Hydropobicity and Improved Localized Corrosion Resistance of Grain Boundary Etched Stainless Steel in Chloride-Containing Environment

Won Tae Choi,a Kkochnim Oh,b Preet M. Singh,b Victor Breedveld,a and Dennis W. Hessa,b,*

aSchool of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA
bSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

Localised corrosion of stainless steels by chloride ions in seawater leads to metal degradation while fouling of marine organisms increases the occurrence of localised corrosion. We describe a simple method to increase hydrophobicity of austenitic stainless steel using grain boundary etching that can also inhibit adhesion of bio-organisms present in seawater as well as increase the localized corrosion resistance of stainless steel in chloride-containing aqueous environments. This paper describes the corrosion behavior of stainless steel as a result of grain boundary etching to achieve hydrophobicity. Potentiostatic polarization on stainless steel 316L in a nitric acid solution at an anodic potential of 1.3 V vs. saturated calomel electrode (SCE) results in a grain boundary etched structure and a Cr- and Mo-rich passive film as confirmed by scanning electron microscopy and X-ray photoelectron spectroscopy. This modified stainless steel 316L surface exhibits enhanced corrosion resistance to a 0.6 M sodium chloride solution. Specifically, potentiodynamic polarization studies indicate that the breakdown potential increases and the sample-to-sample variability decreases. The modified surfaces show a narrow range of breakdown potentials (0.96 to 1.05 V vs. SCE) compared to as-received stainless steel 316L (0.32 to 0.86 V vs. SCE).

Due to the ubiquitous use of metals in infrastructure, production and manufacturing, transportation, and utilities, corrosion results in compromised safety and recurring repair costs. One of the most commonly employed approaches to control corrosion is the use of corrosion resistant alloys. Stainless steels (SSs), which are defined as steel alloys containing at least 10.5% chromium content by mass, are the most frequently used materials in aqueous environments because of their enhanced corrosion resistance relative to carbon steels. Chromium participates in the formation of a stable passive film on SSs that protects the bulk metal against corrosion. However, SSs still suffer from localized corrosion when exposed to chloride-containing aqueous environments, including seawater and bleach plants associated with pulp and paper industries.

Strategies to improve the localized corrosion resistance of SSs include enrichment of Cr and Mo at the SS surfaces and removal of surface inhomogeneities. These SS surface treatments include mechanical polishing, passivation, and electro-polishing. Mechanical polishing results in Cr-rich SS surfaces. Surface passivation of SS using a nitric acid solution removes surface inhomogeneities and enhances the formation of a Cr-rich passive film. Electro-polishing is a technique to control the surface finish of a metal by anodic electrochemical dissolution to yield a smooth metal surface. Electro-polishing removes surface inhomogeneities from the SS surface and simultaneously forms Cr- and Mo-rich passive films. Electro-polished SS surfaces show higher localized corrosion resistance than mechanically polished and passivated SS surfaces. Chromium oxide/hydroxide (Cr₂O₃/Cr(OH)₃) in the passive film hinders movement of cations into the electrolyte and thereby delays local breakdown of the passive film. The Mo component also stabilizes the passive film.

Fouling by marine organisms on submerged SS surfaces increases the probability of localized corrosion on SS surfaces due to metabolic activity of the bio-organisms. Traditionally, coatings of antifouling materials have been employed to solve these problems, but antifouling agents can kill and destroy marine organisms and thus cause environmental concerns. Recently, many studies have been devoted to the development of non-toxic strategies to prevent biofouling by mimicking surface topographies of marine species that naturally resist biofouling such as sharks, shells, and crabs. The combination of microscale topography and surface hydrophobicity is known to effectively reduce the fouling of marine organisms. The SS surface treatments described above enhance localized corrosion resistance but generate smooth, hydrophilic surfaces. Therefore, it is of great interest to develop micro-structured, hydrophobic SS surfaces with resistance against localized corrosion for maritime applications.

Grain boundary etching is a common metallographic technique used to delineate the grain structure of metals and metal alloys, thereby allowing analysis of size and orientation of grains. Its application to modify SS surfaces for specific performance enhancement instead of metallography is rare: one report applies grain boundary etching to a drug-eluting SS stent surface to increase the surface area and, as a result, the drug loading. Recently, we demonstrated that potentiostatic polarization in a nitric acid solution can be used to create/control surface structures on stainless steel 316L (SS316L), which enabled tunable water wettability. The grain structure of SS316L surfaces was accentuated by selective grain boundary etching and the resulting roughness yielded a hydrophobic surface. This etching process provided the appropriate length scales of surface roughness for excellent wetting control. In the current study, we report the localized corrosion behavior of the hydrophobic, grain boundary etched SS316L and compare the results to as-received SS316L, as well as electro-polished SS316L, which is known to possess improved localized corrosion resistance, albeit with hydrophilic properties.

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Experimental

Materials.—Nitric acid (ACS reagent, 70%) was purchased from Sigma Aldrich. Sodium chloride (ACS reagent, ≥ 99.0%) was

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purchased from J. T. Baker. Both chemicals were used without further purification. SS316L plates (30 × 20 × 0.05 cm²) were purchased from Maudlin Products; chemical compositions of the SS316L plates were obtained by X-ray fluorescence (XRF, Oxford Instruments X-MET 8000) and were compared with the material test report provided by Maudlin Products in Table I; the compositions are in good agreement. A platinum foil (2.5 × 2.5 × 0.0025 cm³, 99.9%) was purchased from Alfa Aesar. Insulating tape (Electroplating Tape 470) was purchased from 3M.

Sample preparation: potentiostatic polarization.—Two different sizes (2.5 × 1.5 × 0.05 cm² and 2.5 × 2.5 × 0.05 cm²) of SS316L samples were cut from the as-received sheets using a water jet cutter. These two samples served as working and counter electrodes, respectively, for the potentiostatic polarization. Prior to potentiostatic polarization treatments, the SS316L substrates were washed with acetic acid, methanol, and isopropyl alcohol to remove surface organic contaminants, and the samples were air-dried at ambient temperature. Stainless steel wires were attached to the electrodes via spot welding to establish electrical connections. Insulating tape was employed to mask the working electrode, leaving an active area (0.13 cm²) exposed for electrochemical treatments. Nitric acid (48% by weight) was used as the electrolyte. A saturated calomel electrode (SCE) served as the reference electrode in the three-electrode system. All potential values reported in this paper are relative to SCE. The distance between working and counter electrodes was maintained at 3 cm. A potentiostat (Gamry Reference 600) was used to perform potentiostatic polarizations at anodic potentials of 1.3 V and 2.4 V for 300 s at room temperature; images of droplets were obtained by dispensing 4 μL deionized water droplets onto the SS316L samples at room temperature; images of droplets were captured with a CCD camera and analyzed via the goniometer software. Chemical composition of the SS316L samples was determined by XPS using a Thermo Fisher Scientific K-Alpha XPS with a 400 μm micro-focused monochromatic Al Kα X-ray source.

SS316L surface characterization.—Surface morphologies of the SS316L samples were characterized by SEM (Hitachi SEM S8010, Japan) at 3 kV acceleration potential. A goniometer (Ramé-Hart 290) was used to measure water contact angles. Water contact angles were obtained by dispensing 4 μL deionized water droplets onto the SS316L samples at room temperature; images of droplets were captured with a CCD camera and analyzed via the goniometer software. Chemical composition of the SS316L samples was determined by XPS using a Thermo Fisher Scientific K-Alpha XPS with a 400 μm micro-focused monochromatic Al Kα X-ray source.

Results and Discussion

Surface modification of SS316L.—As shown in Figure 1, the surface structure of SS316L was modified by potentiostatic polarization. An applied anodic potential of 1.3 V results in a grain boundary etched SS316L surface with accentuated 5–20 μm intrinsic grain structures (Fig. 1b), while 2.4 V leads to a smooth electro-polished SS316L surface (Fig. 1c). The roughness features that are evident on the as-received SS316L (Fig. 1a) were created during the sheet manufacturing processes. Grain boundaries are preferential etching sites under certain potential conditions.38,39 In this system, highly selective grain boundary etching is achieved at an applied potential of 1.3 V, which accentuates the intrinsic grain structures on the SS316L surface. Potentiostatic polarization at an anodic potential of 2.4 V shows little to no selectivity toward grain boundary etching, thereby generating an electro-polished SS316L surface. The effects of modifying the SS316L surfaces via potentiostatic polarization on corrosion behavior in 0.6 M sodium chloride solution and on wettability are discussed in the following sections.

Table I. Chemical composition of the stainless steel 316L, wt%; remaining content is Fe.

|     | Cr | Ni | Mo | Mn | Cu |
|-----|----|----|----|----|----|
| XRF | 16.78 | 9.94 | 2.09 | 1.34 | 0.29 |
| Maudlin Products | 16.54 | 10.17 | 2.10 | 1.41 | 0.29 |

SEM images of SS316L samples: (a) as-received SS316L, (b) grain boundary etched SS316L, (c) electro-polished SS316L.
Figure 2. Corrosion behavior of SS316L samples in 0.6 M NaCl solution. Potentiodynamic polarization curves for eight samples each of (a) as-received SS316L, (b) grain boundary etched SS316L, (c) electro-polished SS316L. (d) Direct comparison of representative potentiodynamic polarization curves for each SS316L sample. (e) Summary of E_{BD} values for all three SS316L sample types; columns and error bars represent averages and standard deviations of the E_{BD} values, respectively. Scattered dots represent the spread of E_{BD} values for each curve. (f) Summary of E_{OC} values for all SS316L samples; columns and the error bars represent averages and standard deviations of the E_{OC} values, respectively. Scattered dots represent the spread of E_{OC} values for each sample type. (See Fig. S2 in supplementary material for re-passivation behaviors of each SS316L samples).

Corrosion behavior of SS316L surfaces.—Figure 2 shows anodic potentiodynamic polarization curves of as-received, grain boundary etched, and electro-polished SS316L samples. These curves display onset points of SS316L sample dissolution, passivity, and rapid increases in current density due to localized corrosion. Since the SS316L samples were polarized in the anodic direction from open circuit conditions, the starting point of each curve represents the open circuit potential (E_{OC}). The sharp increase in current density at high potential (i.e. flat section of the graph) represents the onset of localized corrosion, and the potential at which this occurs is referred to as the breakdown potential (E_{BD}). In order to capture the stochastic nature of localized corrosion, eight samples were prepared for each SS316L surface and potentiodynamic polarization measurements were performed on all samples (Figs. 2a–2c). Representative potentiodynamic polarization curves for each substrate are displayed in Fig. 2d to facilitate direct comparison of polarization curves (E_{OC} and E_{BD} values) for as-received, 1.3 V and 2.4 V samples. Specifically, the curves in Fig. 2d were selected from Figs. 2a, 2b, and 2c, as having E_{OC} and E_{BD} values closest to the population average of the eight recorded curves. The average values of E_{BD} and E_{OC} and their standard deviations are summarized in Figs. 2e and 2f. The as-received SS316L samples exhibit spikes in current density in potential ranges from open circuit potentials to 0.2 V, while sharp increases in current density were observed in the potential range 0.32 V to 0.86 V; these increases represent metastable localized corrosion and stable localized corrosion, respectively (Fig. 2a). In the potentiodynamic polarization curves of grain boundary etched and electro-polished SS316L samples, no characteristic metastable localized corrosion was observed; passivity was observed at potentials up to 0.9 V. Beyond the passivity region, stable localized corrosion occurred for the grain boundary etched and the electro-polished SS316L samples in fairly narrow potential ranges: 0.96 to 1.05 V for grain boundary etched, and 0.99 to 1.07 V for electro-polished samples (Figs. 2b, 2c). The lack of metastable localized corrosion and the high E_{BD} values with a narrow distribution indicate superior localized corrosion resistance compared to the as-received SS316L sample (Fig 2e). In addition, the E_{OC} values for the grain boundary etched and electro-polished SS316L samples were higher than for the as-received SS316L sample, which can be attributed to a higher rate of cathodic reaction on electrochemically treated SS316L samples (Fig. 2f). The corrosion behavior of SS316L mechanically ground with 600 grit paper was also tested in 0.6 M sodium chloride solution. Results demonstrate that the breakdown potential occurred in the range of that of as-received SS316L samples (Fig. S1a). In addition, we prepared mechanically ground and grain boundary etched SS316L samples and tested the corrosion behavior, which was consistent with potentiodynamic polarization curves of grain boundary etched SS316L without the mechanical grinding pretreatment (Fig. S1b).

The morphology of localized corrosion sites on SS316L samples after potentiodynamic polarization was also investigated using SEM (Fig. 3). The as-received SS316L samples showed formation of mouth pits with lacy pits around the mouth pit peripheries (Fig 3a). The grain boundary etched and electro-polished SS316L samples showed localized corrosion in the form of pitting and crevice corrosion (Figs. 3b, 3c). Cavities formed inside the active area (see experimental details) of grain boundary etched and electro-polished SS316L surfaces represent pitting corrosion (Fig. 3b1, 3b2, and 3c1, 3c2), while cavities along the periphery of the active area are indicative of crevice corrosion (Fig. 3b3, 3c3). We hypothesize that the confined space between masking tape and SS316L surfaces along the periphery of the active area can act as an initiation site for crevice corrosion by limiting access of bulk electrolyte to the space. Further study is necessary to
Figure 3. Morphology of localized corrosion on SS316L samples after potentiodynamic polarization: (a) Pitting corrosion on as-received SS316L samples; insets represent magnified images. (b) Pitting and crevice corrosion on grain boundary etched SS316L samples. (c) Pitting and crevice corrosion on electro-polished SS316L samples. (See Fig. S3 in supplementary material for depth profiles of pits).

establish the relationship between surface modification and types and morphology of localized corrosion.

Chemical composition of SS316L surfaces.—The chemical composition of passive films on SS316L surfaces plays a pivotal role in corrosion behavior. Figure 4 shows XPS spectra of as-received, grain boundary etched, and electro-polished SS316L surfaces. Potentiostatic polarization of SS316L samples in nitric acid solution leads to increases in Cr and Mo content in the passive films. (Figs. 4a, 4b). After potentiostatic polarization, the Mn content in the passive films decreases slightly (Fig. 4c). In contrast, no definitive changes in Fe content were observed in the passive films of SS316L samples after potentiostatic polarization (Fig. 4d). O1s XPS spectra show that the passive films on surface-modified SS316L samples possess more oxide than hydroxide components (Fig. 4e). Enrichment of Cr and Mo and the removal of Mn at SS surfaces are known to improve

Figure 4. XPS spectra of SS316L samples. (a) Cr2p scans; (b) Mo3d scans; (c) Mn2p scans; (d) Fe2p scans; e. O1s scans.
potential values from 0.32 to 0.86 V. This enhanced localized corrosion resistance of the grain boundary etched SS316L can be attributed to the formation of Cr- and Mo-rich passive film of SS316L during the potentiostatic polarization surface treatment. The corrosion resistance of the etched samples is similar to electropolished substrates, the current benchmark, but the grain boundary etched SS316L also displays microscale topography at the appropriate roughness length scale to yield a hydrophobic surface with a water contact angle of 135.7 ± 2.6°. In contrast, electropolished SS316L is hydrophilic. The combination of microscale topography and hydrophobicity on grain boundary etched SS316L offers the potential to prevent biofouling in maritime environment and thus further deter the occurrence of localized corrosion.

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Figure 5. Water contact angles of as-received, grain boundary etched, and electro-polished SS316L samples.