V and Nb Influence on the Austenitic Stainless Steel Corrosion in 0.1 M HCl

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Abstract: Vanadium and niobium were added in AISI309 austenitic stainless steel composition to modify their structure and pitting corrosion resistance in 0.1 M HCl. The structural characterization was carried out by X-rays diffraction and optical microscopy. Corrosion behavior was investigated using potentiodynamic tests and electrochemical impedance measurements (EIS). Results showed that vanadium and niobium addition precipitated stable carbides (VC, NbC) to chromium carbides’ detriment and improved austenitic stainless steel corrosion resistance.

Keywords: Stainless steel, Intergranular precipitation, Corrosion, Vanadium, Niobium, EIS.

1. Introduction

Austenitic stainless steels (ASS) are well known metallic materials; they are widely used in industry: food and beverage, chemical, nuclear, transport and even, recently, in structural uses [1-8]. They have relatively low cost and excellent resistance to uniform corrosion [9, 10]. However, they are prone to localized corrosion such as crevice, pitting, intergranular and intergranular stress corrosion. The intergranular sensitivity is due to carbides rich in chromium formed along the grain boundaries. This process provokes chromium impoverishment in the immediate vicinity. When chromium percentage is below 12 % the depleted areas become prone to corrosion [11–13].

To protect ASS from corrosion, structural stabilization is necessary. The stabilizing elements’ addition to ASS produces several beneficial effects such as intergranular corrosion reduction, void swelling and precipitate strengthening [14]. MC (M = V, Nb, Ti, Zr, Ta) carbides are very stable and invariably present in ASS. Their aim is to reduce M23C6 (M = Cr, Fe, Mo) carbides’ precipitation and its undesirable consequences, particularly susceptibility to corrosion [14, 15].

Niobium addition in ASS enhances the mechanical properties at high temperatures [16] and increases the localized corrosion resistance in NaCl [2]. Vanadium addition (0.5 - 1.0 %) wt. increases the ASS resistance properties without any effect on ductility [17]. Vanadium and Niobium combined addition in ASS is called double stabilization; it has the following advantages: high resistance to raised temperature and better aqueous corrosion resistance. In this work, we study V and Nb effect on the AISI309 austenitic stainless steel corrosion in 0.1 M HCl.
2. Experimental

2.1. Materials

Alloys chemical composition is cited in Table 1. Samples solution treatment is carried out at a temperature of 1100 °C for 4 h then quenched in water.

For metallographic examination, samples are gradually polished by various abrasive papers: 80, 180, 400, 600, 800, and 1200, followed by paste diamond (3µm) polishing. Then, they are chemically attacked by Catella reagent: 10 cm³ HCl, 6 cm³ CH₃COOH, 2g picric acid, 100 cm³ C₂H₅O₁₄ [18].

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI309 (A)</td>
<td>0.4</td>
<td>1.58</td>
<td>0.74</td>
<td>0.01</td>
<td>0.01</td>
<td>0.3</td>
<td>23.9</td>
<td>14.2</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>AISI309+0.14%Nb+1.2%V (B)</td>
<td>0.4</td>
<td>1.54</td>
<td>0.79</td>
<td>0.01</td>
<td>0.01</td>
<td>0.2</td>
<td>23.9</td>
<td>14</td>
<td>0.14</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The X-rays diffraction is also used to characterize microstructures; the results are shown in Fig. 2. For steel A (Fig. 2a), the phases are mainly: gamma-Fe (Fe_γ), carbides Cr_7C_3, Cr_23C_6 and oxides: Cr_2O_3, CrO_3; whereas, for steel B (Fig. 2b) the identified phase are predominant: gamma-Fe (Fe_γ), carbides M_23C_6, Cr_7C_3, VC, NbC and oxides Cr_2O_3, CrO_3. Table 2 presents the each phase proportion; these results are deduced from diffraction spectra by using Reitveld method and software MAUD.

These results’ analysis show that vanadium and niobium addition in steel A reduces the intergranular precipitation quantity of primary Cr_7C_3 and secondary Cr_23C_6 carbides from 17% to 16% and 15% to 10% respectively.

3. Results and Discussion

3.1. Microstructure

Fig. 1 shows steels A and B microstructures; they are composed of austenitic matrix in beige color and precipitates in green color. These latters are in both grain boundaries and grain interiors; steel B boundaries grains’ precipitates quantity is lower than in steel A. Nevertheless, this technique does not allow each phase identification.

The X-rays diffraction method is also used to characterize microstructures; the results are shown in Fig. 2. For steel A (Fig. 2a), the phases are mainly: gamma-Fe (Fe_γ), carbides Cr_7C_3, Cr_23C_6 and oxides: Cr_2O_3, CrO_3; whereas, for steel B (Fig. 2b) the identified phase are predominant: gamma-Fe (Fe_γ), carbides M_23C_6, Cr_7C_3, VC, NbC and oxides Cr_2O_3, CrO_3. Table 2 presents the each phase proportion; these results are deduced from diffraction spectra by using Reitveld method and software MAUD.

These results’ analysis show that vanadium and niobium addition in steel A reduces the intergranular precipitation quantity of primary Cr_7C_3 and secondary Cr_23C_6 carbides from 17% to 16% and 15% to 10% respectively.
Fig. 2. X-ray diffractograms: (a) steel A; (b) steel B.

Table 2. Phases proportion (%) in both steels.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Fe</th>
<th>Cr&lt;sub&gt;23&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;</th>
<th>Cr&lt;sub&gt;7&lt;/sub&gt;C&lt;sub&gt;3&lt;/sub&gt;</th>
<th>NbC</th>
<th>VC</th>
<th>CrO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>54.9</td>
<td>15.55</td>
<td>17.55</td>
<td>-</td>
<td>-</td>
<td>4.19</td>
<td>7.73</td>
</tr>
<tr>
<td>B</td>
<td>66.4</td>
<td>10.11</td>
<td>16.68</td>
<td>0.027</td>
<td>2.053</td>
<td>2.31</td>
<td>5.23</td>
</tr>
</tbody>
</table>

3.1. Potentiodynamic Polarization Measurements

Fig. 3 shows potentiodynamic polarization curves for steel A and steel B in 0.1M HCl. Both steels curves shape is substantially identical; we note passive domain absence. It is attributed to synergetic interaction that exists between the Cl<sup>-</sup> ions chemisorbed on metallic surface and H<sup>+</sup> ions from the solution. These latter are electrostatically attracted by Cl<sup>-</sup> ions that cover the metallic surface and catalyze the dissolution reactions [19-22].

The obtained electrochemical parameters (E<sub>corr</sub>; I<sub>corr</sub>) are (-449 mV; 0.038 mA.cm<sup>-2</sup>) and (-385 mV; 0.012 mA.cm<sup>-2</sup>) for steel A and steel B respectively (Table 3).

Vanadium and Niobium addition in steel A displaces the corrosion potential towards nobler
values and decreases the corrosion current density. Anodic and cathodic Tafel constants are ($\beta_a$=70.4; $\beta_c$=91.3) mV/decade for steel A and steel B respectively. These results show that Vanadium and Niobium addition reduces partially anodic current.

<table>
<thead>
<tr>
<th>Steel</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (mA/cm²)</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$\beta_c$ (mV/dec)</th>
<th>$R_p$ (Ω.cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-449</td>
<td>0.038</td>
<td>70.4</td>
<td>91.3</td>
<td>390</td>
</tr>
<tr>
<td>B</td>
<td>-385</td>
<td>0.012</td>
<td>49.8</td>
<td>204</td>
<td>1340</td>
</tr>
</tbody>
</table>

3.2. Electrochemical Impedance Measurements

Fig. 4 shows the Nyquist diagrams for steel A and steel B in 0.1 M HCl. Impedance diagrams are composed of capacitive loop at high-frequency and inductive loop at low-frequency.

![Fig. 4. Nyquist plots: (a) steel A, (b) steel B in 0.1 M HCl.](image)

The capacitive loop can be attributed to the charge transfer reaction and time constant of the electric double layer. The capacitive loop radius variation is linked to stainless steel (AISI309) passivation process in an aerated solution [23, 24]. Inductive loop at low frequencies can represent the incubation period beginning for pitting corrosion [13]. Bode plots Fig. 5 refers to equivalent circuit existence that contains a single constant phase element in metal/solution interface.

![Fig. 5. Bode diagrams: (a) steel A, (b) steel B in 0.1M HCl.](image)

![Fig. 6. Equivalent circuit representing impedance spectra of steels A and B.](image)

<table>
<thead>
<tr>
<th>Steel</th>
<th>$R_e$ Ω cm²</th>
<th>$C_d$ μF.cm²</th>
<th>$n$</th>
<th>$R_t$ Ω cm²</th>
<th>$R_L$ Ω cm²</th>
<th>$L$ H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9</td>
<td>316.1</td>
<td>0.873</td>
<td>246</td>
<td>1479</td>
<td>4570</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>189.5</td>
<td>0.883</td>
<td>437</td>
<td>2074</td>
<td>5151</td>
</tr>
</tbody>
</table>

These results’ analysis shows that vanadium and niobium addition in austenitic stainless steel AISI309 increases the charge transfer resistance $R_{ct}$ and reduces the double layer capacitance $C_{dl}$. A large $R_{ct}$ is associated with a slower corroding system. Furthermore, a better protection is associated with a decrease in $C_{dl}$, which results from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer [24].
4. Conclusions

Vanadium and niobium are added in AISI309 austenitic stainless steel composition to modify their structure and pit corrosion resistance in 0.1 M HCl.

Microstructures characterization shows that the addition elements (steel B) reduce the intergranular carbides precipitations’ quantity: primary Cr7C3 from 17 % to 16 % and secondary Cr23C6 from 15 % to 10 %.

Electrochemical parameters values (Ecorr, Icorr) are (-449 mV; 0.038 mA.cm-2) and (-385; 0.012 mA.cm²) for steel A and steel B respectively. Vanadium and Niobium addition displace the corrosion potential towards nobler values and decreases the corrosion current density.

Impedance measurements confirm these results for steel A and steel B respectively: charge transfer resistance (Rct) increases from 246 to 437 Ω cm² and double layer capacitance Cdl decreases from 316.1 to 189.5 µF.cm².

Vanadium and niobium addition in AISI309 austenitic stainless steel provokes vanadium and niobium stable carbides precipitation at the expense of chromium carbides. This microstructure has a better resistance to pitting corrosion in 0.1 M HCl.

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References


