Pitting Corrosion Behavior of 304 SS and 316 SS Alloys in Aqueous Chloride and Bromide Solutions

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ABSTRACT
The importance of the present work falls on the pitting corrosion behavior investigation of 304 SS and 316 SS alloys in 3.5 wt% of aqueous solution bearing with chloride and bromide anion at different solutions temperature range starting from (20-50)°C due to the pitting corrosion tremendous effect on the economic, safety and materials loss due to leakage. The impact of solution temperatures on the pitting corrosion resistance at 3.5wt% (NaCl and NaBr) solutions for the 304 SS and 316 SS has been investigated utilizing the cyclic polarization techniques at the potential range -400 to 1000 mV vs. SCE at 40 mV/sec scan rate followed by the surface characterization employing Scanning Electron Microscope. The results show that a significant decline in the pitting corrosion potential Ep values of both stainless steel alloys in chloride and bromide solution during temperature increase attributed to the pitting corrosion potential decreased arises from the modification of the passive film properties. The surface examination using optical microscope and scanning electron microscope prove the occurring of higher pitting density over 304 SS in chloride solution than that observed in bromide solution with a non-circular lacy cover pitfall out at the center and falls inside the pits hall in comparison to the isolated circular lacy cover pit formed on 316 SS in 3.5wt% NaBr solution at 50 °C.

Keywords: 304 and 316 SS alloys, pitting corrosion, Sodium halide salts, temperature effect.
1. INTRODUCTION

Pitting corrosion is a corrosion mechanism characterized by a highly localized loss of metals particularly passivated materials Schweitzer, 2007. Fe-Cr-Ni alloys, for example 304 and 316 Stainless steel, which are the most popular corrosion-resistance alloys used in many different applications due to their excellent corrosion resistance arises from the formation of a thin protective passive film with a thickness of several nm covering the stainless steel alloys surfaces at different environments and different experimental conditions. Ahmed, 2006, Shreir, et al., 1994.

Despite their characteristic properties, these alloys are susceptible to pitting corrosion in halide containing solutions. The 304 SS alloy is susceptible to pitting corrosion attack at 10°C in seawater while 316 SS alloy is more resistance than 304 SS and will suffer the same pitting attack at a temperature higher than that for 304 SS. Numerous studies have demonstrated that increasing the solution temperatures in the presence of halide anion will promote pitting corrosion attack to the Fe-Cr-Ni alloys Wang, et al., 1988, Pardo, et al., 2000.

Pitting corrosion of SS alloys mostly occurs in an environment bearing with ions such as Cl⁻, Br⁻, and I⁻ in perceivable concentration with chloride being the most aggressive one and as well as in marine environments. A shifting in the pitting corrosion potential Ep towards an active direction was associated with increasing the solutions temperature or chloride concentration Ahmed, 2006, Talbot, 1998. Liu et al., 2014, finds 13Cr Stainless steel is susceptible to severe pitting corrosion attack in heavy brine 1400 g/L KBr solution.

The aim of the present work was to determine the pitting corrosion resistance of 304 and 316 SS alloys in 3.5wt% NaCl and NaBr solution at temperature range (20 -50)°C, with comparing the aggressiveness of halide (Chloride and Bromide) towards pitting corrosion.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The chemical compounds used for the tested solutions preparation were sodium chloride (NaCl) and sodium bromide (NaBr) with analytical grade product manufactured by BDH. A 3.5wt% NaX⁻ solution at pH5 was prepared by adding a 35 g of halides salt in one liter of deionized water, this concentration represents the synthetic seawater concentration and this value was fixed for the Br⁻ halide to compare the aggressivity of the two halides. The specimens under investigation were an alloy of plate cut from stainless steel sheet (304 and 316)SS alloy with a dimension of 1.5cmx1.5cmx2mm. These alloys and their chemical compositions listed in table 1were supplied by HESSCO / Heavy Engineering Equipments State Company / Ministry of Oil/Iraq.

The specimen were first ground using a series of silicon carbide emery paper starting from 80 up to 2000 surface finishing in order to remove surface scratch or defect, followed by degreasing with acetone and washing with distilled water, finally swabbed with ethanol and dried using a stream hot air supplied by heat gun then kept in the desiccator.
2.2 Electrochemical Measurements
The electrochemical measurement including the cyclic polarization techniques for pitting corrosion studies was performed with Wenking M-lab 200 Electronik Germany Bank potentiostat, in a double glass wall three electrode corrosion cell with a 1 cm$^2$ surface area. The opening face of the holder was exposed to the tested solution acts as working electrode, a saturated calomel electrode and a high purity platinum rod with 10 cm long were used as reference and counter electrode respectively. Fig. 1 shows the full electrochemical system used for polarization studies. The cyclic polarization measurements were performed at a 10 mV/Sec scan rate starting from -400 mV up to 1000 mV in the anodic direction (forward scan) and back to the starting potential (backward scan). These measurements were done to the tested alloys in the prepared solution (3.5wt% NaCl and NaBr) at different solution temperatures with a heating-cooling circulation unit type HAAKE OOO-3959/ Germany in order to control the desired solutions temperature within ±1 °f, to estimate the pitting potential values which gives an indication of the potential up with the onset of pitting corrosion surfaces attack, while the protection or repassivation potential $E_{rep}$ which is defined as the potential at which the potential above is with no pit nucleation but allowed propagation of the existing pits and below which occurs of pitting corrosion.

Finally, the samples were subject to the surface examination utilizing the FEI Scanning Electron Microscope SEM, model Inspect S50 made in the Czech Republic.

3. RESULTS AND DISCUSSION
The major goal of this paper is to examine and discuss the pitting corrosion behavior of the 304 SS and 316 SS alloys in 3.5wt% of sodium halides salt NaCl and NaBr at different solution temperature due to the massive presence of sodium chloride and sodium bromide in the industry.

3.1 Stainless steel /Chloride System
3.1.1 304 SS/ Chloride system
The cyclic polarization curves of 304 SS tested specimens in 3.5 wt% NaCl solution at 20,30,40 and 50°C are shown in Fig. 2. In general this figure shows that the sample was susceptible to pitting corrosion attack in a solution bearing with chloride halide at different temperature range starting from 20°C up to 50°C from the existence of positive hysteresis loop in cyclic polarization curves, which characterizes the passive film breakdown in the forward scan and subsequent repassivation on the backward scan. Although a decrease in the anodic polarization curves was observed for 304 SS alloy in the chloride halide solutions due to solutions temperature increasing up to 50°C these results coincided with the SEM observation.

According to Wang, et al., 1988, Malik, et al., 1992, Roy, and Basu, 1981, an active shifting of the anodic polarization curves as well as in the pitting potential $E_p$, with a pronounced increase in the passive current density was observed through solution temperature increases. The same results were observed in this study with a slight influence of temperature on repassivation potentials.

One can notice from Fig. 2 that the pitting corrosion potential $E_p$ decreased while the pitting current density $I_p$ in mA/cm$^2$ measured at the $E_p$ values increased with increasing the solution temperature from 20 to 50°C, with no tendency for 304 SS to repassivate in 3.5 wt% NaCl.
solution at the studied temperature which indicates that the 304 SS suffers a severe pitting corrosion attack at these conditions. These results are extracted from the cyclic polarization curve Fig. 2 and illustrated in Table 2.

Fig. 3 shows the effect of the temperature on the Ep, Ecorr values as well as on the potential area difference ΔE between the pitting and corrosion potentials for a chance of the metals surfaces affected by pitting corrosion for 304 SS in chloride containing solution versus solutions temperature, both values Ep and ΔE decreased with temperature increase attributed to decreasing the resistance to pitting corrosion with about 200 mV potential of ΔE higher than Ep curve Munoz, et al., 2006.

The variation in the Ep, Ecorr, ΔE, and Ip values arises from the fact that the passive film undergoes a degradation in its properties with temperature, and becomes more defective, porous and less resistance to film breakdown with an intrinsic modification of their chemical and physical structures Hur, and Park, 2006, Wang, et al., 1988, Manning, and Duquette, 1980.

Fig.4(a and b) shows the SEM micrographs of 304 SS at different magnification after testing the alloy with cyclic polarization techniques applying a potential (-400-1000)mV at 10mV/sec scan rate in 3.5wt% NaCl at 50C. These micrographs show a small shallow open mouth circular pits spreading on the alloy surface with another large noncircular lacy cover pit collapse at the cover center and falls inside a pits hall, as well as a salt film deposit inside the cavities showing bright parts indicates salt film deposition, while the dark cavities gives an indication to the deep pit.

The SEM observation also showed that the pits formed in clusters of numbers of the pit and the pits grow rate increase with temperature increase and subsequently the pits grow into one another to form one large irregular lacy pit shape Tait, 1979.

3.1.2 316 SS/Chloride system

The cyclic polarization curve of 316 SS in 3.5wt% NaCl solution at temperature range is (20, 30, 40 and 50)°C is shown in Fig.5. A clear sign to pitting corrosion occurring on the 316 SS alloy surface in a chloride containing solution at all temperatures arises from the presence of the positive hysteresis loop with the ability of the 316 SS to repassivate at Erep after pitting corrosion occurs in 3.5wt% NaCl at the studied temperature range. The values of the Ep, Ecorr, Erep and Ip are listed in Table3 which are extracted from the cyclic polarization curves (Fig.5) and also is shown in Fig.6. A decrease in the characteristic potentials that distinct the pitting corrosion attack on 316 SS alloy illustrated in Ep, Erep, Ecorr, and ΔE values with solution temperature increases up to 50°C towards an active direction, which can be attributed to the impact of halide solution temperature on the protective oxides passive layer that is covering the SS surface with an indication of decreased resistance to pitting corrosion occurrence during temperature increase Laycock, and Newm, 1998. Moreover, the Ip values show to be increased with temperature increasing as can be noticed from Table 3.

The SEM micrograph of 316 SS surface shows that this alloy incur a pitting corrosion attack in chloride containing medium with a low-density pit were formed on the 316 SS surface which evinces the higher resistance of this alloy toward susceptibility to pitting corrosion in comparison to the 304 SS behavior in the same halide salt solution as can be shown in Fig.7.
3.2 Stainless Steel /Bromide system

3.2.1 304 SS/ Bromide system

To investigate the 304 SS susceptibility to pitting corrosion in a 3.5wt% NaBr solution at different picked temperatures starting from 20°C up to 50°C, a cyclic polarization technique was used to the working electrode (304 SS) from -400 to 1000 mV versus SCE as mentioned previously in the experimental work.

Fig. 8 shows the typical cyclic polarization curves for 304 SS in a solution bearing with 3.5wt% sodium bromide (NaBr) salt over a temperature range (20-50)°C, the results show that bromide halide promotes pitting corrosion to 304 SS at all studied temperature with the metal ability to repassivate under the experimental condition, in addition, a slight decrease in the pitting corrosion potential Ep, Ecorr and the potential area difference ΔE versus the temperature varying was observed. Fig. 9 and Table 4 illustrate the 304 SS pitting corrosion characteristic parameters in a bromide containing solution. Again the influence of environmental condition temperature (20, 30, 40 and 50)°C on the increasing susceptibility of 304 SS towards pitting corrosion results form the aggressive bromide anion in breaking the passive oxide film which then promotes the pitting corrosion to the 304 SS.

Examination the 304 SS surface confirmed the presence of different pits size widespread over the alloy surface with an interrupted area with no pits denote the remaining of passive film cathodic area in comparison with pit (anodic area). Fig. 10 depicted the pitting corrosion occurring on the 304 SS surface using SEM microscope, a deep lacy cover pits the surface with an average pit mouth diameter of about 66.30 µm.

3.2.2 316 SS/ Bromide system

The pitting corrosion behavior of 316 SS in a bromide containing solution at different solution temperatures was done utilizing the cyclic polarization techniques and surface microscopic examination. Fig.11, Fig.12 and Table 5 present the pitting and corrosion parameter for 316 SS in a 3.5wt% NaBr solution at temperature increase from 20°C up to 50°C. Pitting potential and ΔE showed to decrease with temperature increasing with more than 100 mV differences between the two values which gives an indication of increased susceptibility to pitting corrosion through decreasing the resistance to pitting corrosion. An open mouth pits with 69.77 µm were formed on 316 SS with a salt film deposition inside the pit favoring pits growth rate towards gravity Fig.13.

3.3 Comparison between Cl⁻ and Br⁻ anion

It is well known that the presence of aggressive anion would promote the pitting corrosion to SS alloys by penetrating the film which causes breaking the passive film covering the surface of the metal. This can be seen for instance from Fig. 14, this figure illustrates a marked difference in the Ep values for the 304 SS in comparison to the two prepared aqueous halide salts versus temperature and a higher reduction in Ep values was observed in chloride than bromide. Moreover, the chloride values (Ep) shows to be a 100 mV more negative than that of bromide associated with the fact that chloride was more aggressive than bromide ion. In addition, the same behavior was obtained for pitting resistance ΔE as can be shown in Fig.15, with the same behavior obtained by Leckie, and Uligh, 1966, Kolotyrkin, 1963, Refaey, et al., 2005.
Dawood, and Szklarska-Smialowska, 1986 reported that the aggressiveness of halide decreased in the order Cl⁻ > Br⁻, in contrast to the anion radius Cl⁻ < Br⁻.

Pitting corrosion promotes by the presence of halide anion especially chloride anion which is more mobile in solution, small ion size can easily penetrate the passive film and allowed the formation of pitting corrosion due to the halide properties Talbot, 1998, Jones,1996, Loto, 2015.

Pardo et al., 2000, observed a decrease in the ΔE values for two high alloys SS in a solution with different chloride concentration and temperature and mentioned that the higher the ΔE values lead to the higher resistance to the pitting corrosion.

The pits were also imaged in SEM microscope. These observations proved that the surface of the alloy was covered with a high density of pits not only around the MnS inclusion but also upon the surface defect especially in bromide-containing solution as well as these formed at the boundary of grains illustrated in the cavity bottom, these results were in accordance with Tzaneva, et al., 2006.

Abd El Meguid, 2007, stated that the pits morphology of SS alloys under chloride attack are not hemispherical but grew under the metal surface, growth in a numerous point to make a lacy pattern.

Fig. 16 illustrated the difference in pits formed on 316 SS in bromide compared to chloride solutions; one can see that an isolated circular pit with salt deposition in the pit cavity was pronounced in bromide while a one large pit composed of different pits formed in chloride solution, both pits are of open mouth, which enhances the repassivation process.

4. CONCLUSIONS
1. Stainless Steel grades 304 and 316 are susceptible to pitting corrosion attack in chloride and bromide containing media with different extent depending on the anion aggressivity and size.
2. Pitting corrosion resistance decreased as $E_p$, $E_{rep}$, and $\Delta E$ decrease with the solution temperatures increase from 20 to 50°C in both studied halide salt solutions for 304 SS and 316 SS.
3. A 100 mV difference was observed for 304 SS in chloride solution compared to bromide solution (chloride more aggressive than bromide) and this difference increases with solution temperature increase the resistance to pitting corrosion decreased.
4. A non-hemispherical or irregular pit with a lacy cover formed on 304 SS and 316 SS surfaces in chloride containing solution compared to an open mouth isolated circular pits in 3.5 wt% Bromide solution.
REFERENCES


**NOMENCLATURE**

Ecorr. = corrosion potential, mV  
EDX= Energy Dispersive X-Ray  
Ep= pitting corrosion potential, mV  
Erep= repassivation potential, mV  
Ip= pitting current density at Ep values, mA/cm²  
SCE= standard calomel electrode  
Sec= time, second  
SEM= Scanning Electron Microscope  
SS= Stainless Steel  
X= Halide type (Cl⁻ and Br⁻)  
ΔE= potential area difference = Ep-Ecorr, mV

**Table 1.** Chemical composition of studied alloys in wt%.

<table>
<thead>
<tr>
<th>Fe-Cr-Ni. wt%</th>
<th>Ni</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>Mo</th>
<th>S</th>
<th>Cu</th>
<th>P</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 SS</td>
<td>9.7</td>
<td>19.3</td>
<td>0.06</td>
<td>1.37</td>
<td>0.122</td>
<td>&lt;0.005</td>
<td>0.198</td>
<td>&lt;0.005</td>
<td>0.986</td>
<td>Bal.</td>
</tr>
<tr>
<td>316 SS</td>
<td>8.67</td>
<td>17.1</td>
<td>0.09</td>
<td>1.5</td>
<td>2.66</td>
<td>&lt;0.005</td>
<td>0.177</td>
<td>&lt;0.005</td>
<td>0.67</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
**Figure 1.** Full electrochemical system for polarization studies.

**Figure 2.** The cyclic polarization curve for 304 SS in 3.5wt% NaCl solution vs. temperature change (20-50)°C.
**Figure 3.** The variation of pitting, corrosion and potential area difference with temperature for 304 SS in 3.5wt% NaCl.

**Table 2.** Pitting, corrosion and resistance potential characteristic to pitting corrosion for 304 SS at different temperature in 3.5wt% sodium chloride solution.

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>Ep mV</th>
<th>Ecorr mV</th>
<th>Current ip µA/cm² at Ep</th>
<th>ΔE=Ep-Ecorr mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>333.2</td>
<td>-227</td>
<td>4.4</td>
<td>560.2</td>
</tr>
<tr>
<td>30</td>
<td>305.1</td>
<td>-236</td>
<td>9.9</td>
<td>541.1</td>
</tr>
<tr>
<td>40</td>
<td>216.4</td>
<td>-257</td>
<td>15.5</td>
<td>469.5</td>
</tr>
<tr>
<td>50</td>
<td>94.3</td>
<td>-253.3</td>
<td>8.5</td>
<td>407.9</td>
</tr>
</tbody>
</table>

**Figure 4.** The SEM observation of 304 SS after applying cyclic polarization techniques in 3.5wt% NaCl at 50°C at different locations and at(a 50 and b 100) µm magnification.
Figure 5. Cyclic polarization curves for 316 SS in 3.5wt% NaCl at temperature (20-50)°C

Table 3. Pitting corrosion, free corrosion, potential area difference and Ip versus Temperature for 316 SS in 3.5wt% NaCl solution.

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>316 SS in 3.5wt% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ep mV</td>
</tr>
<tr>
<td>20</td>
<td>496.9</td>
</tr>
<tr>
<td>30</td>
<td>412.2</td>
</tr>
<tr>
<td>40</td>
<td>350</td>
</tr>
<tr>
<td>50</td>
<td>237</td>
</tr>
</tbody>
</table>
Figure 6. The variation of Ep, Ecorr and potential area difference vs. solution temperature (20-50°C) for 316 SS in 3.5wt% NaCl.

Figure 7. The SEM observation of 316 SS in 3.5wt% NaCl solution at 50°C.
Figure 8. Cyclic polarization curve of 304 SS in 3.5wt% NaBr at varying temperature range (20-50)°C.

Table 4. Pitting potential Ep, corrosion potential Ecorr, Ip pitting current density and potential area ΔE versus solution temperature for 304 SS in 3.5wt% NaBr.

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>304 SS in 3.5wt%NaBr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ep mV</td>
</tr>
<tr>
<td>20</td>
<td>405</td>
</tr>
<tr>
<td>30</td>
<td>400</td>
</tr>
<tr>
<td>40</td>
<td>362</td>
</tr>
<tr>
<td>50</td>
<td>352</td>
</tr>
</tbody>
</table>

Figure 9. Pitting Ep, corrosion Ecorr, and potential area difference ΔE of 304 SS in 3.5wt%NaBr determined by cyclic polarization test vs. temperature range (20-50)°C.
Figure 10. Scanning Electron Microscopy SEM of 304 SS in 3.5wt%NaBr at 50 °C.

Figure 11. Cyclic polarization curves for 316 SS alloy in 3.5wt% NaBr at temperature (20-50)°C.
Table 5. The pitting potential Ep, Corrosion potential Ecorr, ΔE potential difference vs. temperature in °C for 316 SS in 3.5wt% NaBr.

<table>
<thead>
<tr>
<th>Temp./C</th>
<th>316 SS in 3.5wt%NaBr</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Ep mV</td>
<td>Ecorr mV</td>
</tr>
<tr>
<td>20</td>
<td>450</td>
<td>-213</td>
</tr>
<tr>
<td>30</td>
<td>428</td>
<td>-217</td>
</tr>
<tr>
<td>40</td>
<td>391.8</td>
<td>-212</td>
</tr>
<tr>
<td>50</td>
<td>380</td>
<td>-202</td>
</tr>
</tbody>
</table>

Figure 12. Pitting Ep, corrosion Ecorr, and potential area difference ΔE of 316 SS in 3.5wt%NaBr determined by cyclic polarization test vs. temperature range (20-50)°C.
Figure 13. Scanning Electron Microscope SEM for 316 SS after cyclic polarization test in 3.5wt%NaBr.

Figure 14. Pitting potential Ep comparison between Cl⁻ and Br⁻ halide of 304 SS vs solutions temperature.
Figure 15. The reduction in ΔE values of 304 SS under halide anion effect at different temperatures.

Figure 16. Halide pitting corrosion on 316 SS a for 3.5wt% NaCl while b in 3.5wt% NaBr solution at 50 μm magnification.