process zone [29], though the fundamental details of this interaction are controversial [146-148]. In aqueous environments, electrochemical conditions (chemistry, pH, and electrochemical potential) govern the overpotential (η_H) for hydrogen (H) production which determines the current density for H-ion reduction (i_H) that is proportional to the concentration of hydrogen adsorbed on the metal lattice surface ($C_H \sim \sqrt{i_H}$). (Note that the overpotential is also dependent on the activity of dissolved H_2 at the crack tip, this variable is often assumed to be unity consistent with (1) the often observed bubble generation from the crack, and (2) the log-based dependence on the activity is governed by the Nernst equation, as such the moderate range over which the activity is expected to change will result in a very small impact on the calculated reversible H potential). The ingress, diffusion, and interaction of this surface adsorbed H in the fatigue process zone results in the local material embrittlement and enhancement of crack growth rates. Of particular interest are the electrochemical conditions at the crack tip where active straining can rupture the local passive film and where there are short H diffusion distances to the highly stressed fatigue process zone [57]. For a wide range of high strength steel compositions in aqueous environments, researchers have demonstrated that the occluded crack tip environment deviates substantially from the bulk and is conducive to H-production [61].

Specifically, monotonic loading in low alloy steels are historically reported to have a crack tip pH of 3.5-4 due to dissolution of ferrous ions. For stainless steels, hydrolysis of Cr^{3+} will dominate and further reduce the pH to near 1 [58-61]. A potential drop from the bulk surface to the crack tip has also been reported due to increased resistivity through the narrow crack wake channel [60]. Due to the need to maintain electroneutrality, this acidification process requires and results in a high anion concentration (e.g. $[Cl^-]$; on order of 4-6 M is reasonably expected) at the crack tip [64]. Even extremely low bulk anion concentrations can support the crack tip acidification process, as demonstrated for bulk chloride concentrations below 10^{-6} M and distilled water due to trace impurities or dissolved alloy constituents [64, 65]. This enhanced chloride concentration exacerbates the H-embrittlement process by destabilizing the crack tip passive film [118] and enhancing the H-activity [149]. The film stability is relevant to the cracking process where active crack tip strain can rupture the protective passive film [150, 151]. The kinetics and

stability of the film regrowth [95, 152] at the crack tip will influence dissolution (thus metal ions available for hydrolysis) and can act as a hydrogen permeation barrier to limit ingress [153, 154].

Critically, the evolution of the crack tip chemistry will be strongly influenced by cyclic loading (acutely for frequencies >1 Hz [155]) based upon the enhanced importance of convective transport to the crack tip (due to the pumping effect of the crack walls) to the augment the diffusion based transport in monotonic loading [156, 157]. Critically, for long crack growth the crack tip environment is typically considered to achieve a steady state aggressive condition. However, a comprehensive review of chemically small cracking phenomenon demonstrates that the development of the occluded crack conditions depends on the specimen width, loading frequency, the R-ratio, and the crack size/geometry; each of these factors influences the mass transport through the crack, potential drop from the crack mouth to tip, and the bulk flow down the crack [50, 55, 66, 67, 155]. Such influences motivate the investigation of both small- and long-crack kinetics in the context of the current investigation of the effect of $[Cl^-]$ on the fatigue behavior.

4.3.2 Long Crack Growth

The long crack growth rate data from LEFM testing of SEN specimens in Figure 3 demonstrate two important findings. First, they do not show a trend of increasing growth rate with increasing $[Cl^-]$ rather data from all NaCl (0.0006-1.5M) environments fall in a cluster that is typical of what would be expected from replicate testing at a single loading-environmental condition. Second, the da/dN cluster for NaCl environments shows enhanced crack growth kinetics when compared to testing in the humid N_2 environment. Both findings are consistent with the crack chemistry arguments put forth in Section 4.3.1. Specifically, an aggressive crack chemistry likely develops and enhances the HEE process which produces growth rates exceeding those observed in a moist N_2 environment. Furthermore, the similarity in crack growth kinetics for different bulk $[Cl^-]$ conditions suggests a similar crack tip environment which would be expected for an acidified crack tip since the need for electroneutrality is expected to strongly concentrate the $[Cl^-]$ in the crack tip independent of the bulk $[Cl^-]$ [64, 65].

A LEFM-based computational model is employed to investigate how the faster long crack growth rates observed for the NaCl testing (as compared to the humid N_2 results) influence overall fatigue life. Specifically, for the S-N dog-bone specimen geometry in the current study, the life prediction software (AFGROW [158]) is used to predict the fatigue life to failure using the humid N_2 and 1.5 M NaCl growth rates (Figure 3). The modeling was performed specifying an initial 100 μm semi-elliptical surface crack, $R=0.5$, and $\sigma_{max} = 50\% \sigma_{ys}$; where final failure criteria is due to either net section yielding or a K_{max} in excess of the fracture toughness. These simulations result in a ≈ 1.5 -fold decrease in the predicted fatigue life using the faster 1.5 M NaCl environment crack growth rates. This result suggest that chloride-containing environments will cause faster growth rates but the difference in rates and their net implication on fatigue life in C465-H950 is small compared to the order of magnitude reduction in fatigue life reported for

testing in $[Cl^-]$ in Figure 5 and in the literature for similar steels [31-38]. These results demonstrate that the $[Cl^-]$ dependence observed in Figure 5 for the pre-corroded Condition 4 specimens is likely not due to bulk $[Cl^-]$ effects on the long crack kinetics.

4.3.3 Small Crack Growth

It is well established that there is a break-down in fracture mechanics similitude for small cracks; classic reviews categorize such effects in terms of mechanically- (excess plasticity), microstructurally- (non-continuum), physically- (lack of closure due to crack shape), and chemically-small [48, 159, 160]. While the important issues of the breakdown of linear elastic assumptions in calculating the crack tip driving force and differences in short-long crack closure considerations are recognized, the current discussion focuses on the microstructurally- and chemically-small effects. In contrast to the steady state aggressive chemistry expected for long crack growth experiments (Figure 3), for small crack depths there is the potential for sufficient interaction with the bulk solution such that a steady state occluded crack chemistry is not achieved and thus the bulk solution $[Cl^-]$ may be important [55, 66, 67].

For stress corrosion cracking (monotonic loading) in a variety of high strength steels [61] Brown et al. suggests that beyond roughly 1 mm the small crack geometry effects will cease. As such with increasing crack size, a consistent-aggressive chemistry develops and fracture mechanism similitude is observed [55]. However, such a simplistic approach does not rigorously account the variation in chemistry that has been reported for cyclic loading and other small crack size/geometry effects. While there is no broadly applicable analytical solution for the effect of crack depth on development of the aggressive crack chemistry, several reviews have identified critical variables controlling the observed enhancement of the acidity for chemically small cracks that is postulated to control the enhanced crack kinetics [41, 55]. Furthermore, Gangloff et al. proposed an oxygen-inhibition based mechanism for 4130 steel cycled in NaCl environments where localized transport (related to the crack mouth opening) and reaction processes (related to the crack surface area to occluded solution volume ratio) produce a crack size dependent oxygen concentration at the tip. Specifically, hydrolytic acidification is enhanced for small cracks due to lower levels of oxygen for small crack situations where there are lower levels of convective pumping (thus reduced oxygen supply) and higher surface area to volumes (thus increased oxygen consumption). This concept was supported by modeling of the crack chemistry and indirectly by growth rate and fracture surface correlations [55].

Direct extension of these mechanistic studies to predict/understand the $[Cl^-]$ dependence in C465 is complicated by two factors. First, researchers have found that the addition of Cr (even at 1 wt% levels) will drastically enhance the acidification process, as such this behavior may overwhelm the inhibiting effect of oxygen [66, 157]. Second, recent work [161] has reported an effect of bulk solution $[Cl^-]$ on the chemically short ($\approx 300\mu m$) crack behavior. Specifically, for low $[Cl^-]$ (thus low conductivity), there is a high potential drop down the crack, despite lowering the η_H (assuming a constant pH). This more noble potential may enable a

dissolution-based cracking mechanisms. Furthermore, Zhou et al. suggests that dissolution of Cr during this process may actually lead to a lower pH which would have the net effect of increasing the H generation (i_H) [161]. While detailed measurement and modeling of the crack chemistry is outside of the scope of this study, the current data can be used to quantify how the bulk $[Cl^-]$ will influence fatigue crack progression from 5-500 μm in the 12%Cr Custom 465 steel. Such data will inform the relative influence of oxygen inhibition, Cr-enhanced acidification, and solution conductivity on the small crack effect for bulk solution $[Cl^-]$ pertinent to atmospheric exposures.

Fracture surface marks from the periodic marker band loading sequences are used to quantitatively establish the dependence of da/dN versus crack depth (from the formation site) on the bulk $[Cl^-]$ for small cracks ($<500 \mu m$). Small crack growth rates (da/dN) are calculated by measuring the distance between discrete marker bands and dividing by the known number of cycles from the marker sequence, following previously validated techniques [162]. Figure 15 provides a visual representation of the marker band identification process for a Condition 4 specimen tested in 0.6 M NaCl at $-200 mV_{scc}$. Where Figure 15a is an overview of the crack front progression from ≈ 200 -500 μm , Figure 15b shows the first $\approx 200 \mu m$ of growth proximate to the pit, and Figure 15c shows the morphology of a single marker band. Figure 16 reports the growth rates (da/dN vs. crack depth from the formation site) for the dominant crack that lead to failure in each of the Condition 4 specimens (note, IG morphologies did not produce reliable marker bands thus are not included in this dataset). Obviously, the da/dN vs. crack depth relationship does not utilize fracture mechanics similitude. As such, there are likely subtle differences in the crack tip driving force which could potentially complicate the comparison of results across different environmental conditions. This concern is ameliorated by (1) the macro-pit sizes are each similar, so the stress gradients through which the small cracks are propagating would be similar, (2) as observed in Figure 13, the crack formation location is randomly clustered in a relatively small area, (3) there is no preferential clustering for certain environmental conditions, and (4) the crack growth measurements were taken along a consistent vector for each of the samples. A recent study of the stress intensity of a large data-base of small crack data (tested at constant $\Delta\sigma$) proximate to corrosion damage in an Al-alloy demonstrated that at 25 μm from the corrosion surface, ΔK varied $\pm 16\%$ about a mean value. This variation fell to $\pm 9\%$ at a depth of 100 μm . Similar (or less) variation would be expected in the current study where the crack formation behavior was much more homogenous (Figure 13); this level of variation is unlikely to compromise the comparison between environments in Figure 16.

Overall, the small crack growth rates for Condition 4 in Figure 16 for various $[Cl^-]$ levels increase with increasing distance from the initiation point, however, there are two noteworthy features pertinent to rigorous interpretation of the data. First, for a single crack path, there is significant oscillation about the general trend. Second, significant variability is observed when comparing trends from replicate environmental conditions. Both findings are reasonably expected since such short cracks only span one to several grains, as such crack growth is highly

dependent on grain-specific properties and interactions with local microstructural (e.g. grain boundary or impurity particle) features. Prior work has demonstrated this microstructure dependence experimentally [83, 163, 164] and through computational models [165-168]. Furthermore, such cracking proximate to the initiation site is highly dependent on the stress field of the initiation feature, and crack geometry [83, 169, 170]. Critically, as the crack length increases, da/dN variability decreases which reflects a more regular shaped crack that intersects many grains simultaneously. Such a continuum crack represents the aggregate material response rather than that of a single or a few grains.

With this understanding of the expected level of microstructure induced variability, the da/dN vs. a data in Figure 16 is interpreted as not showing a strong dependence on bulk $[Cl^-]$ ranging from 0.0006-3 M NaCl. The lower $[Cl^-]$ environments produce marginally slower growth rates than higher $[Cl^-]$ environments, but this change is not significant compared to the previously reported chemically short crack effects. Similarly, the 1.5 and 3M NaCl data tend toward the upper portion of the scatter-band but do not definitively demonstrate a $[Cl^-]$ dependence. Furthermore, these data suggest that for this material and loading conditions that there is no crack length dependent behavior for the low conductivity solution (e.g. 0.0006 M NaCl) as was previously reported [161]. Fracture morphology (and thus mechanism) shows some dependence on environmental conditions and bulk $[Cl^-]$; specifically, at $[Cl^-]$ below 1.5 M the fracture morphology is purely transgranular (Figure 10a) whereas some 3 M tests show a region of intergranular cracking from ≈ 250 to $600 \mu m$ (Figures 10b). The intergranular nature of the fracture surface precluded quantitative marker band analysis of the crack growth rates (thus they are not plotted on Figure 16), however, the IG morphology likely represents a change in mechanism associated with higher levels of H-embrittlement. Such behavior is likely analogous to the previously discussed time-dependent cracking (Section 3.1) observed for long crack growth rate testing at these high $[Cl^-]$, but full mechanistic interpretation of this morphology change is outside the scope of this effort.

In toto, the analysis of the crack propagation behavior has demonstrated that neither the long nor short crack growth behavior exhibits a strong enough dependence on bulk $[Cl^-]$ to account for the observed 4-9 fold increase in fatigue life as $[Cl^-]$ decreased from 3.0 to 0.0006 M at this stress level. This finding motivates the investigation of the crack formation life associated with the Condition 4 tests to understand the $[Cl^-]$ dependent behavior in Figure 5.

4.3.4 Crack Formation Behavior

The crack formation life to the first marker band (N_i) is calculated for each of the Condition 4 experiments enabling analysis of it depends on bulk chloride concentration. A previously established approach is used to quantify the number of cycles to the first marker band, this value is considered the crack formation life [42]. While the first marker band is consistently found $< 5 \mu m$ from the initiation feature, the initiation life for the crack to grow to $25 \mu m$ (N_{i-25}) is also calculated in order to demonstrate complete consistency. The propagation life (Figure 17)

from the first markerband to failure is calculated (based on the known loading sequence) and subtracted from the total life.¹ The propagation life (cycles from the first marker band to failure) increases slightly with decreasing $[Cl^-]$, but there is no more than a two-fold variation between the data at 0.0006M and 3.0M. This lack of significant decrease in crack propagation life with increasing $[Cl^-]$ is fully consistent with the observed long crack trends (Figure 3) and small crack trends (Figure 16). These data further support the contentions from Section 4.3.2 and 4.3.3; specifically, that the effect of $[Cl^-]$ on the propagation life is of secondary importance in contributing to the order of magnitude decrease in total fatigue life going from 0.0006 to 3 M NaCl.

Figure 18 plots N_f , N_i , and N_{i-25} for pits that formed cracks in Condition 4 specimens tested in various aqueous $[Cl^-]$. Only the total life is reported for humid N_2 test data due to complications in marker band analysis caused by intergranular fracture character. At high $[Cl^-]$ of 0.6, 1.5 and 3.0M, 60% of the crack forming pits caused initiation before the first marker band sequence was applied (indicating formation life was within the first 1,000 cycles). The remaining 40% formed in less than 4000 cycles. As $[Cl^-]$ decreases to 0.06M, N_i increases to $\approx 8,000$ -10,000 cycles. As $[Cl^-]$ decreases further to 0.006M and 0.0006M, the shortest crack initiation life is approximately 20,000 cycles and the longest is well over 100,000. *In toto*, as $[Cl^-]$ decreases from 3.0M to 0.0006M, N_i increases by as much as two orders of magnitude. A similar trend is observed for the N_{i-25} demonstrating that any small difference between the depths of the first markerband is irrelevant. These data strongly suggest that for a constant pit geometry the effect of $[Cl^-]$ on the total life is largely due to the bulk solution chemistry effects on the crack formation life.

Three aspects of this behavior must be considered for mechanistic interpretation: (1) the crack initiation life increases with decreasing $[Cl^-]$, (2) a comparison between the 3D WLI images taken prior to fatigue loading and the fractographic images of the corrosion damage demonstrate that there is no substantial additional corrosion damage observed (within the fidelity of the WLI measurement technique), and (3) the lack of further broad scale dissolution in the pit suggests that an aggressive pit chemistry does not develop throughout the pit. Researchers have demonstrated that cyclic straining will enhance local film rupture, this rupture is dependent on the magnitude of the local stress, film thickness, nature of the film, and the loading environment [40, 41]. Such rupture would be exacerbated within the pit where there is a strong stress concentration. After film rupture, the extent of further dissolution will be controlled by interactions between the loading frequencies, the repassivation kinetics, and the rate of dissolution (controlled by activity for a given local strain, chemistry, and exposed microstructure features) [40, 41, 128, 171]. Even in instances where significant levels of material dissolution

¹ As the crack grows beyond $\approx 1000 \mu m$ the fracture surface marks are more difficult to distinguish. To provide further confidence in the long crack marker band measurements, they are compared to a LEFM-based fatigue life prediction software (AFGROW) prediction of the expected crack progression. For long crack growth ($\approx 1000 \mu m$) the rigor of continuum fracture mechanics is well established. In each case the marker band data was well-aligned with the AFGROW predictions using the environment specific crack growth rate law (Figure 3).

does not take place (as is the case for the current results), Magnin et al. propose that highly localized dissolution (possibly enhanced by local slip steps) can occur during the rapid film rupture/repassivation process [172]. Such localized dissolution would enable the highly localized production and uptake of H at the highly stressed regions within the pit where the film rupture is most likely. Such a mechanism is fully consistent with Figure 13 that demonstrates crack formation within the high stress region of the pit. Furthermore, the deleterious effect of increasing $[Cl^-]$ on the stability and the repassivation behavior of the surface film would lead to enhanced localized dissolution and H production/uptake, which is fully consistent with the decreasing N_i with increasing bulk $[Cl^-]$ (Figure 18).

4.4 Macro-scale Modeling Impact

The detailed efforts above demonstrate that for the current mechanical and environmental loading conditions, C465-H950 does not experience sufficient pitting during the testing duration to drive the crack formation behavior away from microstructural features, as demonstrated by Condition 2/3 results. Furthermore, testing of samples with a constant, controlled precorrosion morphology show a significant decrease in total life with increasing $[Cl^-]$. Systematic evaluation of the crack formation, microstructurally/chemically small crack propagation, and long crack propagation regimes demonstrate that the crack formation life is most strongly influenced by the changes in $[Cl^-]$. Analysis in Section 4.4.2 demonstrate that the secondary effects of increasing $[Cl^-]$ on the overall fatigue life can be captured by integrating environment specific material growth relationships (da/dN vs. ΔK) into LEFM-based life prediction models. However, modeling efforts that aim to capture the primary effect of $[Cl^-]$ on the fatigue life must be focused on prediction of the crack formation life.

Kondo et al. proposed the prevalent model (though lacking mechanistic rigor [41]) of environmentally assisted fatigue crack initiation which involves actively evolving corrosion damage [39, 41, 173]. This model calculates a stress intensity based on the 2D projection of the corrosion damage and predicts that the pit-to-crack transition occurs when the ΔK of the pit exceeds the long crack threshold [122]. Such models are not applicable to the current pre-corroded conditions where the corrosion geometry is fixed and broad scale dissolution is not occurring within the pit. Computationally intensive and mechanistically rigorous efforts have been put forth to model the crack formation life from fixed local defects [174]. However, empirically-based stress/strain life models of crack formation [175] that capture the effects of local defect geometry on the stress/strain inputs have been demonstrated to be accurate and are likely more feasible for engineering applications [42, 170, 176-178]. Specifically, a mean stress modified Smith-Watson-Topper [175] based approach was highly accurate in predicting the crack formation life from pre-corrosion damage in aerospace Al-alloys [42]. Critically, these approaches use empirical constants that are typically established from S-N testing in laboratory air. Use of such data is justified for conditions where the local stress/strain conditions at the notch dominate the failure process with a secondary role of loading environment. However, the current data suggest a strong role of the bulk environment (apart from the evolution of corrosion

damage during testing) on the crack initiation behavior (Figure 18). Critically, this work shows that environment specific stress/strain life constants are necessary to for accurate modeling of the crack formation life for the environments and loading conditions examined.

5.0 Conclusions:

Fatigue testing (both S-N and fracture mechanics-based long crack growth rate) of Custom 465-H950 was performed in various NaCl environments and with different levels of pre-exposure. These data are used to characterize the effect of pre-exposure and $[Cl^-]$ on the crack nucleating feature, crack formation life, microstructurally/chemically small crack growth rates, and long crack growth rates. The following conclusions are established:

- Custom 465-H950 exhibits a strong resistance to corrosion for various combinations of polarization, NaCl concentration, and exposure duration. Concurrent exposure and loading does not result in enhanced pit size or density.
- Crack nucleation for Condition 1 (pristine specimens in humid air) is governed by microstructure features. Interspersed intergranular and transgranular facets are observed on the fracture surface, suggesting an environmental influence despite the relatively inert moist air environment.
- Conditions 2 and 3 (broad surface exposure at various $[Cl^-]$ and polarizations) fail to produce sufficient pitting damage (size or density) and/or subsequent local material embrittlement to drive the crack nucleation process away from microstructural features (primarily TiC).
- For Condition 4 (isolated galvanostatically induced pits; mean pit depth $\approx 40 \mu m$ and surface diameter of $\approx 175 \mu m$) the total fatigue life of C465-H950 increases by 4-9 fold as $[Cl^-]$ decreases from 3.0M to 0.0006M for loading at 70% of σ_{ys} and $R=0.5$.
 - o The existing precorrosion damage does not evolve during cyclic loading in any of the NaCl environments.
 - o While the pit-nucleated fatigue in Condition 4 consistently demonstrates the shortest fatigue lives as compared to Condition 1-3, in many instance there is only slightly better performance than the microstructure feature nucleated fatigue in Condition 2/3.
 - o Fracture surface marking load protocols successfully isolate the exact crack formation location, and quantified the crack formation life and microstructurally/chemically-small crack growth rates.
 - o Crack nucleation occurs at the high stress locations associated with the macro-geometry of the pit. The nucleation location within the pit is independent of bulk $[Cl^-]$.
 - o Initiation life is the main factor governing fatigue life for the mechanical and environmental conditions tested; initiation life was shown to increase by as much as two orders of magnitude as $[Cl^-]$ was decreased from 3.0M to 0.0006M.

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Custom 465 Composition																	
<i>Fe</i>	<i>Cr</i>	<i>Ni</i>	<i>Co</i>	<i>Mo</i>	<i>W</i>	<i>V</i>	<i>Ti</i>	<i>Al</i>	<i>Si</i>	<i>Mn</i>	<i>S</i>	<i>P</i>	<i>As</i>	<i>Sn</i>	<i>Sb</i>	<i>La</i>	<i>Ce</i>
Balance	11.4	10.9	0.1	0.9	0.7	-	1.6	0.1	65	150	5	18	19	9	6	<1	<1

Table 1: Composition of the Custom 465, bulk measurements (wt %) of Cr, Ni, Co, Mo, W, V, Ti, Al obtained via combustion infrared absorption, bulk measurements of C (wt%) obtained via ICP-AES or IC, and trace element analysis (wppm) of Si, Mn, S, P, As, Sn, Sb, La, and Ce obtained via GDMS.

	Preconditioning			
	<i>Exposed Area</i>	<i>Solution</i>	<i>Polarization</i>	<i>Time</i>
<i>Condition 1</i>	None	None	None	None
<i>Condition 2</i>	200 mm ²	0.6, 1.5, or 3 M NaCl	-200 mV _{SCE}	24 h
<i>Condition 3</i>	200 mm ²	0.6, 1.5, or 3 M NaCl	Between 100-150 mV _{SCE}	24 h
<i>Condition 4</i>	4 coplanar 50 μm diameter circles	1 M NaCl (acidified with HCl to a pH of 3)	Galvanostatic hold at 18 mA	20 min

Table 2: Details of the pre-fatigue preparations for the dog-bone specimens used in S-N testing.

wt %	wppm
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Figure 1: Orientation maps of Custom 465 via electron backscatter diffraction at (a) low (step size of 250 nm) and (b) high magnification (step size of 12 nm). White arrows denote islands of retained austenite.

Figure 2: SEM (a) and White Light Interferometry (b) images of a Condition 4 corrosion pit on Custom 465-H950, where a line scan depth profile is presented in (c).

Figure 3: Fatigue crack growth rates versus increasing ΔK of Custom 465-H950 tested on a SEN specimen at a constant $\sigma_{\max}$ (300 MPa), R (0.5) and frequency (2 Hz) for humid N_2 and various NaCl concentrations at a fixed applied potential of $-200 \text{ mV}_{\text{SCE}}$.

Figure 4: SEM images of SEN fatigue crack surfaces of Custom 465-H950 taken at $\Delta K \approx 20$ $\text{MPa}\sqrt{\text{m}}$. Specimens were stressed at σ_{max} (300 MPa), R (0.5) and frequency (2 Hz) in (a) humid N_2 , (b) 0.006 M NaCl, and (c) 1.5 M NaCl ((b-c) both at a fixed applied potential of -200 mV_{SCE}).

Figure 5: Cycles to failure for dog-bone Custom 465-H950 specimens with various pre-exposure conditions (1-4) stressed at σ_{max} (1153 MPa), R (0.5) and frequency (2 Hz). Testing is performed in humid N_2 and various NaCl-based environments at a fixed applied potential of -200 mV_{SCE}.

Figure 6: SEM of the fracture surface of a pristine (Condition 1) dog-bone Custom 465-H950 specimen stressed at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz) in humid N₂. An overview is shown in (a), with the boxed region show in higher magnification (b). Three distinct regions are identified: (e) a quasi-cleavage transgranular morphology at the initiation site, a mixed transgranular and intergranular morphology at intermediate lengths (d), and transgranular morphology for long cracking (c).

Figure 7: WLI and SEM images of Custom 465-H950 in the (a-b) pristine condition, (c-d) after Condition 2 (Condition 3 is similar) pre-exposure, and (e-f) after Condition 3 pre-exposure (such large pits occur at a very low density (3 per 1 mm²)).

Figure 8: Cycles to failure for dog-bone Custom 465-H950 specimens with various pre-exposure conditions (1-4) stressed at σ_{max} (1153 MPa), R (0.5) and frequency (2 Hz). Testing is performed in humid N_2 and various NaCl-based environments at a fixed applied potential of $-200\text{ mV}_{\text{SCE}}$. Indicated on the plot are the nucleating feature and the size of the features.

Figure 9: SEM images and EDS characterization of the crack formation features typically observed for fatigue testing of Custom 465-H950 for Condition 2/3. Specifically, (a) a blocky TiC-based inclusion, (b) a more rounded TiC-based inclusion, (c) a Si-based particle, and (d) an area of intergranular failure.

Figure 10: SEM of the fracture surfaces of two precorroded (Condition 4) dog-bone Custom 465-H950 specimens stressed at $\sigma_{\max}$ (1153 MPa), R (0.5), frequency (2 Hz) held at a fixed applied potential of $-200 \text{ mV}_{\text{SCE}}$ in (a) 0.6 M NaCl and (b) 3 M NaCl.

Figure 11: Cycles to failure versus (a) initiating particle depth and (b) cross-sectional particle area for Condition 2/3 dog-bone Custom 465-H950 specimens at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz). Regression trend-lines are included along with the corresponding R^2 -values.

Figure 12: SEM and WLI of a dog-bone (Condition 4) Custom 465-H950 specimen stressed at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz), showing (a) the fracture surface, (b) the corroded surface after fracture, (c) the corroded surface before fracture, and (d) WLI image from before fracture. These images are used to precisely identify the crack formation location (green box).

Figure 13: An idealized quadrant of a pit is represented (due to pit symmetry) and the crack formation locations for dog-bone (Condition 4) Custom 465-H950 specimens stressed at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz) in humid N₂ and various NaCl-based environments at a fixed applied potential of -200 mV_{SCE}. Circled points indicate that there were inclusion particles at the initiation site.

Figure 14: Cycles to failure versus initiating pit depth for Condition 4 dog-bone Custom 465-H950 specimens at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz) in humid N_2 and various NaCl-based environments at a fixed applied potential of $-200 \text{ mV}_{\text{SCE}}$.

Figure 15: SEM of the fracture surface of a Condition 4 dog-bone Custom 465-H950 specimen stressed at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz) in 0.6M NaCl environments at a fixed applied potential of -200 mV_{SCE}. An overview is shown in (a), with the boxed region show in higher magnification (b), in both the marked lines indicate locations where load-induced marks ((c) indicated by white arrows) were found on the surface.

Figure 16: Fatigue crack growth rates versus distance from the formation site for Condition 4 dog-bone Custom 465-H950 specimens stressed at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz) in humid N_2 and various NaCl concentrations at a fixed applied potential of $-200 \text{ mV}_{\text{SCE}}$.

Figure 17: Propagation cycles from the first observed fracture surface markerband until failure for Condition 4 dog-bone Custom 465-H950 specimens stressed at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz) in various NaCl concentrations at a fixed applied potential of $-200\text{ mV}_{\text{SCE}}$.

Figure 18: Cycles to failure, cycles to the first observed fracture surface markerband, and cycles to 25 μm away from the formation site for Condition 4 dog-bone Custom 465-H950 specimens stressed at $\sigma_{\max}$ (1153 MPa), R (0.5) and frequency (2 Hz) in humid N₂ and various NaCl concentrations at a fixed applied potential of -200 mV_{SCE}.