Evaluation of Oxide/Metal Interfaces Formed in Type 304/304L Stainless Steel During Environmentally Enhanced and Retarded Fatigue Crack Growth in Deaerated Pressurized Water Using High Resolution Analytical Electron Microscopy

Bryan D Miller and Denise J Paraventi
Bechtel Marine Propulsion Corporation – Bettis Laboratory, PO Box 79, West Mifflin, PA 15122

ABSTRACT

Environmentally enhanced and retarded crack growth has been previously reported to occur during corrosion fatigue (CF) testing of Type 304/304L stainless steel (SS). As hypothesized by W.J. Mills, enhanced crack growth, prevalent at short rise times in low sulfur heats, occurs by a hydrogen-based mechanism. Retarded crack growth, observed at long rise times and in heats with higher sulfur levels, was attributed to an injected vacancy enhanced creep (IVEC) mechanism. Direct experimental confirmation of either of these mechanisms is extremely challenging due to the nature of microstructural features (e.g., hydrogen and vacancies) believed responsible for each. However, indirect evidence could be construed from understanding the type and chemistry of oxides formed under these two regimes of growth. To this end, the oxide on fracture surfaces and at crack tips in the enhanced and retarded crack growth regimes for two heats of SS has been thoroughly characterized using analytical electron microscopy (AEM). A two layer oxide is observed in the crack tip of a high sulfur heat of SS under retarded crack growth conditions. Conversely, a single layer oxide is found in the crack tip of a low sulfur heat of SS under nearly identical test conditions but where enhanced crack growth rates are measured. Specific differences in the oxides observed between high and low sulfur heats and implications on CF crack growth will be discussed.

Keywords: Corrosion Fatigue, Enhanced Fatigue Crack Growth, Retarded Fatigue Crack Growth, Corrosion Film, Fractography, Focused Ion Beam, Analytical Electron Microscopy

1. BACKGROUND

Knowledge of the formation of oxide structures in the crack tip enclave of a growing fatigue crack is critical for developing a comprehensive understanding of the fundamental mechanisms responsible for environmentally enhanced and retarded crack growth observed in some heats of Type 304/304L stainless steel (SS) during corrosion fatigue (CF) testing in deaerated pressurized water at elevated temperatures [1]. Crack growth during these tests is believed to be related to a combination of corrosion and mechanical processes. Depending on CF test conditions, such as temperature, hold time, or rise time, one of these processes may dominate and lead to instances where fatigue crack growth (FCG) is enhanced or retarded. As will be described, identification of the similarities and difference in the microstructure and chemistry of the oxides formed during corrosion fatigue are a critical factor in determining the mechanism that is operating. This information can be used to guide the development of appropriate models for predicting crack growth behavior.

Analysis of CF test data and surface fractography led W.J. Mills to propose that environmentally enhanced crack growth observed in Type 304/304L SS during CF testing was attributable to enhanced planar slip resulting from the uptake of hydrogen, generated during the corrosion process, into the heavily strained region immediately ahead of the crack tip [1]. Enhanced crack growth was expected to be prevalent at short rise times, short hold times, and low stress ratios during cyclic loading. Mills attributed environmentally retarded crack growth to an injected vacancy enhanced creep (IVEC) mechanism [1] that operated during both long rise and hold times and at low values of ΔK. Under the IVEC process, vacancies generated in response to the corrosion process would diffuse to dislocations formed ahead of
the crack tip and induce a climb process that would relax stresses at the crack tip and subsequently retard crack growth. Fractographic evidence to support the IVEC mechanism is in the form of the lack of cleavage-like facets on the fracture surface which is indicative of wavy slip (dislocation slip on multiple crystallographic slip planes).

Experimental work to directly test the validity of the IVEC mechanism by the direct observation of vacancies would be extremely challenging for several reasons. First, the direct observation of vacancies within the microstructure ahead of the crack tip would require high resolution electron microscopy (HREM) and the preparation of very thin samples from the region immediately ahead of the crack tip using the focused ion beam (FIB) technique. While both the FIB and HREM techniques are readily available, specimens would need to be very thin (on the order of a few atomic planes) in order to directly identify the presence of vacancies in high resolution images. High quality specimens of this type would be very difficult to produce using the FIB technique. Second, large numbers of vacancies in a material tend to cluster together and coalesce into dislocation loops. While observation of dislocation loops might provide indirect evidence of the presence of vacancies, ion damage imparted by the FIB ion beam during specimen preparation can also lead to the formation of dislocation loop structures. Thus, it would not be clear in the analysis if any observed dislocation loops were formed from coalescence of vacancy clusters or if the loops were a result of ion damage during specimen preparation. Third, individual vacancies are formed during interactions that occur between dislocations that are mobile on different slip planes. Thus, even with direct observation of vacancies in the region ahead of a propagating crack, there will be uncertainty in the analysis as to whether the vacancy was generated as a result of corrosion or from dislocation-dislocation interactions that occur in the high stress region immediately ahead of the propagating crack. As a consequence, experimental observations to test the IVEC mechanism will have to rely on indirect evidence of vacancy mechanisms. One potential characterization path for this is to examine the oxide structures formed by corrosion during testing to determine which elemental species contribute to potential vacancy mechanisms. These observations can then provide input for the development of models for predicting how vacancy injection mechanisms may influence crack growth rates.

The majority of observations of oxides formed in austenitic SS under nuclear plant operating environments reported in the open literature are from the study of stress corrosion cracking (SCC) where the corrosion process strongly influences the cracking behavior of SS under constant load. A summary of the types of oxides was presented in a recent paper [2]. In general, a two layer oxide structure consisting of an outer oxide of magnetite (Fe$_3$O$_4$), with some incorporated Cr and Ni, and an inner Cr-rich spinel (typically a non-stoichiometric form of (Fe, Cr)$_2$O$_3$ or FeCr$_2$O$_4$) is most often observed in austenitic SS exposed to a simulated primary water environment.

A number of studies have also been performed to understand the oxide formation in a variety of water chemistries. These studies tend to focus on the use of coupons exposed to high temperature water chemistries in an autoclave. Based on the work of Stellwag, the outer (surface) oxide layer is thought to form due to Fe diffusion from the base metal and from dissolved Fe ions present in the water from the autoclave while the inner oxide layer is believed to form in parallel to the outer layer by a solid state growth process [3]. Imperfections in the microstructure, due to grain boundaries, dislocation structures, etc., likely increase mass transport due to increased movement of ions along these structures. Recent work by Kuang, et al. [4, 5] has proposed a different mechanism to describe the formation of both the outer and inner oxide layers. In the proposed model for oxide growth in this work, based on experimental observations of surface oxides formed on coupons of 304 SS exposed to water with dissolved oxygen content (3 ppm) at 290°C for times ranging from 1 hour to 1000 hours, both magnetite (Fe$_3$O$_4$) and hematite (Fe$_2$O$_3$) are observed in the outer oxide layer along with a thin inner (spinel) oxide. Based on these observations, and different from that proposed by Stellwag, it was proposed by Kuang, et al. that a solid state reaction initiates the growth of the observed hematite (Fe$_2$O$_3$) which subsequently grows by a precipitation process driven by metallic ions present in the water environment of the autoclave. It should
be noted that direct comparison of the oxides formed on coupons may be difficult due to differences in water chemistry in the crack tip enclave compared to that in the autoclave environment.

Composition of the inner oxide formed in primary water environments is found to vary due to the temperature and water chemistry (particularly the pH, conductivity, and oxygen content) under which the oxide forms. While the inner oxide retains a spinel crystal structure, the ratio of Fe and Cr may be non-stoichiometric and small amounts of Ni may be incorporated into the corrosion product. In some cases, elevated levels of Ni are observed at the interface between the inner oxide and the base metal. This is believed to result from the corrosion process; because Ni is more noble than Fe or Cr, it is rejected from the growing oxide layer and tends to be concentrated at the oxide/metal interface [2].

Formation of the oxides during corrosion fatigue appears to be a less studied topic. No open literature papers were found that focused on oxide structures developed during corrosion fatigue testing of austenitic SS in simulated primary water conditions. In comparison to the oxide structures formed during static (or nearly static) load imposed during SCC testing, oxide formation in fatigue testing, and its influence on the mechanisms responsible for crack growth, may differ depending on the test conditions (e.g., rise time, hold time, $\Delta K$, etc.) used during corrosion fatigue testing. As mentioned earlier, crack growth during corrosion fatigue is likely influenced by a combination of corrosion and mechanical processes. For example, during test conditions promoting enhanced crack growth, the mechanical response may contribute more to the overall crack growth than the corrosion process.

In this work, a FIB system was used to extract specimens from the fracture surface of compact tension (C(T)) specimens and from the crack tip enclave from two different heats of Type 304/304L SS that had undergone corrosion fatigue testing that promoted enhanced and retarded crack growth. These two heats of material, A16830 and D2739, exhibited markedly different fracture surfaces and fatigue crack growth behavior. The former exhibited a heavy, thick corrosion product which obscured the fine structure of the fracture surface while the latter possessed a relatively light corrosion product. Analytical electron microscopy (AEM) was used to characterize the corrosion product and the interface between the oxide and the base metal. The goal of this work was to identify similarities and differences between the oxides and the oxide/metal interfaces to understand how the corrosion processes may be different and affect the corrosion fatigue crack growth rate response to different loading conditions. Further, experimental observations of the oxide formation process will provide input to support ongoing modeling efforts related to corrosion and could provide information to indirectly test the validity of the IVEC mechanism.

2. EXPERIMENTAL

2.1 Corrosion Fatigue Crack Flank and Crack Tip Specimens

Compact tension, C(T), specimens, one inch thick (1.0T), machined from round bar stock in the L-R orientation were evaluated following CF testing in deaerated pressurized water (DPW). The room temperature pH level was 10.1 to 10.3, the oxygen concentration was less than 20 ppb, and the nominal hydrogen concentration was 30 cc H$_2$/kg H$_2$O. Two heats of Type 304/304L SS were examined, A16830 (made to ASTM A276 specifications) and D2739 (made to MIL-DTL-23195F specifications). The composition for each heat is shown in Table 1, but the primary difference in the composition of these two heats is the S content. C(T) specimens were fatigue tested in DPW at 288°C or 338°C with a stress ratio of 0.7 and $\Delta K$ of ~8.8 MPa$\sqrt{m}$. CF testing was performed to generate specimens for both fracture surface and crack tip analysis. In tests used to generate fracture surface specimens from both heats of material, four different rise times (using an 85% rise/15% fall cycle) were evaluated in the following progression: 5.1s, 510s, 51s, and 5100s. In this progression, at the conclusion of testing, the region of the fracture surface tested using a 5.1s rise time was in the oldest region of the crack (with the longest exposure time to the environment) while the region tested using a 5100s rise time was in the youngest portion of the crack (with the least exposure time to the environment). Fatigue crack tip specimens from both heats of material were generated under the same temperatures and $\Delta K$ value, but using rise times of 51s and 5100s.
2.2 FIB Specimen Preparation

The FEI NovaLab 600 FIB system at Carnegie Mellon University was used to prepare site-specific foils for analysis using analytical electron microscopy (AEM). Foils were extracted from regions of the fracture surface rise times of 5.1s and 5100s and from crack tips that were tested at rise times of 51s and 5100s; these conditions were found to consistently produce enhanced and retarded FCG at the temperatures and low values of $\Delta K$ that were tested. Thus, given the manner in which each phase of the test was conducted, specimens extracted from the fracture surface in these locations enabled cross-sectional examination of the corrosion product formed in the oldest and youngest portions of the crack. All foils were typically ~25 microns wide x 10 microns deep in size. In the high S heat of material, all AEM foils were extracted from regions of the fracture surface that were far from indications of dissolved Mn sulfide inclusions.

2.3 AEM Characterization

Characterization of oxide films and oxide/metal interfaces were performed using an FEI Tecnai TF20 AEM operating in scanning transmission electron microscopy (STEM) mode with a beam voltage of 200 kV. For each specimen, composition data was collected at a minimum of three locations. Electron diffraction data of oxide films was collected using a Phillips CM300 AEM operating at 300 kV. Composition data for all specimens was collected using an Oxford Instruments energy dispersive spectrometer (EDS) equipped with the Inca Microanalysis software calibrated against a Ni standard. EDS data were collected using acquisition live times ranging from 60 to 90 seconds (depending on specimen thickness). Composition profiles across the oxide/metal interface were acquired primarily at a magnification of 225,000x using a sequence of 17 to 29 discrete points. The resolution of the individual profiles depends on the spacing between these discrete points; for this work, typical values for spatial resolution ranged between 8 nm and 13 nm. All composition data were determined using standardless quantification of EDS data; this was accomplished in the Inca software using a modified Cliff-Lorimer approximation with theoretical k-factors. Where possible, these data were acquired from a minimum of three regions of interest in each sample.

3. RESULTS/DISCUSSION

CF crack growth rate testing was performed under conditions known to promote environmentally enhanced and retarded crack growth in both materials at elevated temperature in DPW. The main difference between these two heats was the S content. The results of the CF testing are summarized in the plot of fatigue crack growth rate (FCGR) as a function of rise time presented in Figure 1. This plot includes data from specimens generated for fracture surface and crack tip evaluations. For comparison, two baseline FCGRs, one for elevated temperature air and the second based on testing in elevated temperature DPW using a 5.1s rise time, are indicated by the black and red dashed lines, respectively. FCGR values above the DPW baseline are considered to be enhanced while those below the line are considered retarded. For the shortest rise time, 5.1s, both the high and low S materials exhibit nearly the same FCGRs which are elevated above the elevated temperature air baseline; relative to this baseline, these values would be considered enhanced for both heats of material. Similarly, for longer rise times, 51s, 510s, and 5100s, the FCGRs for the low S material are generally found to be enhanced. However, at these longer rise times, FCGRs for the high S material tend to be below the DPW baseline and are considered to be retarded. Indeed, for the 5100s rise time, the FCGR in the high S material may be very near the value of the baseline FCGR measured for elevated temperature air.

A comparison of the oxide structures formed on the fractures surfaces in the low and high S materials under enhanced and retarded fatigue crack growth is presented in Figures 2 and 3. The fracture surfaces show primarily transgranular (TG) cracking in both materials. One exception noted in the low S material where at the longest rise time, some isolated intergranular (IG) cracking was found interspersed with the
TG cracking. Consistent with the work of Mills [1], the low S material also has a less extensive corrosion product compared to the high S heat under nearly identical test conditions. Two different sizes of oxide particles are observed on fracture surfaces in both materials. As shown in Figures 2a and 3a, in the oldest portion of the crack (with the longest exposure to the environment) in both the high and low S materials, these oxide particles can be quite coarse in size (up to ~5 microns). These coarse particles are absent in the youngest portion of the crack, shown in Figures 2c and 3c, where the oxide particles typically range from less than 100 nm to 1 micron in size. Using electron diffraction in subsequent AEM evaluations, both the fine and coarse surface oxide particles were identified as Fe$_3$O$_4$.

Figures 2 and 3 also show secondary electron (SE) images of cross-sections of the oxide extracted from the fracture surfaces in the enhanced and retarded crack growth regimes using FIB. These images reveal the presence of a second oxide layer between the base metal and the outer layer of Fe$_3$O$_4$ particles. In both the low and high S heats, Figures 2b and 3b, respectively, this inner oxide layer is observed in the oldest region of the crack (tested using the 5.1s rise time) which exhibited enhanced crack growth. The thickness of the layer is much higher in the high S material (~400 nm) than in the low S material (~100 nm at most) despite the low S material being tested at 338°C (vs. 288°C for the high S material) and both materials being exposed to environment for similar lengths of time. Further, the inner oxide/metal interface in the low S material is rough with regions where the oxide has penetrated more deeply than in others; the red arrows in Figure 2b designate regions of base metal near the fracture surface devoid of an extensive penetration of the inner oxide. Electron diffraction patterns from this layer in both heats of material was consistent with a spinel oxide structure, however, a definitive identification could not be determined for reasons that will be discussed below.

In contrast, there is a marked difference in the formation of the inner oxide layer formed in the youngest portion of the crack when comparing the low and high S materials as shown in Figures 2d and 3d, respectively. In the low S material, high magnification SE images show only Fe$_3$O$_4$ particles on the surface with no obvious inner oxide layer present. In contrast, in the high S material at lower magnification, both surface Fe$_3$O$_4$ particles and a thin, seemingly continuous inner oxide layer are present. The FCGR measured in each of these regions was also different despite test conditions being nearly identical (the only difference being that the low S material was tested at 338°C while the high S material was tested at 288°C). In the low S material, FCGRs were considered to be enhanced, while the FCGR in the high S material was considered retarded. Thin pockets of inner oxide were identified in the youngest portion of the crack in the low S material, but only in a sample extracted from a region that was ~200 microns behind the location of the crack tip.

Crack tip specimens generated under enhanced and retarded crack growth conditions are primarily TG and exhibit similar types of oxide structures to those observed on fracture surfaces in the youngest portion of the crack. Figure 4 compares the structure and oxides formed at crack tips in the low S material and the high S material. At low magnification, crack tips in the low S material generated under enhanced crack growth conditions, Figure 4a, are relatively sharp, and contain very small, discrete oxide particles. As with the fracture surfaces, regions of these cracks exhibit IG cracking during testing at the 5100s rise time. In contrast, at the same magnification in the high S material, crack tips generated under retarded crack growth conditions, Figure 4c, are generally more open and exhibit the presence of a heavier oxide product. Bright-Field (BF) STEM images of the crack tip oxides following FIB lift-out show that in the crack tip of the low S material, Figure 4b, only fine oxide particles, identified as Fe$_3$O$_4$ by electron diffraction, are present; there is no obvious inner oxide layer present in the crack tip enclave. However, as with the fracture surface from the low S material described above, the inner oxide layer was found in a sample extracted at a distance of ~125 microns behind the crack tip in a secondary crack tip. In contrast, in the high S material, Figure 4d, both very fine Fe$_3$O$_4$ oxide particles and an inner oxide layer were identified. These observations suggest that the Fe$_3$O$_4$ forms before the inner oxide layer in the low S material, likely due to a precipitation mechanism. Given the inward growth of this oxide layer, the growth process may be influenced by underlying dislocation structures formed during crack advance.
Further, the absence of an inner oxide in the youngest part of the crack in the low S material is a key difference that was found between the types of oxides formed in the crack tip enclave in both materials tested under nearly identical fatigue conditions. This finding suggests that the inner oxide layer in the low S material does not form initially in the crack tip enclave as the crack tip is actively advancing, but some time after the active crack has advanced within the material. In the high S material, the inner oxide layer begins to form as soon as the fresh metal surface is created as the crack advances.

In general, the inner oxide layer in the high S material and in the low S material (when observed) exhibited no porosity in either the oldest or youngest portions of the crack. Further, electron diffraction patterns in this layer in both materials exhibit a ring structure implying the inner oxide layer has a very fine-grained structure. Combined, these two observations suggest that the inner oxide layer likely forms due to a solid state growth process. Under both enhanced and retarded crack growth conditions in the high S heat, the interface between the inner oxide layer and the base metal is relatively rough suggesting the corrosion process into the base metal does not occur uniformly. When the inner oxide is observed in the low S material, a similar rough interface is observed between the inner oxide and the base metal. The roughness of this interface may indicate the solid state growth process that forms the inner oxide layer either (1) does not proceed uniformly or (2) may be influenced by the presence of a dislocation substructure formed by the advancing crack. Further, the differences in the thickness of the inner oxide layer also suggest the growth rate of this layer is likely different between the high and low S materials.

Semi-quantitative STEM-EDS spot analyses of the different oxides and composition profiles across the oxide/metal interface in regions extracted from the fracture surface and crack tip enclave exhibiting enhanced and retarded crack growth were obtained to determine if differences in the composition of the oxides were present. In general, spot analyses of the Fe$_3$O$_4$ particles present on fracture surfaces and in crack tip specimens in both the low and high S materials were found to only have trace amount of Cr and Ni. Identification of the inner oxide based on electron diffraction data was inconclusive as the measured crystallographic d-spacings corresponded to both an A$_2$O$_3$ and an AB$_2$O$_4$ spinel oxide structure. Spot measurements of the inner oxide using STEM-EDS showed that, in the oldest parts of the crack in both the high and low S materials, the Fe and Cr content were nearly equal (~15 – 20 at.%). In the youngest portions of the crack, near the oxide/metal interface, a higher concentration of Fe (20 – 30 at.%) was found relative to the Cr content (which varied between 10 – 15 at.% in these locations). This non-stoichiometric oxide is consistent with other observations [6, 7], with the exception that, in locations close to the oxide/metal interface, the Fe content in the localized region of the oxide is higher than the Cr content.

Composition differences between the metal and the adjacent oxide layer in the oldest and youngest regions of cracks in the low and high S materials were examined using STEM-EDS semi-quantitative composition profiles. Representative results from crack flanks and crack tips are presented in Figures 5-7. The composition profile plots are divided into specific regions (oxide, metal, etc) by black lines; these lines represent the approximate interface between the metal and oxide and include sections labeled as “overlap/transition” regions. Because of overlap between the metal and oxide layers, care should be taken in interpreting the composition results in these locations.

In the oldest portion of the cracks in both the low and high S material, where the Fe-, Cr-rich inner oxide is thickest in both materials, Figure 5a and 6a respectively, both materials exhibit a significant decrease in the Fe content across the oxide/metal interface. Little change in the Cr or Ni content is generally observed, however, in the low S material, Figure 5a, an elevated level of Ni is observed at the interface between the overlap and transition regions. This was the only instance of a significant elevation in the Ni content that was observed in this work. Given the distance between points in Figure 5a, this interface is likely not in the overlap region between the oxide and the metal. Further, as described above, in the oldest portion of cracks in the low S material, the inner Fe-, Cr-rich oxide tended to have a very irregular interface as if the solid state growth process were still underway. In this case, the presence of the elevated level of Ni may possibly be explained by the segregation of the metal from the oxide due to its higher
nobility as was described in [2]. Further, the composition profiles show difference in the stoichiometry of the oxide as a function of distance from the oxide/metal interface. In Figure 6a, where corrosion was faster, shows the Fe and Cr content of the inner oxide layer is nearly the same whereas in Figure 5a, where corrosion was slower, the Fe content of the inner oxide is generally higher than the Cr content (which remains nearly the same as in the metal). Near the interface between the inner and outer oxide, points 6 and 7 in Figure 5a, the Fe and Cr content of the oxide is similar to that shown in Figure 6a. This suggests the composition of the inner oxide reaches some equilibrium as a function of time.

In the youngest portion of the cracks, Figures 5b, 6b, and 7, the oxide composition shows subtle differences. In the low S material, Figures 5b and 7a, the inner oxide layer is absent and the Cr and Ni contents of the Fe-rich oxide show similar reductions relative to the base metal. However, in the high S material, there is a difference in the amount of Fe and Cr in the inner oxide layer as a function of distance from the oxide/metal interface. In Figure 6b, for the crack flank specimen, the Fe and Cr concentration converges at a distance ~70 nm from the interface (indicated by the black arrow in Figure 6b), while in the crack tip specimen shown in Figure 7b, the Fe content of the oxide remains higher than the Cr content. This difference is likely related to the rate of the corrosion process occurring in the crack tip region in that it takes some amount of time for the solid state reaction forming the inner oxide to reach an equilibrium composition due to corrosion process that is occurring.

As stated above, both the fracture surface and the crack tip enclave of the high S heat exhibit a substantially greater amount of corrosion product relative to the low S heat when tested under nearly identical fatigue conditions. The accelerated corrosion process responsible for this has been attributed to the presence of S at the inner oxide/metal interface in the high S heat which is known to promote a breakdown of the protective passive surface film in some materials leading to enhanced metal dissolution [1]. The role of S in promoting accelerated metal dissolution and corresponding reductions in FCGRs is supported by experimental work where direct injection of sulfide into the crack tip enclave in a low sulfur containing heat of Type 304/304L SS during testing was shown to decrease crack growth rates greatly and promote a heavier coverage of oxide [8]. In the high S heat used in this work, the source of any S present in the water in the crack tip enclave would be from the dissolution of MnS stringers. In the C(T) specimens of the high S heat used in this work, S is concentrated in stringers consisting of small, globular MnS particles which are widely spaced and orientated perpendicular to the crack plane. As such, dissolution of stringers would occur when the crack intersects these small particles. Given the wide spacing of the MnS particles, this would lead to localized “bursts” of sulfide entering the environment in the crack tip enclave. Depending on how far the S species diffuse upon entering the water, the concentration of S measured within the corrosion product may vary considerably.

In this work, AEM specimens were extracted from regions of the fracture surface well away from any indications where MnS particles were dissolved. STEM-EDS spot measurements of the inner oxide and oxide/metal interface in the high S material showed only low concentrations of S (ranging from 0.2 – 0.5 wt.%) are present at the oxide/metal interface. The concentration of S was found to vary non-uniformly along the oxide/metal interface and was often co-located with a slight elevation in the Ni concentration (10 – 12 wt.%) relative to base metal Ni content. The latter may imply the presence of discrete Ni and S concentrations at the interface; although the potential for the formation of a Ni-S phase at the interface can not be ruled out.

Summary illustrations comparing the similarities and differences in the oxide structures observed in the crack tips and on the crack flanks of the low and high S materials are presented in Figures 8 and 9, respectively. In the low S heat, Figure 8, under enhanced FCGRs, cracks exhibited regions of TG and IG fracture (for the longest rise time). In both of these regions, only Fe$_3$O$_4$ (magnetite) particles were observed in the crack tip enclave and in the youngest region of the crack. In older portions of the crack, a thin, discontinuous layer of Fe-,Cr-rich oxide is found between the surface magnetite particles and the base metal. In contrast, in the youngest region of the crack in high S material, Figure 9, between the magnetite and the base metal is a thin layer of Fe-, Cr-rich oxide. Given that this is observed in the high
and low S materials under nearly identical CF test conditions, this is a key difference between the oxide structures formed in the crack tip enclave. In the low S material, the absence of the inner oxide layer could potentially make hydrogen ingress easier, thus promoting the enhanced FCGRs that are observed by promoting enhanced planar slip as postulated by Mills [1] or by increased localization of dislocations on planar slip bands via a mechanism such as hydrogen-enhanced localized plasticity (HELP) [9].

While accelerated metal dissolution is evident in the high S material tested at long rise times and low values of ΔK, how it influences the observed reduction in the corrosion FCGR is not understood. The IVEC mechanism attempts to explain retardation by vacancy-induced climb of dislocations which subsequently relaxes stresses ahead of crack tips resulting in reduced FCGRs. In this work, the differences observed in the oxide film between the high and low S materials, suggest more vacancies may be generated in the high S heat due to the early initiation of the Fe-, Cr-rich oxide in the crack tip enclave which could support the IVEC mechanism. Alternatively, the presence of S at the interface raises additional possibilities for potential mechanisms for retarded CF crack growth. For example, S is a known recombination poison for hydrogen [10], thus, its presence at the interface might be expected to enhance the uptake of hydrogen into the material. Since the accelerated corrosion process associated with retarded crack growth in the high S material would be expected to generate more hydrogen in the crack tip environment relative to the low S material, a larger concentration of hydrogen would potentially be available for ingress into the metal during retarded crack growth. However, this would be thought to promote enhanced crack growth via increased planar slip; this has not been observed in the high S material based on analysis of the fracture surface in regions exhibiting retarded crack growth [1].

Based on this, three alternative hypotheses for the observed retardation in crack growth in the high S material could be: (1) the inner oxide prevents hydrogen from being adsorbed into the metal, (2) the hydrogen is captured by some other microstructural feature, such as vacancies, thereby limiting the amount of hydrogen available to enter the material, or (3) the excess hydrogen is adsorbed into the metal and promotes activation of multiple slip systems in the region ahead of the crack tip leading to relaxation of the stress concentrations in the region ahead of the crack tip. Hypothesis 1 could be tentatively supported by the results of this work because the low S material, which exhibits some degree of enhanced crack growth, lacks the inner oxide layer in the crack tip enclave and thus the potential barrier to hydrogen ingress into the material. Likewise, hypothesis 2 could be tentatively supported as vacancies are postulated to capture up to six hydrogen atoms. Thus, higher numbers of vacancies generated during corrosion in the high S material could potentially capture the excess hydrogen that is generated and prevent it from accelerating the crack growth. Further work is planned to explore all the potential hypotheses and their implications for environmentally enhanced and retarded fatigue crack growth.

CONCLUSIONS

1. In the high S heat, a two layer oxide structure, consisting of an outer layer of Fe₃O₄ and an inner layer enriched in Fe and Cr, was observed in the crack tip enclave following CF testing under conditions known to promote retarded crack growth.

2. In low S heat, the inner Fe-, Cr-rich oxide layer does not initially form in the crack tip enclave during CF testing known to promote enhanced crack growth; it likely forms sometime after the crack has advanced and the region is exposed to the environment for some period of time.

3. For both enhanced and retarded crack growth, Fe was identified as the predominant species associated with corrosion in both the high and low S heats of Type 304/304L SS. Thus, vacancy injection may be supported by Fe diffusion out of the material.

4. Differences observed in the oxidation process in the crack tip enclave support the hypothesis that the outer layer of Fe₃O₄ forms by the diffusion of Fe ions out of the base metal and prior to the initiation of the solid state reaction which forms the inner Fe-, Cr-rich oxide layer in low S material. In the high S material, both oxidation processes occur concurrently.
ACKNOWLEDGEMENTS

W.J. Mills is acknowledged for inspiring this work and for many helpful discussions related to CF testing and the mechanisms related to environmentally enhanced and retarded crack growth. Discussions with J.A. Savchik, E.C. Johns, and T.W. Webb regarding the corrosion process and hydrogen/metal behavior are gratefully appreciated. G. Smith and D. Gasparovic are gratefully acknowledged for sectioning and metallographic polishing of specimens as is J.K. Heuer for Fuji image plate processing. FIB specimen preparation was carried out at Carnegie Mellon University under the auspices of BMPC membership in the Advanced Microscopy Consortium. Dr. N.T. Nuhfer at CMU is gratefully acknowledged for many helpful discussions related to sample preparation.

REFERENCES


Table 1. Composition of materials (weight %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D2739</strong></td>
<td>0.019</td>
<td>1.6</td>
<td>0.025</td>
<td>&lt; 0.0025</td>
<td>0.4</td>
<td>18.3</td>
<td>9.4</td>
<td>0.14</td>
<td>0.38</td>
<td>510 ppm</td>
</tr>
<tr>
<td>(Low S Heat)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>A16830</strong></td>
<td>0.02</td>
<td>1.71</td>
<td>0.026</td>
<td>0.031</td>
<td>0.41</td>
<td>18.31</td>
<td>8.13</td>
<td>0.24</td>
<td>0.34</td>
<td>0.087</td>
</tr>
<tr>
<td>(High S Heat)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Plot of DPW FCGR vs. Rise Time (seconds) from the different test phases used to generate the crack flank and crack tip specimens evaluated in this work. Testing was performed at R=0.7 and ΔK of ~8.8 MPa√m. Consistent with Mills [1], the baseline FCGR in DPW was taken for the rise time (5.1s) where FCGRs for the two heats of material were nearly identical. FCGR values above the DPW baseline are considered to be “enhanced” while those below the baseline are considered to be “retarded”. The baseline air FCGR (for testing at 288°C), which is independent of rise time, is included for comparison. Retarded FCGRs are slightly above this elevated temperature air baseline.
Figure 2. SE SEM images showing the fracture surface and FIB cross sections from low S heat from (a, b) initial test phase (oldest region of the crack) and (c, d) final test phase (youngest region of the crack). CF testing was conducted at 338°C and at a rise time of 5.1s in (a,b) and 5100s in (c,d). The total test duration was 2500 hours; specimens extracted from the oldest region of the crack were exposed for this length of time. The specimen extracted from the youngest region of the crack was exposed for ~50 hours. White arrowheads in (a) denote coarse Fe3O4 particles. Red arrowheads in (b) denote regions of the metal that are surrounded by localized penetrations of the inner oxide layer.
Figure 3. SE SEM images showing the fracture surface and corresponding FIB cross sections from high S heat from (a, b) initial test phase (oldest region of the crack) and (c, d) final test phase (youngest region of the crack). CF testing was conducted at 288°C and at a rise time of 5.1s in (a,b) and 5100s in (c,d). The total test duration was 2810 hours; specimens extracted from the oldest region of the crack were exposed for this length of time. The specimen extracted from the youngest region of the crack was estimated to have been exposed for between 24 and 1000 hours due to the orientation of the FIB sample (parallel to the crack growth direction). Because the FCGR was so low in this region, the different ends of the FIB specimen were exposed to water for a large time differential as the crack advanced. White arrowheads in (a) denote the very coarse Fe$_3$O$_4$ particles observed in the oldest region of the crack and are absent in the youngest region of the crack (c).
Figure 4. SE SEM images of crack tips and crack tip cross-sections generated in (a, b) the low S material under CF test conditions promoting enhanced crack growth (288°C at a rise time of 51s) and (c, d) in the high S material under CF test conditions promoting retarded crack growth (288°C at a rise time of 5100s). (e) Schematic showing the orientation of the FIB foils that were extracted from the crack tip regions of the bulk C(T) specimen.
Figure 5. Representative BF-STEM image and AEM semi-quantitative composition profiles across the inner oxide/metal interface formed in regions of the low S material exhibiting (a) enhanced crack growth in a region of transgranular cracking (in the oldest portion of the crack) and (b) enhanced crack growth in region of intergranular cracking (in the youngest portion of the crack) following corrosion fatigue testing at 338°C at a rise time of 5.1s in (a) and 5100s in (b). Distance between points in the composition profiles in (a) and (b) is ~13 nm.
Figure 6. BF-STEM image and AEM semi-quantitative composition profiles across the inner oxide/metal interface formed in regions of the high S material where (a) enhanced crack growth (in the oldest portion of the crack) and (b) retarded crack growth was observed (in the youngest portion of the crack) during corrosion fatigue testing at 288°C at a rise time of 5.1s in (a) and 5100s in (b). Distance between points in (a) is ~13 nm and in (b) is ~11 nm.
Figure 7. Comparison of oxide/metal interfaces in crack tips generated in (a) low S material under CF test conditions promoting enhanced crack growth (288°C at a rise time of 51s) and (b) high material under test conditions promoting retarded crack growth (288°C at a rise time of 5100s). Distance between points in (a) is ~10 nm and in (b) is ~8 nm.
Figure 8. Evolution of oxide layers in Low S material
Figure 9. Evolution of oxide layers in High S material.