Original Article

Effect of elevated temperature variations on the corrosion resistance of S31603 and SS2562 austenitic stainless steels in chloride-sulphate environments

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ABSTRACT
Effect of environmental temperature variation at 308K, 318K, 333K and 353K on the corrosion resistance of S31603 and SS2562 austenitic stainless steels in 2.5M H₂SO₄/3.5% NaCl solution was studied by potentiodynamic polarization, potentiostatic measurement and optical microscopy. S31603 exhibited higher general corrosion resistance compared to SS2562 with values of 0.529 mm/y and 8.701 mm/y (308K and 353K) compared to 0.911 mm/y and 17.492 mm/y for SS2562. The corrosion potential of SS2562 shifted to cathodic values compared to S31603 which varies between cathodic and anodic values. At 308K, SS2562 exhibited metastable pitting activity at potential of 0.02 V. Passivation occurs at 0.09 V before breakdown of the protective oxide. Beyond 308K, passivation was absent on SS2562. S31603 exhibited unstable passivation behaviour at 308K and elevated temperatures. The protective oxide of S31603 formed at certain potentials before collapsing at all temperatures studied. Images of both steels showed localized corrosion deterioration at the grain boundaries. Larger micro-pits were visible on SS2562 compared to S31603 which had numerous shallow pits on its surface. At 353K, the extent morphological deterioration has advanced further on SS2562 compared to S31603 with the grain boundaries becoming more visible. The microstructural deterioration on S31603 at 308K and 353K is comparatively minimal.

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1. Introduction
Corrosion is the progressive degradation of materials, metals and alloys by chemical or electrochemical interaction with their environment [1–6]. Industrial environments produce variety of compounds corrosive to stainless steels. Stainless steels have extensive industrial and diverse applications due to their renowned corrosion resistance. Nevertheless they are susceptible in most cases to localized deterioration in specific industrial environments. Localized deterioration is one of the most catastrophic causes of failure of stainless steel parts and components [7–13]. Corrosion in aqueous industrial
environments at elevated temperatures such as in chemical processing plants, petrochemical plants, heat exchangers, automobile radiators, energy generating plants, fertilizer production etc. is a major factor for appropriate material selection of stainless steel alloys for equipment parts and components, building and structure, and extended service life prediction. Elevated temperature causes increased agitation and reaction of environmental molecules and corrosive anions (e.g. \( \text{SO}_4^{2-}, \text{Cl}^- \) depending on the industrial process) resulting in the deposition of oxides, carbides, sulfides etc. This leads to thinning of the metal, loss of structural integrity, performance degradation, unsightly appearance, possible equipment failure and decrease in reliability and service lifespan [14]. Ability of stainless steels to form resilient protective oxide when exposed to these environments is very important. This depends to a large extent on the nominal weight composition of alloying elements (Cr, Ni, Mo etc.), their interaction with the main metal substrate and the resulting microstructure [15,16]. However, elevated temperatures agitate molecular interactions with metallic alloys causing the breakdown of the protective oxide, constituting one of the very major failure mechanisms. Previous research has shown that elevated temperature strongly influences the passivation behaviour of metallic alloys [17,18]. The protective oxide properties of stainless steels are limited by pitting corrosion; a major problem resulting from the breakdown of the protective oxide [19–23]. Corrosion pits are microscopic, insidious and difficult to detect while its propagation is random, leading to perforations, leakages and fracture after getting to advanced stages. SS2562 austenitic stainless steel contains very low C content but has high Cr, Ni and Mo content responsible for its high corrosion resistance. Its high nickel content helps maintains its austenitic structure. The steel is extensively applied in the manufacture of equipment in chemical processing and petrochemical plants where high temperature is prevalent during service though it was originally developed to resist corrosion in dilute sulfuric acid. SS2562 is cost effective as against the costly Ni based super-alloys with strong resistance to hot crack formation [24,25]. Focus on the development of metallic alloys with sufficient corrosion resistance in sulphate-chloride environments at differential temperatures is of utmost importance. S31603 austenitic stainless steel is an extra-low C type of the S31600 steel alloy. The lower C content significantly reduces carbide precipitation due to welding. The steel has high corrosion resistance and high temperature applications. S31603 austenitic stainless steel is particularly effective against corrosion caused by acid reagents, alkalines and chlorides. The austenitic structure of the steel gives it excellent toughness down to cryogenic temperatures and high creep, stress to rupture and tensile strength at elevated temperatures. The steel is used in the construction of exhaust manifolds, furnace parts, equipment components and structures in chemical and petrochemical industry, heat exchangers, in food processing, jet engine parts, pharmaceutical and photographic equipment, medical devices, valve and pump parts, chemical processing equipment, tanks, and evaporators etc. However, the corrosion resistance of S31603 is limited in warm sea water and some marine environments. Assessing the corrosion resistance of metallic alloys for application in aqueous environments at elevated temperature is of utmost importance. This research aims to study the pitting corrosion resistance of S31603 and SS2562 austenitic stainless steel in chloride-sulphate environments at elevated temperatures.

2. Experimental methods

SS2562 and S31603 austenitic stainless steel obtained from Vienna University of Technology, Vienna, Austria have nominal (wt.%) content shown in Table 1 from energy dispersive spectroscopy characterization with Phenom ProX Scanning Electron Microscope (Model No. MVE0224651193) at the Materials characterization Laboratory, Department of Mechanical Engineering, Covenant University. The austenitic stainless steels were cut, machined and subsequently grinded with emery papers of different grits (80, 120, 220, 600 and 1000 grit size) and subsequently polished to 6\( \mu \)m with diamond polishing paste. They were thereafter sanitized with distilled water and dimethyl formaldehyde. The exposed steel surface for analysis is 1 cm by 1 cm. Analog grade NaCl (sourced from Loba Chemie Pvt. Ltd, India) was prepared into volumetric concentration of 3.5% in 200 mL of 2.5 M \( \text{H}_2\text{SO}_4 \) solution by the addition of 7 g of NaCl into 200 mL of the acid. 2.5 M \( \text{H}_2\text{SO}_4 \) solution was prepared from analar grade of reagent of the acid (98%, obtained from Sigma Aldrich, USA) by adding 27.17 mL of concentrated \( \text{H}_2\text{SO}_4 \) into 172.83 mL of deionized H\(_2\)O. 2.5 M \( \text{H}_2\text{SO}_4/3.5\% \) NaCl solution was prepared in 4 test solutions. Each electrochemical test for the steels at specific temperature was performed in 100 mL of 2.5 M \( \text{H}_2\text{SO}_4/3.5\% \) NaCl solution. Potentiodynamic polarization test was performed at 308K, 318K, 333K and 353K with portable heating device using a ternary electrode configuration within a glass containing 2.5 M \( \text{H}_2\text{SO}_4/3.5\% \) NaCl solution and a mercury thermometer immersed therein. The electrodes were linked to Digi-ivy 2311 potentiostat interfaced with a computer. The temperature was thermostatically controlled. Potentiodynamic polarization plots were produced at specific scan rate of 0.0015 V/s from of \(-0.7\) V and +1.75 V. Corrosion current density \((j, \text{A/cm}^2)\) and corrosion potential \((E_{corr}, \text{V})\) were gotten from Tafel extrapolation of the plots. Corrosion rate \((\text{Cr})\) was calculated from the formulae below;

\[
\text{CR} = \frac{0.00327 \times j \times E_q}{D}
\]

\( E_q \) is the sample equivalent weight in grams. 0.00327 is a constant for corrosion rate calculation in mm/y and \( D \) is for density in g/cm\(^3\). Optical images of S31603 and SS2562 stainless steel surfaces at 308 K and 353 K were studied and compared before and after the corrosion test using Omax trinocular metallurgical microscope.

3. Results and discussion

3.1. Polarization studies

Potentiodynamic polarization plots of SS2562 and S31603 corrosion in 2.5 M \( \text{H}_2\text{SO}_4/3.5\% \) NaCl concentration at 308 K, and elevated temperatures of 318 K, 333 K and 353 K are shown from Figs. 1(a) to 2(b). Figs. 1(a) and 2(a) shows the polariza-
Table 1 – Nominal Content (wt. %) of S31603 and SS2562 austenitic stainless steel.

<table>
<thead>
<tr>
<th>Element Symbol</th>
<th>P</th>
<th>S</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Composition</td>
<td>0.035</td>
<td>1</td>
<td>0.02</td>
<td>21</td>
<td>23</td>
<td>0.8</td>
<td>0.045</td>
<td>1.5</td>
<td>0.1</td>
<td>48.5</td>
<td></td>
</tr>
<tr>
<td>S31603</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Composition</td>
<td>0.045</td>
<td>0.03</td>
<td>0.03</td>
<td>18</td>
<td>13</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>62.9</td>
</tr>
</tbody>
</table>

Fig. 1 – a): Potentiodynamic polarization plots of SS2562 corrosion in 2.5 M H₂SO₄/3.5% NaCl at 308 K, 318 K, 333 K and 353 K and (b) Close up view of the anodic-cathodic portions of the polarization plots.

Table 2 – Potentiodynamic polarization data of SS2562 and S31603 corrosion in 2.5 M H₂SO₄/3.5% NaCl at 308K, 318K, 333K and 353K.

<table>
<thead>
<tr>
<th>SS2562 Sample</th>
<th>Temp (K)</th>
<th>SS2562 Corrosion rate (mm/y)</th>
<th>Corrosion current, I (A)</th>
<th>Corrosion Current density, J (A/cm²)</th>
<th>Corrosion potential, I_corr (V)</th>
<th>Polarization resistance, R_p (Ω)</th>
<th>Cathodic potential, B_c (V/dec)</th>
<th>Anodic potential, B_a (V/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>308</td>
<td>0.911</td>
<td>8.48E-05</td>
<td>8.48E-05</td>
<td>−0.220</td>
<td>561.60</td>
<td>−1.122</td>
<td>7.401</td>
</tr>
<tr>
<td>B</td>
<td>318</td>
<td>4.681</td>
<td>4.36E-04</td>
<td>4.36E-04</td>
<td>−0.191</td>
<td>58.97</td>
<td>−3.040</td>
<td>9.081</td>
</tr>
<tr>
<td>C</td>
<td>333</td>
<td>9.067</td>
<td>8.44E-04</td>
<td>8.44E-04</td>
<td>−0.186</td>
<td>11.78</td>
<td>−5.763</td>
<td>4.088</td>
</tr>
<tr>
<td>D</td>
<td>353</td>
<td>17.492</td>
<td>1.63E-03</td>
<td>1.63E-03</td>
<td>−0.191</td>
<td>58.97</td>
<td>−2.866</td>
<td>0.058</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S31603 Sample</th>
<th>Temp (K)</th>
<th>S31603 Corrosion rate (mm/y)</th>
<th>Corrosion current, I (A)</th>
<th>Corrosion Current density, J (A/cm²)</th>
<th>Corrosion potential, I_corr (V)</th>
<th>Polarization resistance, R_p (Ω)</th>
<th>Cathodic potential, B_c (V/dec)</th>
<th>Anodic potential, B_a (V/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>308</td>
<td>0.529</td>
<td>4.93E-05</td>
<td>4.93E-05</td>
<td>−0.238</td>
<td>521.70</td>
<td>−11.52</td>
<td>24.290</td>
</tr>
<tr>
<td>B</td>
<td>318</td>
<td>2.581</td>
<td>2.40E-04</td>
<td>2.40E-04</td>
<td>−0.246</td>
<td>107.00</td>
<td>−8.689</td>
<td>11.660</td>
</tr>
<tr>
<td>C</td>
<td>333</td>
<td>6.868</td>
<td>6.39E-04</td>
<td>6.39E-04</td>
<td>−0.212</td>
<td>40.20</td>
<td>−7.050</td>
<td>8.058</td>
</tr>
<tr>
<td>D</td>
<td>353</td>
<td>8.701</td>
<td>8.10E-04</td>
<td>8.10E-04</td>
<td>−0.228</td>
<td>31.73</td>
<td>−6.434</td>
<td>7.584</td>
</tr>
</tbody>
</table>

The corrosion plots of both steels while Figs. 1(b) and 2(b) shows the close up view of the anodic-cathodic portions of their polarization plots. Table 2 shows the polarization data obtained. The corrosion rate result of S31603 (0.529 mm/y) is relatively more resistant to general surface deterioration than SS2562 (0.911 mm/y) at 308 K. These values corresponds to corrosion current densities of 8.48 × 10⁻⁵ A/cm² and 4.93 × 10⁻⁵ A/cm², though the assertion of S31603 being more corrosion resistant is subjective considering the higher polarization resistance of SS2562 at 561.6 Ω. Increase in temperature (308 K to 333 K) caused a significant increase in corrosion rate of both steels to 4.681 mm/y and 2.581 mm/y, respectively, due to increased agitation of the molecular and corrosive species in the acid solution. Comparison of the polarization plots of both steels from 308 K to 333 K shows a large increase in cathodic and anodic slopes for SS2562 signifying a higher susceptibility to H₂ evolution, O₂ reduction and surface oxidation reactions. The minimal difference in anodic-cathodic slopes for S31603 shows slight increase in temperature has little influence on the activation processes of corrosion. At 333 K and 353 K, the vulnerability of SS2562 to surface degradation is higher with respect to the large variation in corrosion rates (9.067 mm/y and 17.492 mm/y) compared to S31603 at 6.868 mm/y and 8.701 mm/y. At 353 K, the anodic-cathodic slope of both steels [Figs. 1(b) and 2(b)] significantly increased signifying increased accelerated corrosion reaction mechanism. The visible poten-
The transients on the cathodic portion of SS2562 polarization plot at 353 K shows increased vulnerability to H₂ adsorption, a precursor to H₂ embrittlement. This is further proven from the cathodic shift in corrosion potential from −0.220 V at 308 K to −0.186 V at 353 K. The anodic–cathodic Tafel slope values of S31603 is significantly higher than SS2562 due to lower anodic and cathodic exchange current densities hence higher polarization resistance and lower vulnerability to corrosion at elevated temperatures.

### 3.2. Potentiostatic studies

**Fig. 3(a) and (b)** shows the metastable pitting, passivation, transpassive and stable pitting portion of the polarization plots for SS2562 and S31603 stainless steels. **Table 3** shows the potentiostatic data obtained. At 308 K, SS2562 exhibited significant metastable pitting activity following anodic polarization at corrosion potential of 0.02 V, corresponding to corrosion current of 7.92 × 10⁻³ A due to breakdown of the protective oxide on the alloy surface. This results in the formation and propagation of corrosion pits. However, at corrosion potential of 0.09 V and corrosion current value of 1.48 × 10⁻³ A passivation of the steel occurs signifying the pitting phenomenon is transient in nature. The passivation is due to the reformation of Cr₂O₃ on the steel surface, i.e., competitive adsorption of dissolved O₂ (instead of Cl⁻ and SO₄²⁻ ions) which dominated the surface reaction processes, leading to extended passivated region of the polarization plot. Breakdown of the protective oxide occurs at the transpassive portion of the polarization plot (1.06 V, 3.93 × 10⁻⁴ A) leading to stable pitting corrosion. Beyond 308 K, passivation behaviour was completely absent due to inability of the steel to passivate in the presence of agitated corrosive anions. This assertion is corroborated by the geometric increase in corrosion rate of SS2562 with respect to temperature which increased the kinetic energy of the corrosive species in the acid test media. The rate of destruction of the protective oxide accelerates due to enhanced electrochemical action of Cl⁻ and SO₄²⁻ ions which displaced O₂ from adsorbing onto the steel surface, hence the SS2562 could not repassivate but deteriorated in a localized manner which will be discussed in the optical characterization section. S31603 exhibited unstable passivation behaviour at ambient and elevated temperatures. At 308 K, the passivated region of the polarization plot extended from 0.02 V (4.65 × 10⁻³ A) to 0.52 V (1.03 × 10⁻³ A). The passivation region at 0.5 V is significantly shorter than the value obtained for SS2562 at 0.97 V. The limited passivation behavior of S31603 abruptly collapsed without any sign of transpassivity. This phenomenon obviously signifies weak protective oxide compared to SS2562, however the corresponding corrosion rate values of S31603 shows the steel
Table 3 – Potentiostatic data for SS2562 and S31603 corrosion.

<table>
<thead>
<tr>
<th></th>
<th>SS2562 Temp. (K)</th>
<th>S31603 Temp. (K)</th>
<th>Corrosion potential (V)</th>
<th>Passivation potential (V)</th>
<th>Pitting potential (V)</th>
<th>Passivation range (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>308</td>
<td>308</td>
<td>−0.22</td>
<td>0.09</td>
<td>1.06</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td>−0.238</td>
<td>0.04</td>
<td>0.52</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td></td>
<td>−0.212</td>
<td>0.07</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td></td>
<td>−0.228</td>
<td>0.03</td>
<td>0.21</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Fig. 4 – Optical images of (a) SS2562 and (b) S31603 before corrosion test.

Fig. 5 – Optical images of (a) SS2562 and (b) S31603 after corrosion at 308K.

is generally more corrosion resistant than SS2562. Increasing the temperature of the corrosive test solution gave important results. It is observed that limited passivation behaviour occurred for S31603 signifying that despite the agitated molecular activity and increased electrochemical action of the corrosive ions, the protective oxide of S31603 formed at certain potentials before collapsing, i.e., the properties of the passive film formed on S31603 allowed for O₂ adsorption for transient protective oxide. This observation and phenomenon shows S31603 is more resistant to the onset of localized corrosion reactions on its surface than SS2562.

3.3. Optical microscopy characterization

Optical images (mag. ×40 and ×100) of SS2562 and S31603 before corrosion and after corrosion at 308K and 353K are shown from Figs. 4(a) to 6(b). At 308K, the images of both steels showed evidence of localized corrosion deterioration at the grain boundaries signifying intergranular corrosion. Grain structures were revealed without etching. Comparatively large but relatively fewer micro-pits are visible on the morphology of SS2562 compared to S31603 which had numerous micro-pits on its surface though the pits lack meaningful depth to pose any serious threat to the surface integrity of both steels. At this temperature (308K), it is quite obvious that both steels exhibited strong resistance to electrochemical deterioration which agrees with the corrosion rate result in Table 2. At 353K, the extent morphological deterioration has advanced further on SS2562 [Fig. 6(a)] compared to S31603 with the grain boundaries becoming more visible. This shows that the corrosion resistance of SS2562 is more dependent on the properties of its microstructural constituents. There is no evidence of pitting corrosion despite the loss of passivity from potentiostatic studies. Localized corrosion is more visible at the grain boundaries signifying significant surface deterioration. On S31603, the difference in microstructural deterioration between Figs. 5(b) and 6(b) is minimal, Fig. 6(b) show evidence of sufficient resistance to the formation of corrosion pits and intergranular corrosion compared to SS2562. This observation agrees with the results from polarization resistance technique.
However, it must be noted that the agitated molecular species of the solution played a major role in the resulting microstructural configuration of both steels. Previous research as earlier mentioned has shown that increased kinetics of electrolyte molecules due to high temperature is more statistically relevant than the corrosive anions of sulphates and chlorides in causing corrosion. It is probable that the lack of significant corrosion pits prevalent on metal surfaces in the presence of chlorides is due to the surface erosion activity of the molecular species, hence the appearance of the grain boundary configuration. Nevertheless S3160’s proves to be more resistance in these environments.

4. Conclusion

S31603 and SS2562 stainless steels exhibited differential rates of surface deterioration in the presence of sulphate and chloride corrosive anions at ambient and elevated temperatures. However, S31603 proves to be more resistant to general and localized corrosion. The corrosion resistance of both steels was marginally comparable at 308 K. Increase in temperature to 353 K caused accelerated corrosion on SS2562 compared to S31603. Passivation behaviour was completely absent on SS2562 after 308 K, compared to S31603 which showed limited passivation behaviour till 353 K. Despite the agitated molecular activity and increased electrochemical action of the corrosive ions, the protective oxide of S31603 formed at certain potentials before collapsing. Optical images of both steels showed evidence of localized corrosion deterioration at the grain boundaries at 308 K. At 353 K, the extent morphological deterioration on SS2562 is higher than S31603.

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