Corrosion behavior of cold-rolled and post heat-treated 316L stainless steel in 0.9 % NaCl solution

K. Bin Tayyab¹, A. Farooq¹, A. Ahmed Alvi¹, A. Basit Nadeem¹, K.M. Deen¹,²*

¹Corrosion Control Research Cell, Department of Metallurgy and Materials Engineering, University of the Punjab, Lahore, Pakistan
²Department of Materials Engineering, The University of British Columbia, Vancouver, V6T 1Z4, BC, Canada
*Corresponding Author: kmdeen.ceet@pu.edu.pk; deen@mail.ubc.ca

Abstract
The effect of cold rolling and post-rolling heat-treatment on the microstructural and electrochemical properties of the 316L stainless steel is investigated. The two passes and four passes cold-rolled stainless steel specimens were heat-treated by annealing at 900 °C followed by quenching in water. The microstructure of the as-rolled specimens transformed from austenite to strain-induced α'-martensite due to the significant plastic deformation that also resulted in significant grain elongation (~28 to ~54 µm). The hardness of the heat-treated specimens decreased from 190 to 146 HV due to the recovery and recrystallization of the austenite grain structure. The cyclic polarization scans of the as-rolled and heat-treated specimens were obtained in 0.9% NaCl solution. The pitting potential of the four passes rolled specimen was significantly increased to 930.5 mV from 322.3 mV after post-rolling heat treatment. The beneficial effect of the heat treatment process was evident from ~10 times lower corrosion current density and two orders of magnitude lower passive current density of the heat-treated specimens compared to as-rolled specimens. Similarly, appreciably lower corrosion rate (0.013 mpy) and higher pitting resistance (1115.5 mV) was exhibited by the post-rolled heat-treated specimens compared to as-rolled 316L stainless steel specimens.

Keyword: Cold rolling; Quenching; Cyclic polarization; Re-passivation tendency

1. Introduction
Now a day’s stainless steel is considered to be one of the most important classes of engineering materials as it is widely used in surgical industries owing to its good corrosion resistance and mechanical properties. Austenitic stainless steels are mostly utilized for biomedical applications like implants, fixtures, pharmaceuticals, and surgical instruments. The extensive use of 316L stainless steel can be ascribed to its biocompatibility, affordable cost, easy fabrication, good mechanical strength and better corrosion resistance [1,2]. High corrosive resistance and toughness have remained the key prerequisite for the production of surgical instruments [3]. For instance, austenitic stainless steel is widely
used in the manufacturing of spatula, scissors because of its nonmagnetic behavior and better corrosion resistance. Hardenability of such stainless steel is achieved not by heat treatment but via cold working. Heat treatment of stainless steel can cause Cr and C depletion from the grain boundaries and may cause intergranular corrosion. However, the grain refinement of stainless steel could play a significant role in improving the corrosion resistance by decreasing the diffusion path for carbon and chromium across the fine grains. This eliminates the possibility of chromium depletion at the vicinity of grain-boundaries, which as a result would promote the formation of uniform passive oxide film on the surface thus restricting the dissolution of the 316L stainless steel [2,4]. Corrosion resistance is ascribed to the stability of the film generated on the surface. The outer part of the generated passive film is oxides of iron while the inner part is formed by oxides of chromium because of its less mobility, which is due to decreased diffusion property of chromium as that of iron [5–7]. The growth of protective film is facilitated by the decrease in the diffusion length for chromium atoms due to a reduction in grain size. It has been reported in the literature that fine austenite grain structure ensures the formation of uniform chromium enriched surface film [8–12]. Fine microstructure due to rapid interface boundary diffusion can cause more uniform and compact film generation [7,13]. Stainless steel and Vitallium (CoCrMo alloy) have resembled results for the manufacturing of surgical equipment [14]. One of the advanced usages of stainless steel is in the biopharmaceutical companies. Since austenitic stainless steels are not heat-treatable, mechanical properties can be increased only by work hardening [15]. There are several methods (i.e. nanotexturing, mechanical vibrations, electromagnetic forces, arc oscillation, and cold rolling) that are reported in the literature to refine the grains of stainless steel [7,16,17]. Cold working can help in the formation of strain-induced martensite from the austenite phase, where the level of formation of martensite is connected to the range of cold working [15,18–19]. The mechanical martensitic modification takes place whenever external-field-induced strain is applied instead of thermal-shock-induced stress. This martensite develops in two different states: the ε-martensite phase with a hexagonal close-packed (HCP) structure and ferromagnetic α'-martensite phase with a body-centered cubic (BCC) structure. The α'-martensite phase is thermodynamically more substantial than the ε-martensite phase [15]. Moreover, to increase the strength and hardness, coldworking considerably influence the corrosion behavior of austenitic stainless steels [15,20]. As a result of previous studies, cold-worked steel might be more liable or even more corrosion resistant when exposed to a corrosive environment in contrast with the same stainless steel in an annealed state [18,21]. 316L stainless steel is shielded by a thin oxide film which shows resistance against corrosion in aggressive environments. Breakdown of this passive film can cause localized corrosion i.e. crevice/pitting corrosion. The capability of stainless steel to re-passivate after the breakdown of the film determines its corrosion
resistance [22–24]. Some of the researchers highlighted that pitting potential is reduced by cold working, while others have revealed that pitting potential enhanced as a result of coldworking [25,26].

This research aims to investigate the effects of plastic deformation induced during the cold rolling process and influence of post heat-treatment (i.e. annealing and quenching) on the microstructure, hardness and corrosion behavior of 316L stainless steel in 0.9 % NaCl solution. This information may be for the selection of suitable parameters to process and/or to manufacture medical grade instruments from 316L stainless steel. In addition, the objective of this study is to highlight the corrosion-related issues of as-rolled 316L stainless steel surgical instruments that come under interaction with the human body during surgical procedures or as orthopedic implant material within the body. The 0.9% NaCl solution was used to simulate the total salinity of the human blood that contains 9 gm of total salts dissolved in 991 gm of water. The same physiological solution is most often used as a saline infusion for humans.

2. Experimental Work
A rectangular sheet of stainless steel 316L having 3.35 mm thickness with dimensions of 24 × 6 inches was purchased from the local market. Before cold rolling, sheets were annealed at a temperature of 900 °C. The furnace cooled sheets were cleaned in a 5 vol. % sulfuric acid solution to remove any oxide scale before the cold rolling process. During the rolling process, the thickness of the stainless steel sheets was reduced to 1.9 mm (43% reduction in thickness) and 1.6 mm (52% reduction in thickness) after applying 2 and 4 passes rolling steps, respectively as illustrated schematically in Figure 1.

![Figure 1](image)

Figure 1: Schematic diagram of the cold rolling process
After rolling, sheets were allowed to air cool and then subjected to heat treatment at 900 °C for an hour in the muffle furnace followed by quenching in tap water as elaborated in Figure 2.

**Figure 2:** Schematic of the post-rolling heat-treatment process showing the heating and cooling cycle

The specimens were designated based on the number of rolling passes and post-rolling heat-treatment process as given in Table 1.

**Table 1:** Designations of the specimens used in the study

<table>
<thead>
<tr>
<th>Specimens/Treatment</th>
<th>Designations</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>AR</td>
</tr>
<tr>
<td>Two rolling passes</td>
<td>2R</td>
</tr>
<tr>
<td>Four rolling passes</td>
<td>4R</td>
</tr>
<tr>
<td>Quenched as-received</td>
<td>RQ</td>
</tr>
<tr>
<td>Quenched two rolling passes</td>
<td>2RQ</td>
</tr>
<tr>
<td>Quenched four rolling passes</td>
<td>4RQ</td>
</tr>
</tbody>
</table>

For microstructure and hardness analysis, small specimens of 1 cm² surface area were cut from the rolled sheet samples. These specimens were cold mounted in polyester resin and grinding was performed sequentially by using silicon carbide paper from coarse P60 to fine P2000 grit sizes. All the specimens were chemically etched in a freshly prepared aqua regia (5 vol. % HNO₃, 95 vol. % HCl) solution. To examine the microstructural details, optical microscopy was used (*Leica Model DM 15000M, Germany*). The grain size (length of the grains) was measured from the micrographs (at 100X magnification).
magnification) obtained from the optical microscope by using the Image J software package by following the ASTM E–112 standard practice. The grain size is the general term that may either represent the grain area or length of the elongated grains. In this article, the grain size values correspond to the length of the elongated grains produced during the rolling process. X-ray diffraction (XRD) of these specimens was carried out to observe any phase transformation during cold rolling and quenching processes. Hardness was measured by using Vickers hardness tester (Shimadzu, Japan) by 300 g load for 10 sec and by using a diamond pyramid indenter.

For electrochemical testing, the disk shape specimens (16 mm in diameter) of as-received, cold-rolled and rolled-heat treated 316L stainless steel specimens were carefully cut by using a diamond wire without generating a significant amount of heat that could otherwise deteriorate the microstructure. To prepare the working electrodes, these disk specimens were individually connected with the copper wire by using silver epoxy and mounted in the polyester resin by leaving the top surface (2.0096 cm²) exposed. A three-electrode electrochemical cell was used that has a working electrode, Ag/AgCl reference electrode and graphite rod as a counter electrode as shown in Figure 3. Commercially prepared 0.9 wt. % NaCl (UNISA pharmaceuticals Industries Ltd.) (represented as 0.9% NaCl solution) was used as an electrolyte for electrochemical analysis. Open circuit potential (E_{oc}) was measured for 1 hr to stabilize the surface potential and to maintain the equilibrium between the working electrode and electrolyte. Cyclic polarization tests were performed by sweeping the potential from –0.5 V vs E_{oc} to apex potential of +1.5 V vs E_{oc} with a forward scan rate of 2.5 mV-s\(^{-1}\). The potential was reversed from the apex potential to final potential –0.5 mV-s\(^{-1}\) vs E_{oc} with the same scan rate.
Figure 1: Electrochemical test system showing the electrical connection of a three-electrode cell with a potentiostat

3. Results and Discussion

3.1 Microstructure and Grain size analysis

Figure 4 illustrates the optical micrographs of 316L stainless steel AR, 2R and 4R specimens. The AR specimen (Figure 4(a)) consists of equiaxed austenite grains having an average grain size of 21.31 ± 0.5 µm. In the case of 2R and 4R specimens as shown in Figure 4(b) and (c), respectively present elongated grains in the rolling direction.
Figure 2: Microstructures of 316L stainless steel (a) AR, (b) 2R and (c) 4R specimens. The white arrow signs in the micrographs represent the rolling direction.

The average grain size of the specimen is found to be $28.28 \pm 1 \, \mu m$ due to two-pass rolling that resulted in a 43% decrease in thickness and a 33% increase in grain length compared to AR specimen. This is due to the fact that the larger deformation during the rolling process lead to a 52% reduction in the sheet thickness and produced preferentially elongated grain structure with an average grain size of $68.87 \pm 4.5 \, \mu m$ as shown in Figure 5.
Similarly, this excessive deformation of the 4R specimen resulted in a 144% increase in the grain’s length compared to the 2R specimen. After a four-pass rolling process (4R specimen), the 223% increase in grain elongation is observed compared to the AR specimen. Due to the serve plastic deformation of the austenite grain structure, a preferentially oriented lamellar grain structure is formed in 4R specimen as illustrated in Figure 4(c).

During the rolling process, the applied stress level could range between 350 – 500 MPa (estimated based on the % reduction in thickness and yield strength (210 MPa) of the annealed 316L stainless steel). The stress level greater than the yield strength of 316L stainless steel but lower than the ultimate strength (550 MPa) is always required to induce plastic deformation during the cold rolling process. However, the strain-hardening of the 316L stainless steel specimens during the rolling process would increase as a function of rolling passes and the required stress level in the successive rolling passes would become high. Due to the application of multiple rolling passes, the exact stress level after and before each rolling pass was not calculated due to the complexity in the phase transformation and induced strain hardening. However, the detailed microstructural analysis revealed the concentration of strain-induced martensite increased with an increase in the number of rolling cycles.
Figure 6(a) represents the presence of a well-formed polygonal shape grain structure that is formed due to sequential annealing and quenching of as-received 316L stainless steel [27]. The austenite grain shows the formation of annealing twins as indicated by the arrow signs in the microstructure. In the RQ specimen during quenching, the fast cooling rate restricts the formation of martensite due to larger solubility of carbon in the austenite phase and its slow diffusion from the austenite solid solution during the quenching process. However, the carbon depletion at the austenite grain boundaries and formation chromium carbide precipitated cannot be neglected [28] as highlighted in Figure 6(a). The average grain size in the RQ specimen is found to be 43.93 ± 2.0 µm, which is higher than the AR specimen due to the annealing heat treatment (at 900 °C for 1 hour) and recrystallization of the grains prior to quenching. During the annealing process, the recrystallization and growth of new austenite grains would occur depending on the extent of the pre-existing stresses in the grains associated with the prior thermo-mechanical treatment history of the specimen. In 2RQ specimen, the formation of relatively coarse austenite grains during the annealing process and the average grain size of 54.72 ± 0.5 µm is observed. This is found to be approximately 25% larger than the austenite grains present in the RQ specimen. In the case of 4RQ specimen, the relatively coarse austenite grain structure and recrystallization of the pre-deformed grains (grains that experienced excessive deformation during the rolling process) would occur along with the annealing twins as evident in Figure 6(c). Apparently, the relatively dark grains in Figures 6(b) and 6(c) indicate the restoration of the excessively deformed grains during the recovery and recrystallization process. These are the retained austenite grains in the microstructure that had experienced sever mechanical deformation during rolling process. These grains would release induced stresses during thermal treatment and would co-exist with the recrystallized austenite grains. In other words, due to excessive mechanical deformation of 316L stainless steel during the rolling process, the appreciable recovery of the austenitic grains and recrystallization would take place along the twin lines as evaluated from the microstructural analysis. This also resulted in the formation of relatively coarse grains (average grain size of 55.10 ± 1.5 µm) as evident in Figure 5 and presented slight elongation (0.7%) along the rolling direction in the 4RQ compared to 2RQ specimen. Twins structure with the austenite grains would form due to serve mechanical deformation or due to the mismatch in the grain orientation during the recrystallization process [29] as evident in Figure 6(a – c).
Figure 6: Microstructures of 316L stainless steel (a) RQ, (b) 2RQ and (c) 4RQ specimens, and T = twinning in the asutentite grain structure, and RC = recrystallized grains
3.2 XRD Analysis

To illustrate the grain orientation and any phase transformation during the cold rolling and quenching process, the XRD patterns were obtained as shown in Figure 7(a) and (b). The diffraction pattern of the AR specimen confirmed the existence of the austenite matrix phase. However, a small collar peak at 44.5° could be affiliated with the formation of α'-martensite in the microstructure as indexed by (110) crystallographic plane. Briefly, the diffraction peaks observed at 43.6°, 50.7°, 74.6°, and 90.5° correspond to the austenite (γ-phase) with preferential grain orientation along the (111), (200), (220) and (222) crystal planes, respectively.

Austenite to α'-martensite conversion could happen due to the arrangement of Fe and C atoms and the transformation of FCC to BCC crystal structure during thermo-mechanical treatment [29] of 316L stainless steel. As evident in the diffraction pattern, the characteristics diffraction peaks corresponding to the HCP ε-martensite phase were not observed. Whereas, the direct γ → α' transformation could result due to serve plastic deformation of the grain structure as reported in the literature [30–31]. In the case of 2R and 4R specimens, the relatively small diffraction peak at 2θ = 44.5° highlighted the formation of α'-martensite phase within the γ-austenite matrix phase. Compared to AR, in addition to the diffraction peaks at 43.6°, 50.6°, 90.3°, an additional peak at 95.8° was originated, which corresponds to (311) crystallographic plane of the γ-phase. However, the diffraction peak at 74.6° associated with the γ-phase peak disappeared after the rolling process as shown in Figure 7(a). Due to mechanical deformation, the increase in peak intensities at 43.7°, 50.8°, 90.5° and emergence of a peak at 95.8° in the diffraction pattern of the 2R and 4R specimens compared to AR highlighted the preferred grain orientation in the (111), (200), (222) and (311) direction, respectively. The austenite contents were also calculated by using Equation 1 [32].

\[ VA = \frac{1.4I_\gamma}{I_\alpha + 1.4I_\gamma} \]

Where, \( V_A \), \( I_\alpha \), and \( I_\gamma \) are the austenite fraction in the matrix, integrated intensities of the (110)\( _\alpha \) and (111)\( _\gamma \) diffraction peaks, respectively. The relatively large amount of austenite contents (~82%) was calculated from the diffraction pattern of 2R and 4R specimens compared to 68% austenite contents in AR specimens.
Compared to the diffraction pattern of AR specimen an appreciable increase in the peak intensity at $2\theta = 74.6^\circ$ in the RQ specimen indicated the preferred orientation of austenite grain structure in the (220) direction. Similarly, the diffraction peak (at $96.1^\circ$) associated with the (311) plane was also present in the XRD patterns of 2RQ and 4RQ as shown in Figure 7(b). In contrast to the 2R and 4R specimens, the origin of peak associated with the (220) plane was evident in the diffraction pattern of 2RQ and 4RQ specimens. However, the relative increase in the peak intensities associated with the \(\gamma\)-phase at 43.4°, 50.8°, 74.7°, 90.5°, and 95.8° corresponded to the recrystallization of the \(\gamma\)-phase. The diffraction peak at 44.5° related to the formation of \(\alpha'\)-martensite was evident in both 2RQ and 4RQ specimens. However, based on Equation 1, no significant change in the austenite concentration was observed in the RQ (68%), 2RQ (80%), and 4RQ (83%) specimens, which highlighted the least effect of post-rolling heat-treatment on the austenite contents. Austenite to martensitic transformations is possible when the applied stress level during the mechanical deformation is higher than the yield strength of the austenite phase and is known as strain-induced martensitic transformation. Whereas, the austenite transformation to martensite at lower applied stress level than its yield strength is called stress-induced martensite [33–34].

### 3.3 Hardness measurement

The hardness of AR, 2R, 4R, RQ, 2RQ and 4RQ 316L stainless steel specimens is illustrated in Figure 8. The severe plastic deformation could induce excessive stresses in the grains that could affect the hardness of the 316L stainless steel [35–36]. The hardness of the 4R specimen was found to be 285 HV which is greater than that of 2R (267 HV) and AR specimen (190 HV) as shown in Figure 8. Due to excessive deformation of the grain structure by the repetitive rolling passes, the
considerable strain hardening of the grain structure increased the hardness of 2R and 4R 316L stainless specimens [37–38].

Figure 8: Hardness profile of as-received, cold-rolled and quenched 316L stainless steel specimens

The hardness of RQ, 2RQ and 4RQ specimens was significantly decreased to 146 HV, 151 HV, and 147 HV respectively as shown in Figure 8. The relatively lower hardness of RQ, 2RQ and 4RQ specimens than AR, 2R and 4R specimens were due to the formation of retained austenite during annealing and quenching process. The presence of strain-induced martensite would revert back to austenite during the annealing process. The large solubility of carbon in the austenite grain structure and its restricted diffusion during the quenching process would stabilize the austenite phase. However, α'-martensite formation was favored by a diffusion-less shear mechanism that may produce during the cold rolling process. Microstructural changes occur during the annealing recovery process that could appreciably reduce the strain hardening within the grain structure [39–40].

3.4 Electrochemical Characterization

3.5.1 Open circuit potential

The open-circuit potential (OCP) or free potential of AR, 2R, 4R, RQ, 2RQ and 4RQ specimens was measured in 0.9% NaCl solution and the values are shown in Figure 9. The 316L stainless steel AR specimen showed more negative OCP –150.7 mV vs Ag/AgCl as compared to 2R (–102.7 mV) and
4R specimens (−108.1 mV) which represents its higher corrosion tendency in 0.9% NaCl solution. In other words, the relatively negative OCP of AR specimen and a gradual shift in potential towards positive value indicated its delayed electrochemical process. In the case of 2R and 4R 316L stainless steel specimens, the OCP slightly shifted towards a positive potential possibly due to the rapid reaction of these specimens with the electrolyte and formation of chromium oxide passive film, which could possibly hinder their further dissolution. The negative OCP of AR, 2R and 4R specimens in 0.9% NaCl solution correspond to the active state of the surface that showed a high tendency to react with the electrolyte. In simple words, the highly deformed grains would preferably promote the dissolution of ionic species from the surface. Under applied conditions, on the surface of 316L stainless steel, the following reactions are expected to occur (reactions 1–3) [41].

\[
\begin{align*}
1. \quad & \text{Fe} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 2e^- \\
2. \quad & \text{Cr(OH)}_2 \leftrightarrow \text{Cr(OH)}_2^+ + e^- \\
3. \quad & \text{Cr(OH)}_2 + \text{H}_2\text{O} \leftrightarrow \text{Cr(OH)}_3 + \text{H}^+ + e^- 
\end{align*}
\]

Figure 9: OCP of as-received, cold-rolled and quenched 316L stainless steel specimens
On the other hand, after annealing and quenching of AR and rolled specimens, the recovery and recrystallization process would decrease the surface reactivity of 316L stainless steel. Significantly positive OCP values of RQ (−70.6 mV vs Ag/AgCl) and 2RQ (4.70 mV vs Ag/AgCl) highlighted their lower corrosion tendency compared to AR and 2R specimen under same conditions. However, the OCP of behavior indicated that the severely deformed grain structure of 4RQ specimen and the possible formation of strain-induced martensite within the austenite matrix was not fully retrieved during the recovery and recrystallization process. In other words, the restoration of the pre-deformed austenite grain structure was incomplete during the annealing process. Grain size also influences the corrosion tendency of 316L stainless steel as described in the literature [2,7]. The relatively fine grain of 2RQ (54.72 ± 0.5 μm) compared to RQ and 4RQ specimens may also be the possible reason for its low corrosion tendency.

3.4.2 Cyclic polarization
The cyclic polarization trends of AR, 2R, 4R specimens in 0.9% NaCl solution are also shown in Figure 10. The quantitative information obtained from these polarization curves is given in Table 2.

![Figure 10](image)

**Figure 10:** Comparison of cyclic polarization curves of 316L stainless steel AR, 2R, 4R, RQ, 2RQ and 4RQ specimens.
To measure the effect of mechanical deformation and post-heat-treatment, the intrinsic corrosion tendency of the specimen was estimated from the polarization curves. In this regard, the scans were initiated from the more negative potential (−500 mV lower than the OCP of the respective specimens) to estimate the influence of pre-existing oxide species on the surface [42]. These species may abruptly form on the surface of 316L stainless steel upon exposure to air or electrolyte. No significant difference in the cathodic polarization curves was observed as shown in Figure 10, which indicated the possible reduction of oxide species (reverse of reactions 1–3) and water during cathodic polarization. These reduction reactions depend on the thermodynamic stability of water and kinetic activity of the surface species towards water reduction according to reaction 4.

$$\text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(4)}$$

On the other hand, a considerable difference in the anodic polarization curves was evident in Figure 10, which corresponds to the surface oxidation and/or active dissolution of 316L stainless steel in 0.9% NaCl solution as a function of mechanical deformation induced during the cold rolling process. The current generated by both AR and 2R specimens and the anodic polarization trends were found to be almost similar.

The corrosion current density ($i_{corr}$) and the corrosion rate were calculated by the fitting of the cyclic polarization curves within the Tafel region by using Echem Analyst software. The quantitative information of the kinetic parameters is given in Table 2. The results show that the $i_{corr}$ value for AR is found to be appreciably higher (23.401 μA.cm$^{-2}$) than the as-rolled and heat-treated specimens. For instance, the AR 316L after annealing and quenching heat treatment, the QR specimen presented appreciably lower $i_{corr}$ value (0.782 μA.cm$^{-2}$). Interestingly, compare to AR, the six fold decrease in $i_{corr}$ was presented by 2R specimen (4.440 μA.cm$^{-2}$). After four passes rolling of 316L stainless steel (4R specimen), the $i_{corr}$ value was further decreased to 1.550 μA.cm$^{-2}$, which highlighted the positive effects of mechanical deformation on its corrosion resistance. For instance, the lowest corrosion rate (0.6725 mpy) value registered by the 4R specimen indicated its appreciably low dissolution rate in 0.9% NaCl solution. When the AR 316L specimens were heat-treated and quenched, the formation of twin structure was nucleated from the strain induced martensite phase as evident in RQ could further decrease the $i_{corr}$ value i.e. 0.782 μA.cm$^{-2}$ relative to AR, 2R and 4R specimens. Similarly, the annealed+water quenched 2QR and 4QR specimens, the $i_{corr}$ values of these specimens were further decreased to 0.132 μA.cm$^{-2}$ and 0.030 μA.cm$^{-2}$ respectively. This indicated the positive effects of heat treatment procedure that has significantly improved the corrosion resistance of as-rolled 316L stainless steel.
During anodic polarization of these specimens, a gradual increase in current with potential was observed, which may be attributed to the formation and growth of the passive oxide film on their surface. However, an abrupt increase in the current by the 4R specimen at a relatively low potential; 322.3 mV vs Ag/AgCl (designated as \( E_{\text{pit}} \) breakdown or pitting potential). This increase in current represented the instability of the passive oxide film that may break above this potential leading to the accelerated localized dissolution of the surface [43]. This clearly highlights the deleterious effects of mechanical deformation on the passive film stability formed on 4R specimen. Both Fe and Cr oxide/hydroxides may coexist in the passive film that may form on the surface of 316L stainless steel at a potential > \(-0.2 \) V vs Ag/AgCl. However, the Fe(OH)\(_3\) species could interact with the Cl\(^-\) ions present in the solution under applied conditions (at potential > \(-0.2 \) V vs Ag/AgCl) and may form Fe(OH)Cl\(^+\) complex via reaction 5 [44]

\[
\text{Fe(OH)}_3 + \text{Cl}^- \leftrightarrow \text{Fe(OH)Cl}^+ + 2\text{OH}^-
\]

Due to severe mechanical deformation as evident from the microstructure of 4R specimen, the continuity of the surface oxide film may be disturbed as could be indicated from the origin of a large positive current loop and very negative protection potential (\( E_{\text{prot}} \)) during reverse polarization scan. The in-ability of the 4R specimen surface to re-passivate in the 0.9% NaCl solution is indicated from the \( E_{\text{prot}} < E_{\text{corr}} \) and the development of a large positive current loop corresponded to its accelerated pitting tendency. The rapid increase in current during anodic polarization is attributed to the formation of soluble FeCl\(_{2}^+\) species (reaction 6) at the local defect sites (where local pH is significantly dropped) that is depleted with Cr result in the pit nucleation and growth [44].

\[
\text{Fe(OH)Cl}^+ + \text{H}^+ \leftrightarrow \text{FeCl}_{2}^{+}(\text{aq}) + \text{H}_2\text{O}
\]

Also, at potentials larger than \( E_{\text{pit}} \), the oxidation of Cr\(_{\text{III}}\) to Cr\(_{\text{VI}}\) species (via reaction 7) could further promote the accelerated dissolution of the 316L stainless steel [41].

\[
\text{Cr(OH)}_3 + \text{H}_2\text{O} \leftrightarrow \text{CrO}_4^{2^-} + 5\text{H}^+ + 3\text{e}^- 
\]

However, AR and 2R specimens represented almost similar anodic polarization trends and the current density increased gradually with an increase in potential and approached to 0.1 mA cm\(^{-2}\) at approximately 1200 mV vs. Ag/AgCl. For instance, the continuous increase in anodic current density in the range of 1 – 100 \( \mu \text{A/cm}^2 \) highlighted the larger dissolution tendency of AR and 2R specimens. The abrupt increase in current at potential beyond 1200 mV vs. Ag/AgCl could either be associated with the water oxidation or to the localized dissolution of the specimens due to the breakdown of a passive oxide film. This increase in current and formation of a positive current loop during the reverse...
scan validated the hinderance in the re-passivation of the surface. This behavior also indicated the occurrence of vigorous localized reactions that could accelerate the pitting corrosion of AR and 2R specimens in 0.9% NaCl solution.

The appreciably large current response (current greater than the forward anodic current) during the reverse scan dictates that once the passive film is broken, the pitting corrosion may proliferate in an uncontrolled manner. From these polarization trends, it was evaluated that the continuous increase in current during anodic polarization and abrupt increase in current at high potential (> 1000 mV vs. Ag/AgCl) suggested the formation of unstable passive film that decreased the protection tendency of the AR and 2R specimens. In other words, during a reverse scan of both AR and 2R specimens, the reverse anodic curves formed a hysteresis loop that intersected the forward anodic curve at $E_{\text{prot}}$ (~187.5 and ~145.0 mV vs Ag/AgCl, respectively) slightly higher than the $E_{\text{corr}}$ corresponded to the protection tendency of 12.5 mV and 40 mV, respectively as given in Table 2. The protection tendency represents that once the potential of AR and 2R specimens is increased by 12.5 and 40 mV, respectively from their respective $E_{\text{corr}}$, there are fair chances of uncontrolled pitting corrosion on the surface under applied conditions. On the other hand, the significant mechanical deformation of the grain structure in 4R specimens deleteriously affected the passive film stability as confirmed from the very low $E_{\text{pit}}$ and from the rapid increase in current density beyond 322.3 mV (measured at 10 $\mu$A-cm$^{-2}$). This reverse anodic scan of 4R specimen intersected the forward scan at more negative potential than its $E_{\text{corr}}$ value (~112.5 mV), which represented its poor passivation tendency and accelerated localized dissolution.

Table 2: Electrochemical parameters calculated from Cyclic Polarization curves of 316L stainless steel

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$I_{\text{corr}}$ (µA-cm$^{-2}$)</th>
<th>CR (mpy)</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$E_{\text{prot}}$ (mV)</th>
<th>$E_{\text{pit}*}$ (mV)</th>
<th>Pitting resistance (mV)</th>
<th>Protection tendency (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>23.401</td>
<td>10.161</td>
<td>-200.0</td>
<td>-187.5</td>
<td>-</td>
<td>-</td>
<td>12.5</td>
</tr>
<tr>
<td>2R</td>
<td>4.440</td>
<td>1.933</td>
<td>-185.0</td>
<td>-145.0</td>
<td>-</td>
<td>-</td>
<td>40.0</td>
</tr>
<tr>
<td>4R</td>
<td>1.550</td>
<td>0.672</td>
<td>-112.5</td>
<td>-</td>
<td>322.3</td>
<td>434.8</td>
<td>-</td>
</tr>
<tr>
<td>RQ</td>
<td>0.782</td>
<td>0.340</td>
<td>-118.5</td>
<td>-</td>
<td>975.3</td>
<td>1160.8</td>
<td>-</td>
</tr>
<tr>
<td>2RQ</td>
<td>0.132</td>
<td>0.057</td>
<td>-175.0</td>
<td>-</td>
<td>762.3</td>
<td>937.3</td>
<td>-</td>
</tr>
<tr>
<td>4RQ</td>
<td>0.030</td>
<td>0.013</td>
<td>-185.0</td>
<td>-</td>
<td>930.5</td>
<td>1115.5</td>
<td>-</td>
</tr>
</tbody>
</table>

*Measured at 10 $\mu$A/cm$^2$

Figure 10 shows the cyclic polarization curves of RQ, 2RQ and 4RQ specimens. Significant improvement in the passive film stability and appreciable decrease in current response during anodic potential sweep was evident, which attributed to the decrease in the dissolution tendency of post rolling heat-treated 316L stainless steel. Almost similar polarization trends of RQ, 2RQ and 4RQ specimens
indicated the beneficial effects of recovery and recrystallization process that may homogenize the microstructure leading to the increase in the passive film stability. For instance, at 500 mV vs Ag/AgCl, the current density of the RQ specimen was almost three times lower than the AR specimen. However, at the same applied potential, the anodic current density of the 4R specimen was approximately two orders of magnitude higher than the 4RQ specimen. Similarly, approximately 10 times lower \( i_{\text{corr}} \) of these specimens highlighted the decrease in the dissolution rate of the post rolling heat-treated specimens. Most interestingly, the \( E_{\text{pit}} \) of 4RQ was considerably increased to approximately 930.5 mV from 322.3 mV vs. Ag/AgCl (as registered by the 4R specimen) as evaluated form the polarization trends. Based on these results, the pitting resistance of the 4RQ specimen was calculated to be 1115.5 mV, which was almost four times higher than the 4R specimen. However, slightly low pitting resistance (937.3 mV) was observed in the case of 2RQ after annealing + quenching treatment. During reverse polarization scans, the origin of positive hysteresis loop and very low intersection potential (at potential more negative than \( E_{\text{corr}} \)) presented by all RQ, 2RQ and 4RQ specimens ensured that once the pit is initiated on the surface, it would grow rapidly in an uncontrolled manner [45–46]. Also, from these trends it can be evaluated that once the passive film formed on the rolled and post heat-treated specimens is broken on the surface, the re-passivation/self-healing tendency of these specimens would become very difficult in the 0.9% NaCl solution.

4. Conclusions
i. The austenite grain structure of 316L stainless steel was transformed to strain-induced martensite during cold rolling and hardness was considerably increased from 190 to 285 HV. However, the post annealing + quenching of the as-rolled specimens relieved the induced stresses and converted the strain-induced martensite back to austenite due to the recovery and recrystallization process.

ii. As evident from the cyclic polarization scans, the positive shift in \( E_{\text{corr}} \), appreciable decrease in \( i_{\text{corr}} \) and anodic current density were registered by post-rolling heat-treated (annealing + quenching) AR, 2R and 4R specimens. In other words, the corrosion rate and pitting tendency of the post rolling heat-treated specimens (2RQ and 4RQ) was significantly decreased. This also highlighted the beneficial effects of post-heat-treatment on improving the passive film stability of the rolled 316L stainless steel.

iii. The formation of large hysteresis loop and the intersection of reverse polarization curve at potential < \( E_{\text{corr}} \) represented that once the passive film is broken, the localized dissolution of the as-rolled and post-rolled heat-treated specimens would proceed in an uncontrolled manner.

iv. The beneficial effects of post-rolling heat-treatment was evident from the considerably large pitting resistance of the 4RQ specimen (1115.5 mV), which is found to be approximately 4 times higher than the severely deformed 4R specimen.
References


