Biomass hydrothermal liquefaction (HTL) is operated in a harsh reaction medium, which contains hot pressurized water, inorganic acidic or basic catalyst, and inorganic/organic corrosive components released during the conversion. Candidate alloys for this application shall have acceptable resistance to both general corrosion and stress corrosion cracking (SCC) to withstand the HTL process conditions (250-374°C and 4-22 MPa). Ferritic Fe-Cr steels are more prone to corrosion but less susceptible to SCC compared to austenitic Fe-Cr-Ni steels. Our recent study has shown that chromizing can significantly reduce corrosion of Type 409 stainless steel (Fe-11Cr) in a simulated aqueous HTL solution. The objective of this study is thus to determine the SCC susceptibility of chromized Type 409 stainless steel, relative to the bare case. The slow strain rate testing (SSRT) technique was used for this purpose. For simplicity of experimentation, SSRT was conducted using simulated HTL water containing 800 ppm KCl, 1 M K₂CO₃ and 10 wt.% acetic acid at ambient temperature and pressure. Complementary potentiodynamic polarization measurements and surface analysis by X-ray photoelectron spectroscopy (XPS) were also made to help interpret the SSRT results. The SSRT results show no significant difference in SCC susceptibility, regardless of the starting surface. Thus, chromizing, while significantly reducing the corrosion of Type 409 stainless steel, does not adversely affect SCC susceptibility, at least under the conditions tested.

1.0 INTRODUCTION

Multiple organically sourced industries such as the pulp and paper industry are currently interested in the implementation a more optimal approach to organic waste disposal. The traditional method of waste incineration is deemed inefficient, and landfilling is an impractical do to growing concerns over groundwater pollution [1]. Recently, there has been widespread interest in the application of hydrothermal liquefaction (HTL) technologies to produce a marketable bio-crude oils from these organic waste feedstocks to generate an additional source of revenue [2], [3]. Intensive studies has demonstrated that HTL is a cost-effective, clean and reliable thermochemical conversion process that produces a bio-crude oils from wet biomass and industrial biowaste feedstock [2]–[4]. The HTL process uses high-temperature (250-374°C) and high-pressure (4-22 MPa) subcritical water, with an appropriate caustic catalyst, to readily dissolve and breakdown organic material into value-added fuel [2]–[4].

HTL technology, although well-established within the laboratory and even at pilot scale, commercial industrial-scale plants have yet to be implemented due to investment capital rooted in structural material selection issues [3], [5], [6]. Operating parameters required for effective conversion are inherently corrosive; structural materials would be subjected to hot, pressurized water with a caustic catalyst along with aggressive anions (e.g. S-based ions and Cl⁻) and organic acids released as bi-products of the conversion [2], [3], [5], [7]. A suitable material to construct the conversion reactor is imperative for effective long-term cost-effective implementation. Austenitic Fe-Cr-Ni steels are currently of interest due to their widespread consideration in multiple hot water systems: supercritical water oxidation (SCWO), Generation IV supercritical water-cooled reactors, current generation light water reactors (LWR), and supercritical fossil-fired power boilers [8]–[10]. Although austenitic Fe-Cr-Ni steels offer excellent general corrosion resistance, as well as exhibit excellent ductility, formability, and weldability, these materials are highly susceptible to stress corrosion cracking (SCC) in hot water [9]–[12]. Ferritic Fe-Cr steels are considered as a more cost-effective and SCC-resistant alternative to austenitic Fe-Cr-Ni steels; however, the lower Cr content (<11 wt%) considerably increases corrosion induced damage [13]. Therefore, surface coatings are being considered to reduce corrosion of the ferritic Fe-Cr steel, while exploiting the low SCC suscetibility and cost-effectiveness to produce a more suitable material for the construction of HTL systems.

Chromizing is a surface treatment which has potential to significantly reduce corrosion of ferritic Fe-Cr steels in HTL systems. Chromizing is expected to provide sufficient protection by forming an adherent Cr₂O₃ scale, which has
a much lower solubility for outward diffusing cations than the (Fe,Cr)₃O₄ scale that would form on ferritic Fe-Cr steel otherwise [8], [14]–[18]. Electroplating Cr metal has been successfully employed to reduce corrosion of metallic materials in various hot water processes [19]–[21]. Electroplating is a simplistic, cost-effective, and well-established technology for the industrial applications of metallic coating to enhance wear resistance, corrosion resistance, and aesthetic appearance. Unfortunately, thermal cycling and drastic differences in the thermal expansion coefficients between the substrate and coating material can produce greater stresses and promote spalling [22]. Further heat-treating a Cr electroplated surface to create a diffusion coating (chromizing) can well address this problem as a stronger metallurgical bond between the substrate and coating will be formed [22]. Alternatively, chromizing can be achieved as a single step process through furnace exposure at high temperature ~1000°C with Cr binders and fillers, consequently promoting the diffusion of Cr into the substrate to produce an adherent coating with lower internal stresses [23]. Alia et al. reported that chromized T91 significantly reduced oxidation susceptibility during short-term steam exposure at 700°C [24]. Kim et al. reported that chromizing Type 316L stainless steel reduced the weight change in supercritical water with 5 wt.% NaCl at temperature up to 500 °C for 50 hours [25].

Our recent study found that chromizing successfully reduced corrosion rate of Type 409 stainless steel (Fe-11Cr) by about 70% in a simulated aqueous HTL solution because of the formation of a protective Cr-rich oxide scale during the immersion [26]. Ferritic Fe-Cr steels are usually less susceptible to SCC than austenitic Fe-Cr-Ni alloys in aggressive environments under loading[27]. However, SCC of ferritic Fe-Cr steels have been observed in aggressive high temperature caustic and chloride solutions such as boiling 42% MgCl₂ (125°C), 60% LiCl (125°C), and 50% NaOH (316°C) [27]–[29]. Plastic deformation has been shown to promote SCC in boiling 42% MgCl₂ by shifting the critical cracking potential to lower values [27], [28]. Nickel additions (over 1%) are also to enhance SCC in (42% MgCl₂) by shifting the corrosion potential to higher value. These results suggest SCC is affected by the relative position of critical potentials, i.e., SCC susceptibility increased when the repassivation potential is higher than the critical cracking potential due to accelerated anodic dissolution at cracks [27]. Thus, the SCC susceptibility of chromized Type 409 stainless steel needs to be clarified before for HTL system construction due to the corrosivity and tensile stresses associated with the hot pressurized water exposure (thermal stresses and pressure-induced hoop and axial stresses for example) [3], [10], [12]. Another concern from an SCC perspective is the formation of acetic acid as a conversion by-product since it can enhance localized oxide scale dissolution [30], [31], and then might facilitate crack initiation. Liu et al. showed that the addition of acetic acid to a simulated aqueous HTL solution resulted in a thicker, more porous scale [5].

Therefore, the objective of this study is to determine the SCC susceptibility of chromized Type 409 stainless steel, relative to the bare (non-chromized) case, in a simulated aqueous solution of relevance to HTL biomass processing (simulated HTL water) using slow strain rate testing (SSRT) technique and electrochemical polarization measurements. During the conversion, the initially alkaline aqueous phase shall become less alkaline as organic acids will be released from the biomass feedstock [2]–[4]. Thus, pH may also be a critical factor, as it can affect the chemical solubility of the protective passive oxide scale. For simplicity of experimentation, SSRT was conducted in simulated HTL water at ambient temperature and pressure to determine relative SCC susceptibility. Complementary electrochemical polarization measurements and surface analysis by X-ray photoelectron spectroscopy (XPS) were conducted to help interpret the relative SCC susceptibility.

### 2.0 MATERIALS AND METHODS

Commercial Ti-stabilized Type 409 stainless steel (SS409) sheet (2.5 mm thick) procured from AK Steels was used as the ferritic Fe-Cr steel substrate. Table 1 lists the chemical composition as reported in the Mill Test Certificate provided by the supplier. The microstructure, as shown in Figure 1a consists of the austenitic matrix phase (average grain size of 22 ± 9 µm) and a random distribution of micro-meter sized Ti-C particles.

Flat tensile samples required for SSRT were prepared from the SS409 sheet with the dimensions shown in Figure 2. The long axis was made parallel to the rolling direction of the sheet. Square (20 mm × 20 mm) samples required for electrochemical measurements were also machined from the SS409 sheet. All surfaces (flat tensile and square samples) were manually ground down to a 600 grit surface finish using SiC papers and distilled water as a lubricant. Samples were rinsed with deionized water, then with ethanol while submerged in an ultrasonic bath for 10 minutes before drying with pressurized air. This surface preparation served as the baseline case (SS409). Samples were then
sent to a commercial lab (Ontario Chrome, Oakville, ON) for Cr metal electroplating. Prior to electroplating, samples were sandblasted to increase the surface roughness and consequently improve coating adhesion. Approximately 50 µm thick of Cr metal was plated onto the samples. Electroplated samples were rinsed with deionized water, and then ultrasonically cleaned in ethanol for 10 minutes before drying with pressurized air. Chromizing involved a furnace exposure at 975°C for 1 hour in an inert Ar atmosphere (to produce SS409-Cr samples). After the furnace exposure, chromized samples were manually lightly ground on all sides using 600 grit SiC abrasive paper and water as a lubricant to remove a thin layer of Cr₂O₃ (presumably) formed from the above treatment. Chromized samples were then rinsed with deionized water, then with ethanol while submerged in an ultrasonic bath for 10 minutes before drying with pressurized air. A cross-sectional image on the chromized surface is shown in Figure 1b. The chromized layer consists of the Cr metal layer, a strike layer of smaller grain size where the voltage was initially increased to improve adhesion, and an Fe-Cr solid solution region at the coating/substrate interface. A few small defects and cracks from the plating process can be seen within the coating. The Fe-Cr solid solution diffusion region is formed during the heat treatment process for improved adhesion and subsurface strengthening.

Small rectangular samples (15 mm × 10 mm) were prepared from the square SS409 and SS409-Cr samples required for the electrochemical measurements to facilitate working electrode construction. The long axis was made parallel to the rolling direction of the sheet. Construction involved mounting the small rectangular sample face down in epoxy after attaching a shield Cu wire to the buried face. After curing, the working surface was manually lightly ground using 600 grit SiC abrasive paper and water as a lubricant. Working surfaces were rinsed with deionized water, then with ethanol while submerged in an ultrasonic bath for 10 minutes before drying with pressurized air. As a final step, the interface between the mount and working surface was sealed using epoxy.

SSRT measurements was made using an Adelaide Testing Machine TTS-25 kN Universal Testing Apparatus. Tests were conducted in duplicate in lab air and in simulated HTL water at ambient temperature and pressure. The simulated solution was comprised of 1M K₂CO₃, 800 ppm KCl, and 10% acetic acid. A strain rate of 5 × 10⁻⁷/s was used for all measurements. Electrochemical polarization measurements were conducted using a computer-controlled Gamry Reference 600+ potentiostat. Measurements were made using a solution with and without 10% acetic acid to simulate the expected chemistry at the beginning and end of the conversion. A scan rate of 0.167 mV/s was used for the potentiodynamic polarization measurements, which were initiated after 1 h conditioning at the open circuit potential (OCP). Triplicate measurements were to ensure reproducibility. Potentiostatic polarization, initiated after 1 h conditioning at the OCP, was used to promote the formation of the passive film for subsequent analysis using X-ray photoelectron spectroscopy (XPS). The applied potential was held constant at +90 mV SCE for 1 hour for this purpose. The hold potential selected was selected from the potentiodynamic measurements. The XPS analysis was conducted using a PHI Quantera I Scanning XPS Microprobe. Spectra were acquired using monochromatic Al Ka X-rays at 1487 eV and a 45° take-off angle.

3.0 RESULTS

Figure 3a and 3b compares the typical potentiodynamic polarization response acquired in the simulated HTL water without (pH about 11) and with (pH about 7) the addition of 10% acetic acid, respectively. Both SS409 and SS409-Cr spontaneously passivate at the corrosion potential in both cases, as indicated by the polarization response (lack of an active to passive transition). Despite spontaneous passivation, SS409-Cr exhibits a substantially lower passive (corrosion) current density (about two orders of magnitude lower) than SS409. There is no significant difference in the polarization response in the two simulated HTL water cases considered, suggesting that pH does not significantly impact passive film stability at the ambient temperature and pressure conditions considered. There is also no distinct breakdown potential associated with localized corrosion initiation despite the presence of 800 ppm Cl⁻ (aq) in both cases. A similar corrosion potential is exhibited by both materials in the near-neutral case (Figure 3a), while a significant difference in observed in the alkaline case, with SS409 exhibiting a higher value than SS409-Cr (Figure 3b).

Figure 4 shows a set of XPS sputter depth profiles acquired through the passive films formed on SS409 and SS409-Cr after potentiostatic polarization in both simulated HTL water cases. Several observations are worth noting. First, the passive film is comprised of a mixed Fe-Cr oxide on SS409 in both test environments, whereas it is compromised of only a Cr oxide on SS409-Cr in both cases. Second, the passive film formed on SS409-Cr is thinner than that formed on SS409 in both cases. Third, the passive film formed in the simulated near-neutral HTL water is comparatively thinner than that formed in the simulated alkaline HTL water. Thus, as expected, the improved
protectiveness imparted by the passive film formed on SS409-Cr is controlled by the passive film chemistry; a Cr-rich oxide being more protective than a mixed Fe-Cr oxide (as defined by a lower passive current density).

Figure 5 presents the duplicate set of SSRT stress-strain curves for SS409 and SS409-Cr, as acquired in lab air and near-neutral simulated HTL water. There are several observations worth noting. First, the SS409-Cr sample exhibits a lower yield point and ultimate tensile strength than the SS409 sample when tested in air. This is likely related to the chromizing heat-treatment, which served to mildly soften the SS409 substrate by inducing some grain growth. Second, there is no significant difference in the stress-strain response between that acquired in lab air versus that acquired in HTL water for both SS409 and SS409-Cr. This indicates that the simulated HTL water chemistry does not significantly affect SCC susceptibility at ambient temperature and pressure. Third, judging by the overlapping strain ranges at fracture (Table 2), chromizing does not alter the SCC of SS409 in any meaningful way, again albeit at ambient temperature and pressure.

Figure 6 shows a set of top-view and side-view images of the fracture surface of the SS409 and SS409-Cr SSRT samples: one from each duplicate test conducted. Both top-view images, regardless of exposure in lab air or the simulated HTL water, show similar physical features, namely a fracture cup cone failure of a more ductile core and shear lips on the outer edge. The side view images of the SS409 sample reveals shear banding, whereas the side-view images of SS409-Cr samples reveal intergranular cracking in the chromized coating. Figure 1b shows that defects and microcracks were present within the coating prior to SSRT. These are relatively short in length and are developed during plating through the formation of decomposition of a metastable Cr hydride compound ultimately leading to volume shrinkage [32]. These microcracks are widely distributed. We found no evidence to suggest that the pre-existing crack propagated from the chromized coating into the substrate. Furthermore, we found little evidence of coating/substrate disbondment (spallation or flaking) of the chromized coating post-exposure (Figure 6). Such disbondment could be expected from a galvanic (dissimilar metal) corrosion perspective. However, the potentiodynamic polarization measurements shown in Figure 3a shows that one does not exist in this solution.

4.0 DISCUSSION

The SSRT results clearly show that the chromizing heat treatment applied does not altered the SCC susceptibility of SS409 in the near-neutral simulated HTL water environment considered, albeit at ambient temperature and pressure. In fact, the results suggest no SCC susceptibility, despite a weaker passive film forming on SS409 in the presence of aggressive anions (Cl− and CH3COO−) and significant plastic deformation. Even the presence of pre-existing cracks in the chromized layer, which might promote the formation of a localized occluded solution at the coating/substrate interface with a chemistry, induce passive film breakdown and then trigger SCC initiation, does not alter SCC susceptibility in this study case. Both SS409 and SS409-Cr failed by the same mechanism: classic void nucleation and growth, as indicated by the cup-cone features. The chromized coating, despite being more brittle than the SS409 substrate, is likely to thin to alter fracture in any meaningful way [33]. SSRT likely served to propagate pre-existing cracks in addition to creating new cracks via a cleavage mechanism [34].

A weaker passive film (higher passive film current density) forms on both SS409 and SS409-Cr in the simulated alkaline HTL water (Figure 3b), despite having a different passive film chemistry (Figure 4). This could be problematic from a SCC perspective at the elevated temperatures (and pressures) associated with HTL processing of biomass. A weaker passive film can drastically increase SCC susceptibility as a film rupture is a common crack initiation precursor event. Here, localized breakdown of the passive film exposes bare metal and the associated enhanced corrosion can pair with slip deformation from the applied stress to initiate SCC [35]. We have shown that SS409 forms a thick (Fe,Cr)3O4 surface film on the surface during exposure in our simulated near-neutral HTL water at elevated temperature (310 °C) and pressure (10 MPa) [26]. The Pilling-Bedworth ratio for this oxide is 2.1, which implies that it is non-protective (prone to disbondment). This, in conjunction with tensile stresses and a corrosive environment, can promote SCC [36]–[39]. The chromized coating can form a thinner Cr2O3 surface film in our simulated near-neutral HTL water at elevated temperature (310 °C) and pressure (10 MPa) [26]. This oxide film is more protective, with low solubility for alloying elements [40], and, in principle, should be less likely to breakdown [35].

Interestingly, a galvanic couple exists between SS409 and SS409-Cr in the simulated alkaline HTL water (Figure 3b). Here, the substrate (SS409) would serve as the cathode and chromized coating as the anode. Thus, there is a possibility for enhanced hydrogen evolution (and associated hydrogen embrittlement), as a cathode process, on the SS409 spot where coating defects exists to the solution to be in contact with both the coating and substrate. However,
SS409 is not traditionally susceptible to hydrogen embrittlement [41]–[45]. Further high temperature testing is required to address this concern.

5.0 CONCLUSION

The primary objective of this study was to determine the SCC susceptibility of chromized SS409, relative to bare SS409, in a simulated HTL water environment (albeit at ambient temperature and pressure) using SSRT measurements. Based on the results presented and discuss, we draw the following conclusions:

1. SS409 is not susceptible to SCC in the near-neutral simulated HTL water environment considered, despite various risk factors: aggressive anions (Cl⁻ and CH₃COO⁻), significant plastic deformation (SSRT) and nickel alloying (0.12 wt.%).
2. Chromizing the surface (electroplating then heat-treating) does not alters the SCC susceptibility of SS409, as exhibited in this environment, despite additional risk factors (more brittle surface/ material and pre-existing cracks).
3. Increasing alkalinity introduces two more possible risk factors that need consideration: somewhat weaker passive film (increased current density) and galvanic corrosion driving force at the coating/ substrate interface.

6.0 ACKNOWLEDGEMENTS

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7.0 TABLES AND FIGURES

Table 1: Composition (wt.%) of SS409 Sheet Product

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>Nb</th>
<th>Si</th>
<th>Ti</th>
<th>Fe</th>
</tr>
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<tr>
<td>SS 409</td>
<td>0.008</td>
<td>10.43</td>
<td>0.30</td>
<td>0.027</td>
<td>0.12</td>
<td>&lt;0.02</td>
<td>0.4</td>
<td>0.21</td>
<td>Bal.</td>
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Table 2: Strain Range to failure (%) for different surface treated samples

<table>
<thead>
<tr>
<th>Exposure</th>
<th>SS409</th>
<th>SS409-Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab Air</td>
<td>6.5-7.1</td>
<td>6.6-6.7</td>
</tr>
<tr>
<td>HTL Water</td>
<td>6.8-6.9</td>
<td>6.4-6.6</td>
</tr>
</tbody>
</table>
Figure 1: Light optical microscopy cross-sectional images of a) etched SS409 and b) etched SS409-Cr.

Figure 2: SSRT flat tensile geometry schematic (measurements in inches).

Figure 3: Potentiodynamic curves for SS409 and SS409-Cr immersed in a) simulated near-neutral HTL water (with 10% acetic acid) and b) simulated alkaline HTL water (without 10% acetic acid).
Figure 4: XPS sputter depth profiles after anodic polarization (+90 mV_SCE for 1 h) for a) SS409 and b) SS409-Cr in the simulated near-neutral HTL water (with 10% acetic acid) and for c) SS409 and d) SS409-Cr in the simulated alkaline HTL water (without 10% acetic acid).

Figure 5: SSRT curves for SS409 and SS409-Cr in lab air and simulated near-neutral HTL water (with 10% acetic acid).
Figure 6: SEM images after SSRT testing: a) SS409 fracture surface in air, b) SS409 fracture surface in simulated near-neutral HTL water, c) SS409-Cr fracture surface in air, d) SS409 fracture surface in simulated near-neutral HTL water, e) SS409 side profile in air, f) SS409 side profile in simulated near-neutral HTL water, g) SS409-Cr side profile in air and h) SS409-Cr side profile in simulated near-neutral HTL water.

8.0 REFERENCES


