A comparative \( \text{H}_2\text{S} \) corrosion study of 304L and 316L stainless steels in acidic media

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\begin{abstract}
\text{H}_2\text{S} \) corrosion of 304L and 316L in oxygen-free \( \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S} \) solution at pH 3 and temperature of 60 °C were investigated by EIS, potentiotodynamic polarisation, multi-component Pourbaix diagrams and microstructure characterization. At similar conditions, lower corrosion rate was observed on 316L, attributed to its denser (1.5 times) and smoother (6%) surface layer and confirmed by SEM micrograph. During polarisation, \( \text{H}_2\text{S} \) increases significantly the critical current density on 304L and passivation current density, \( i_p \), on 316L. Higher \( i_p \) on 316L was associated to simultaneous \( \text{FeS}_2–\text{MoS}_2 \) preservation, confirmed by XRD examination. \( \text{H}_2\text{S} \) could have an inhibiting effect on 304L in passivity region.
\end{abstract}

1. Introduction

In most oil and gas purification processes, the corrosion rate of metals is accelerated by the presence of sulfur containing ions such as \( \text{S}_2\text{O}_3^{2-}, \text{SO}_4^{2-}, \text{HS}^- \) and also \( \text{H}_2\text{S} \) species \[1,2\]. Among these compounds, hydrogen sulfide (\( \text{H}_2\text{S} \)) is an extremely toxic component and with increasing the corrosion rate, accelerates the steel structure deterioration. To obtain a better protection against \( \text{H}_2\text{S} \) corrosion, it is recommended to use special carbon steels or even higher corrosion resistant alloys such as austenitic stainless steels \[1–2\].

The \( \text{H}_2\text{S} \) corrosion mechanism of various alloys is being anticipated, but due to high toxicity of this compound, the available experimental results are limited. \( \text{H}_2\text{S} \) corrosion studies on some carbon steels at laboratory scale and with high safety facilities have been reported by others \[3–7\]. The results indicated that in desired pH and immersion time, \( \text{H}_2\text{S} \) in an acidic media increases the impedance of carbon steel compared to solutions without \( \text{H}_2\text{S} \). This was attributed to the precipitation of a sulfide film on the carbon steel surface in the \( \text{H}_2\text{S} \)-containing solution \[3–8\]. It was stated that depending on the solution pH, the chemical composition of the surface layer is most likely Mackinawite (\( \text{FeS}_{1–x} \)), cubic férrous sulfide or pyrohite (\( \text{FeS} \)), Troilite (\( \text{FeS}_{1+x} \)) and Pyrite (\( \text{FeS}_2 \)) \[6–13\]. In sequential papers, the \( \text{H}_2\text{S} \) corrosion on pure Fe, Cr, and Ni have been studied in simulated experimental conditions with trace amounts of local \( \text{H}_2\text{S} \) produced by added \( \text{Na}_2\text{S} \) dissociation \[14–17\]. It was found that depending on \( \text{H}_2\text{S} \) concentration, solution pH and immersion time, \( \text{H}_2\text{S} \) could have an inhibiting or accelerating effect on the corrosion of pure Fe and Ni \[14–15,17\]. On Cr, although various corrosion reactions could occur, the corrosion rate generally increases by the presence of \( \text{H}_2\text{S} \) \[16\]. However, in referred papers, \( \text{H}_2\text{S} \) corrosion studies on alloys containing Fe, Ni, and Cr were not reported.

Electrochemical impedance spectroscopy (EIS) was found to be effectively useful for characterization of the surface layers and identifying the \( \text{H}_2\text{S} \) corrosion mechanisms \[7,17\]. The difference observed in corrosion behavior of 304L and 316L was associated to the presence of additional molybdenum alloying element in 316L, confirmed by surface analysis techniques \[18\]. It was detected that Mo participates in surface reactions and enhances the protectiveness of surface layer formed on the alloy surface \[18\]. However, up to now, a comparative EIS study of \( \text{H}_2\text{S} \) corrosion of 304L and 316L stainless steel in acidic media at temperatures higher than room temperature has not been carried out \[19–21\].

In this paper, EIS measurements in conjunction with open circuit potential (OCP), linear polarisation resistance (LPR), and potentiotodynamic polarisation (PD) tests and surface microstructural characterization were performed to investigate the \( \text{H}_2\text{S} \) corrosion of 304L and 316L stainless steels in acidic media at 0, 5 and 15 ppm (by mole) concentrations of \( \text{H}_2\text{S} \) and in a temperature of 60 °C. A comparison between the experimental results and multi-component Pourbaix diagrams of Fe, Ni, Cr, and Mo systems in the presence of sulfur components was also performed.

2. Methods and materials

Analytical grade \( \text{Na}_2\text{SO}_4 \), \( \text{Na}_2\text{S} \), and \( \text{H}_2\text{SO}_4 \) reagents were used. To prepare the solution, 1 M \( \text{Na}_2\text{SO}_4 \) solution was buffered by
H₂SO₄ to a pH of 3. To exclusively investigate the H₂S corrosion mechanism, it is common to purge an inert gas into the solution to remove dissolved oxygen [14–17]. Otherwise, several involved cathodic reactions could interfere (oxygen and HS⁻ reduction). Prior to each experiment, the prepared solution was purged by inert gas (Argon) for 15 min. Then a required amount of Na₂S, producing 5 and 15 ppm H₂S, was added to the solution (All concentrations are reported in ppm by mole). According to the following reaction, Na₂S is dissociated to H₂S in acidic solution [2–5,11,12,21–22]:

\[
\text{Na}_2\text{S} + 2\text{H}^+ \rightarrow 2\text{Na}^+ + \text{H}_2\text{S}
\]  

(1)

As a result, a trace amount of H₂S is locally generated at the vicinity of alloy surface. It should be emphasized that the argon purging and deoxygenating were continuously applied during all measurements. A sealed electrochemical flat-cell (with 500 cm² in volume) was used and prior to adding Na₂S, the inert gas was purged into the solution (with 4.5 bar pressure). After adding Na₂S (and producing H₂S), argon was purged above (not into) the solution at a safe distance from the solution surface with lowest possible pressure just to avoid oxygen entrance. This could help to avoid any decreasing in H₂S concentration during measuring time.

All measurements were performed three times to assure reproducibility. All corrosion tests were carried out by an Ivium Potentiostat instrument, using saturated calomel and Pt wire as reference and counter electrodes, respectively. Ivium and EIS Spectrum Analyzer were used to extract the EIS equivalent circuit components. Simulated data was fitted by less than 1% error in calculation.

All measurements were performed in a water bath with a controlled temperature of 60 ± 1°C. This temperature represents actual conditions for gas purification units. To identify the influence of alloying elements, the experimental results were finally compared with multi-component Pourbaix diagrams of Fe-Ni-Cr (304L) and Fe-Ni-Cr-Mo (316L) aqueous systems and in the presence of H₂S species. All Pourbaix diagrams were plotted at 60°C by using Medusa software [23]. An equilibrium concentration of 10⁻⁶ M has been used for dissolved Fe, Ni, Cr and Mo ions (i.e. [Fe²⁺(aq)] = [Cr³⁺(aq)] = [Ni²⁺(aq)] = [Mo⁴⁺(aq)] = 10⁻⁶ M). It should be noticed that in Me-S-H₂O systems (where Me = Fe, Ni, Cr, and Mo), some other species may be also existed which may not be taken into account such as FeCr₂O₄, NiFe₂O₄, NiCr₂O₄, etc. [24]. However, as can be seen in the reference, [24], these compounds are most likely stable at neutral and alkaline conditions. Therefore, most likely they have no contribution in the present study.

Finally, scanning electron microscopy (SEM, Leica Cambridge, S360) and XRD (Bruker model D8 ADVANCE) were used to characterize the samples surface morphology and compositions after exposure to the H₂S corrosive media.

3. Results and discussion

3.1. OCP results

The results of OCP variations are shown in Fig. 1. In all H₂S concentrations, the OCP values associated to 316L alloy are more positive than 304L, but their difference diminishes by increase in H₂S concentration. As seen in Fig. 1, increase in H₂S concentration decreases OCP of both alloys. For instance, in 316L alloy, its decrease is almost three times higher than 304L at 5 ppm H₂S concentration. Decrease in OCP is an indication of alloy nobleness deterioration and surface activity acceleration.

3.2. LPR results

Fig. 2 represents the influence of H₂S concentration on LPR (polarisation resistance, Rp) values. In all H₂S concentrations, the Rp value of 316L is higher than for 304L. However, by an increase in the H₂S concentration, the decrease in Rp value of 316L is quicker than for 304L. This means that the results of the LPR and OCP measurements follow a similar trend. The corrosiveness of the solution increases by an increase in H₂S concentration to 5 ppm. For 316L alloy, the Rp decrease is six times higher than that one for 304L. Accordingly, the corrosion rate of both alloys increases. Although the 316L alloy has a higher corrosion resistance compared with the 304L alloy, the difference reduces by increase in H₂S concentration. This indicates that the influence of H₂S is more profound on the 316L alloy.

The influence of H₂S on cathodic reactions including proton reduction is as follows [14–17]:

\[ \text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^- \]  

(2)

\[ \text{HS}^- \rightarrow \text{H}^+ + \text{S}^{2-} \]  

(3)

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \text{or 2H} \]  

(4)

Table 1

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
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</thead>
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<td>304L</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.30</td>
<td>1.62</td>
<td>0.46</td>
<td>18.13</td>
<td>8.71</td>
<td>Bal .</td>
</tr>
<tr>
<td>316L</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>2.32</td>
<td>1.71</td>
<td>0.49</td>
<td>18.16</td>
<td>8.25</td>
<td>Bal .</td>
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Fig. 1. OCP variations of 304L and 316L alloys vs. H₂S concentration (ppm by mole) in Na₂SO₄ + Na₂S (pH 3).
A decrease in corrosion resistance by introducing H2S in both 304L and 316L alloys can be associated to the increase in proton reduction, equations 2–4, and consequently anodic dissolution. In addition, sulfide ions can act as surface catalysts and speed up the anodic dissolution which can be distinguished in LPR and OCP results. Iron anodic reactions can be represented by the following reactions [14,17]:

\[
\text{Fe} + \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{Fe(HS)}^{-} + \text{H}_3\text{O}^{+} \tag{5}
\]

\[
(\text{FeHS}^{-})_{\text{ads}} \rightarrow (\text{FeSH}^{+})_{\text{ads}} + 2\text{e}^{-} \tag{6}
\]

\[
(\text{FeSH}^{+})_{\text{ads}} + \text{H}_3\text{O}^{+} \rightarrow \text{Fe}^{2+} + \text{H}_2\text{S} + \text{H}_2\text{O} \tag{7}
\]

Consequently, the dissolution of iron is accelerated. In fact, it has been reported that on pure iron, H2S plays an accelerative role on both the anodic iron dissolution and the cathodic hydrogen evolution [14,17]. The difference in corrosion behaviour of 304L and 316L can be related to the chemical reactions involved by other alloying elements such as Cr, Ni, and Mo which is discussed in the following sections.

3.3. EIS results

Figs. 3 and 4 show the Nyquist and Bode plots of 304L and 316L specimens at 60°C and different H2S concentrations. Various equivalent circuits have been proposed for H2S corrosion [7,10,14–17,20]. Certainly, complex reactions could occur on the surface (particularly since the Cr, Ni are active and FeS2 and MoS2 are formed in this pH), but their reaction steps could not be separated. For this reason, the possible and separated reaction steps of the alloying elements were borrowed from the previous studies where H2S corrosion of the pure Cr, Ni, and Fe elements were investigated individually [14–17]. In all conditions, the Nyquist curves indicate a single capacitance loop having a time constant in Bode plots. Therefore, the alloy-electrolyte interface can be simulated by an Randles equivalent circuit as shown in the inserted graph in Fig. 3, where \( R_{\text{s}} \) is the solution resistance, \( R_{\text{p}} \) is the polarisation resistance at the alloy–electrolyte interface (also known as charge transfer resistance) and CPE is the constant phase element. The CPE value can be expressed in the form of \( P(i\omega)^n \) in which \( P \) is proportional to the capacitance, \( n \) is a parameter related to surface roughness and cell configuration, and \( \omega \) is the angular frequency. Applying CPE instead of pure capacitance improves EIS data fitness of the experimental results [25,26]. EIS data simulation on wide frequency spectrum, \( 10^5 \) to \( 10^{-3} \) Hz (not shown here) also indicates that a charge transfer resistance condition occurs in the surface reactions. Although, presence of H2S does not induce any other time constants, however, a decrease in the capacitance loop diameter and charge transfer resistance can be observed by an increase in the H2S concentration. Therefore, the EIS results can be used to identify the corrosion mechanism by the presence of H2S species.

Extracted fitted data from the equivalent circuits are shown in Table 2. The \( R_{\text{p}} \) values obtained by EIS are very similar to the \( R_{\text{p}} \) values obtained by LPR measurements (with less than 5% difference), Fig. 2. Comparing Nyquist curves of the two alloys depicts that in all H2S concentrations, the semicircle diameter associated with 316L is larger than for 304L. In solution without H2S, \( R_{\text{p}} \) of 316L is about three times larger than for 304L. However, by an increase in the H2S concentration, \( R_{\text{p}} \) of both alloys reduce more or less with the same trend. It seems that although the 316L alloy has a greater corrosion resistance at solution without H2S, its superior performance is diminished by an increase in the H2S concentration. Therefore, the EIS results can be used to identify the corrosion mechanism by the presence of H2S species.

The n and C parameters extracted from CPE are shown in Fig. 5. Although in solution without H2S, the n value in 316L is smaller than for 304L, however, as shown in Fig. 5, in solution with H2S, the n values in 316L are greater than for 304L. For the 304L alloy, an increase in the H2S concentration to 5 ppm results in rapid decrease of n value from 0.89 to 0.77. A slight decrease down to 0.77 could be observed by further increase in H2S concentration. For the
316L alloy, the n value decreases slightly from 0.83 to 0.81 by the presence of 5 ppm H$_2$S, but remains almost constant by further increase in H$_2$S concentration. A decrease in the n value is an indication of surface roughening which is due to an increase in the alloy surface dissolution [22,25,26]. Therefore, a more rapid decrease in the n value for the 304L alloy indicates that the H$_2$S influence on the 304L surface roughness is greater than on the 316L alloy. In other words, in 316L, H$_2$S does not affect the surface roughness; consequently the n value does not change significantly. This means that in solution without H$_2$S, the surface roughness of 316L is 7% higher than 304L. In contrast, by producing H$_2$S, the surface roughness on 304L is 6% higher than 316L.

Surface capacitance values were calculated and plotted in Fig. 5(b), according to the following equation [25,26]:

$$ C_{ct} = \frac{n \sqrt{P(R_p)^{1-n}}} $$

In 304L alloy, in presence of 5 ppm H$_2$S, $C_{ct}$ decreases rapidly from 118 to 23.6 $\mu$F cm$^{-2}$ and by further increase in H$_2$S concentration it increases slightly to 37.4 $\mu$F cm$^{-2}$. On the other hand, in 316L alloy, the $C_{ct}$ value increases steadily by an increase in H$_2$S concentration from 27.2 to 56.0 $\mu$F cm$^{-2}$. It is well known that the capacitance is inversely proportional to the surface film thickness according to [22,25,26]:

$$ C_{ct} = \frac{\varepsilon_0 e S}{d} $$

where $d$ is thickness of the surface film, $S$ is surface area of the electrode, $\varepsilon_0$ is the permittivity of air and $\varepsilon$ is the local dielectric constant. Therefore, an increase in $C_{ct}$ is an indication of surface layer dissolution and thinning process. The 316L alloy has a greater $C_{ct}$ in compare with 304L which indicates that it has a thinner surface layer. But since it has greater n, its surface layer is more uniform and condensed. Comparing C values indicates that in H$_2$S-free solution, the surface layer thickness of 316L is 4–5 times thicker than

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<th>Table 2</th>
<th>Extracted fitted data from EIS test.</th>
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<tr>
<td>H$_2$S Conc. (ppm)</td>
<td>$R_s$ ((\Omega) cm$^2$)</td>
</tr>
<tr>
<td>304L</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>316L</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
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<td></td>
<td>15</td>
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</table>
In contrast, by producing H$_2$S, the surface layer thickness on 316L becomes 1.5 times thinner than 304L.  

Fig. 6 shows SEM images of rinsed and dried specimens after exposure to 15 ppm H$_2$S solution. Clearly, a general attack (without any evidence for localized corrosion) was observed on both alloy surfaces. Furthermore, on 304L, the attacked surface is rougher and more heterogeneous than the 316L, confirming the n variations obtained by EIS in Fig. 5. Formation of surface layer on 316L with less porosity can be associated to the beneficial influence of molybdenum alloying element (see Section 3.5). Moreover, it seems that thicker layer with higher porosities formed on 304L leads to crack formation at outmost alloy surface which is clear in SEM images.

In summary, simultaneously C and n comparison can verify that in solution without H$_2$S, surface layer on 304L exhibits a thinner and more uniform characteristic. However, H$_2$S develops a rougher and thicker surface layer. In the case of 316L, in solution with and without H$_2$S, the surface layer is more uniform, compact and does not change significantly.

Based on above EIS (calculated n and C values) and SEM results and to exemplify the alloys surface layer evolution, a sketch of the sample cross section can be drawn. Fig. 7 depicts schematic view of relative surface layer thickness and porosity (roughness) variations on two alloys, at OCP condition, after exposure to 0, 5 and 15 ppm H$_2$S containing media. To simplify, specimen in 0 ppm H$_2$S was chosen as bare and the initial air formed oxide layer, FeO–Cr$_2$O$_3$, was not shown. In fact, air formed oxide is almost dissolved in the present solution and is replaced by the sulfide layer (see Section 3.5). The scheme shows that a thicker and more porous surface layer on 304L is formed. More details of identified layer constituents, FeS$_2$ and MoS$_2$, will be discussed in Section 3.5.

### 3.4. Potentiodynamic polarisation results

Potentiodynamic (PD) polarisation results are shown in Fig. 8. Since in all experimental conditions, the solutions are basically sulfur containing, in the absence and presence of H$_2$S, similar active-passive behaviour is observed in which a critical current density, i$_{cr}$, for both alloys could be obtained. The variations of i$_{cr}$ and passivation current density, i$_{p}$, at 500 mV anodic overpotential (vs. SCE) were plotted in Fig. 9. Generally, in all conditions, i$_{cr}$ in 316L is smaller than in 304L. Therefore, passivation on 316L is easier than on 304L. The i$_{cr}$ value increases in both alloys, five and ten times in 304L and 316L, respectively, by an increase in H$_2$S concentration from 0 to 15 ppm. This means that H$_2$S retards the formation of passive layer on both alloys. However, the influence of H$_2$S on hindering the passivation of 316L alloy is greater than for 304L. In solution with 15 ppm H$_2$S, this ratio decreases to 2.5.

Interestingly, changes in passivation current density, i$_{p}$, are different from i$_{cr}$. In solution with 0 and 5 ppm H$_2$S, i$_{p}$ of 316L is smaller than 304L. In 304L, by an increase in H$_2$S concentration to 15 ppm, i$_{p}$ decreases from 0.69 to 0.077 mA cm$^{-2}$, about 10 times. Conversely, in 316L, by an increase in H$_2$S concentration to 15 ppm, i$_{p}$ increases from 0.17 to 1.12 mA cm$^{-2}$, about 5 times. As a result, in a solution with 15 ppm H$_2$S, i$_{p}$ of 316L becomes higher than 304L. This means that H$_2$S could create a more favorable condition for sulfide layer formation on 304L at high enough potentials in the passivation range (in compare with 316L).

To sum up, considering both i$_{cr}$ and i$_{p}$ values for 304L, it can be concluded that in spite of difficulties for passivation (high i$_{cr}$), the alloy exhibits a passive layer with more integrity (lower i$_{p}$). On the other hand, on 316L, the passivation could occur more easily. However, the passive layer possesses a lower corrosion resistance in compare with 304L. Identifying the current peaks on PD results and analogous surface reactions on alloys surface is discussed below.

### 3.5. Pourbaix diagrams

The passivation behaviour of two alloys can also be investigated in more details by using multi-component Pourbaix diagrams. To do this, a comparison between EIS, PD results and multi-component Pourbaix diagrams of Fe, Ni, Cr, and Mo systems in the absence and presence of sulfur components was performed. According to the Pourbaix diagrams of Fe, Ni, and Cr (alloy constituents of 304L), Figs. 10 and 11, in the presence of H$_2$S and at pH 3 (shown as red dashed line), the passivation of 304L could be associated to the formation of FeS$_2$ in the surface layer (gray region in Fig. 10 (a)–(b)); The following reaction [27–30]:

$$\text{Fe} + 2\text{H}_2\text{S} \rightarrow \text{FeS}_2 + 2\text{H}_2$$

(10)

Regarding to the presence of FeS$_2$ and/or FeS as surface layer constituents, it has been reported that FeS$_2$ and FeS have more stability in acidic and alkaline conditions, respectively, which is similar to the present results, Fig. 10 (b). The following equilibrium reaction exists between FeS$_2$ and FeS [27,28]:

$$\text{FeS}_2 + \text{H}_2\text{S}^{(aq)} \leftrightarrow \text{FeS}_2 + 2\text{H}^+ + 2\text{e}^-$$

(11)
During sample rinsing and drying for SEM imaging and XRD characterization, pyrite may be decomposed to the pyrrhotite as follows [27,28]:

\[
3\text{FeS}_2 + 2\text{H}_2\text{O} \rightarrow 3\text{FeS} + 3\text{H}_2\text{S} + \text{SO}_2
\] (12)

However, studies of pyrite reactions are even more contradictory, the products being listed variously as FeSO₄, Fe₂(SO₄)₃, FeO, Fe₂O₃, FeS, H₂SO₄ or S either as single products or as complex mixture [27–29]. XRD characterization was also performed on rinsed and dried specimens. Figure 13 reveals XRD results on 304L and 316L samples exposed to 15 ppm H₂S containing media. Presence of FeS₂ on both alloys and MoS₂ on 316L is clear. Moreover, FeS and MoO₂ components also exist. This is enough to conclude that the sulfur-bearing Fe compounds and MoS₂ surface layer are formed. Since XRD is an ex-situ technique and it is performed on sample after washing and drying, its results do not exactly resemble the actual corrosion products during aqueous corrosion occurrence [27,28]. Recently, X-ray photoelectron spectroscopy (XPS) studies of surface layer on H₂S attack on 316L also revealed that relatively high concentration of sulfur could be found inside the formed oxide, which indicates that sulfur entered the oxide film through local weakening of the oxide [19]. In fact, using an in situ technique would be further supportive to identify S compounds in the surface layer during corrosion phenomenon.

At higher potentials, FeS₂ is replaced by iron oxide, Fe₂O₃ (and consequently iron hydroxide), as seen in Fig. 10. This means that by detaching the sulfur species from the surface at high enough potentials, hydroxyl ions could take an opportunity to reach the surface and iron oxide could be formed [18,23–24]. This can be confirmed by an extra peak in the passivation region of 304L PD results at a overpotential of about 1000 mV vs. SCE; See Figs. 8 and 9(a). The Pourbaix diagram does not show any stability region for FeS at the present investigated conditions which has been reported previously on carbon steel [6,13].

Moreover, Cr and Ni do not exhibit a passive layer at pH 3, based on Pourbaix diagrams. Following reactions could be proposed for dissolution process [15,16]:

\[
\text{Ni} + \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow (\text{NiHS})_{\text{ads}} + \text{H}_3\text{O}^+ + e^-
\] (13)

\[
(\text{NiHS})_{\text{ads}} \rightarrow \text{NiH}^+ + e^-
\] (14)

\[
\text{NiH}^+ + \text{H}_2\text{O}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2\text{S} + \text{H}_2\text{O}
\] (15)

and

\[
\text{Cr} + \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow (\text{CrSH}^-)_{\text{ads}} + \text{H}_3\text{O}^+
\] (16)

\[
\text{Cr} + \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow (\text{CrSH})_{\text{ads}} + \text{H}_3\text{O}^+ + e^-
\] (17)

\[
(\text{CrSH})_{\text{ads}} \rightarrow (\text{CrSH})_{\text{ads}} + e^-
\] (18)

\[
\text{CrSH}^- + \text{H}^+ \rightarrow \text{Cr}^{2+} + \text{H}_2\text{S}
\] (20)

According to the Pourbaix diagrams of Fe, Ni, Cr, and Mo (alloy constituents of the 316L alloy), Figs. 10–12, the passivation in low anodic overpotential could be mainly associated to formation of FeS₂. Eq. (10) and also MoS₂, as below [19–20,23]:

\[
\text{Mo} + 2\text{H}_2\text{S} \rightarrow \text{MoS}_2 + 2\text{H}_2
\] (21)
This can be confirmed by a decrease in current density after \(i_{cr}\).

At higher potentials, replacement of MoS\(_2\) by MoO\(_2\) could be predicted by the following reaction \([19–20,23]\):

\[
\text{MoS}_2 + 2\text{H}_2\text{O} \rightarrow \text{MoO}_2 + 2\text{H}_2\text{S}
\]

This can be observed as a second current peak in PD results, Fig. 8(b), at overpotential of about 500 mV. Again Fe\(_2\)O\(_3\) (and iron hydroxide in aqueous solution, \([18]\)) could be formed at overpotentials higher than 1000 mV which is similar to the 304L, distinguished by the third current peak in Fig. 8(b).

In brief, the greater corrosion resistance of 316L in H\(_2\)S solutions resulted by LPR and EIS methods can be exclusively associated to its molybdenum content and formation of sufficient MoS\(_2\) component. Research performed on individual alloying elements Cr, Ni, and Mo in media containing reducing sulfur species and H\(_2\)S revealed greater corrosion resistance of Mo in comparison with the two other alloying elements, i.e. Ni and Cr \([18]\). In both alloys, in acidic media, the alloy surface is covered by HS\(^-\) and S\(^2-\). In 304L alloy, Fe tends to thermodynamically form a sulfide compound, FeS\(_2\), which shows some protective ability of the surface layer. Noticeably, Cr and Ni could not help to form a protective layer in the form of Cr\(_2\)O\(_3\) or NiS at pH 3. However, in 316L, MoS\(_2\) could contribute to passivation improvement as seen in the EIS and PD results; Figs. 4 and 8(a) at low potential region. By increase in H\(_2\)S concentration, on 304L, the iron sulfide layer thickness increases as the surface capacitance decreases, Fig. 5(b). However, dissolution of Cr and Ni leads to a rougher porous surface layer as the \(n\) value decreases in Fig. 5(a). On 316L, the surface layer contains both FeS\(_2\) and MoS\(_2\) compounds and contribution of Mo sulfide layer leads to generation of a more compact surface layer (increase in the \(C\) value in Fig. 5(b) on 316L). Meanwhile, the \(n\) value remains almost constant, Fig. 5(a), i.e. the surface is smoother in compare with 304L alloy (despite increase in H\(_2\)S concentration).

In addition, since FeS\(_2\) gives a less protective layer in comparison with FeS\(_2\) + MoS\(_2\), 304L reveals a higher critical current density. On 316L, Mo could improve the passivation by forming MoS\(_2\), particularly in presence of H\(_2\)S. By further increase in H\(_2\)S concentration, however, FeS\(_2\) formation condition is more favorable and the difference between two alloys is reduced.

At higher H\(_2\)S concentrations, high passivation current density on 316L can be associated to the fact that two sulfide compounds, FeS\(_2\) and MoS\(_2\) must be maintained simultaneously on the alloy surface. In contrast, on 304L, the passivation current is only consumed by FeS\(_2\). Therefore, at higher potentials in the passive region, FeS\(_2\) could somewhat induce an inhibiting effect on 304L. This phenomenon has been reported previously on carbon steel where H\(_2\)S begins to exhibit its inhibitive effect with the formation of mackinawite and its conversion to a more protective layer such as troilite \([5,7–13]\). Moreover, it is reported that molybdenum intermittently could cause sulfur species detachment from the surface and thinning of the surface layer \([18,23]\). This can be verified by observing a higher capacitance of the surface layer and passivation current density on 316L in compare with 304L.

It should be noticed that the pH value has inevitably a crucial effect on passivation behaviour as can be seen in Pourbaix diagrams in Figs. 10–12. This is an important issue since in practical...
applications, for instance gas purification processes, an increase in the pH value (due to process variations) could change the situations to the region where chromium oxide and nickel sulfide can be formed, Figs. 10 and 11, and significantly assist the alloy passivation [23]. Interestingly, recent investigations on 316L stainless steel in alkaline solution containing sulfur (NaOH + Na2S) revealed that sulfide has profound effect on the corrosion behaviour. It was stated that sulfide prevents formation of a stable passive film, most probably via adsorption on the surface. As a result, the dominant mechanism of corrosion in sulfide-containing environments becomes similar to active dissolution, which could lead to significant material losses [20]. Betova et al. [20], reported that addition of Na2S has negligible influence on corrosion of pure molybdenum due to the considerably higher kinetic stability of the surface film. This could explain the use of pure Mo as a reference electrode in sulfur-containing solutions.

In addition, in most applications, due to process variables, temperature fluctuations are inevitable which can have a vital effect on H2S corrosion reactions [1–2]. In other words, in addition to the H2S concentration, temperature variations can certainly affect the kinetic parameters, in particular the conditions for surface layer formation [18,25]. Thus, a quantitative study of the temperature influence of H2S corrosion of 304L and 316L stainless steel in acidic media to accurately recognize its importance is needed.

Recent studies on carbon steel (AISI-1020) at high temperature (90 °C) showed that alloy corrosion rate increased significantly.
4. Conclusions

The influence of laboratory-produced H₂S by Na₂S (0, 5 and 15 ppm by mole) on the corrosion behaviour of 304L and 316L austenitic stainless steels in an oxygen-free Na₂SO₄ + Na₂S solution at pH 3 and temperature of 60 °C was investigated. The results can be summarized as follows:

(1) OCP, LPR and EIS results showed almost similar trends in corrosion behaviour of the two alloys. However, a lower corrosion rate could be observed for the 316L alloy. EIS results showed a single capacitive loop containing CPE element representing the surface charge transfer reactions. By an increase in H₂S concentration from 0, 5 and then 15 ppm, the corrosion resistance of both alloys diminishes.

(2) Calculated higher n and C values at the 316L alloy–electrolyte interface indicated formation of a 1.5 times denser and 6% smoother surface layer. This has been confirmed by the SEM image from the alloy surface in which a more porous surface layer could be observed on 304L.

(3) Potentiodynamic polarisation results revealed that both alloys exhibit active–passive behaviour during anodic polarisation in which H₂S significantly increases the critical current density on both alloys and noticeably, the passivation current density on 316L.

(4) Multi-component Pourbaix diagrams of constituent alloying elements revealed that on 304L, the surface layer composition is most likely FeS₂, while on 316L, its composition is mainly FeS₂ and MoS₂. This has been confirmed by XRD examination.

(5) Higher passivation current density on 316L was related to the simultaneous upholding of FeS₂ and MoS₂ on the alloy surface. At higher potentials in the passive region, H₂S could induce a noticeable inhibiting effect on 304L by reducing the passivation current density. The presence of Mo could cause sulfur species detachment from the surface and thinning of the surface, distinguishable by a higher capacitance of the surface layer on 316L in comparison with 304L.

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References


