Effect of Nitrogen on the Corrosion Behavior of Austenitic Stainless Steel in Chloride Solutions

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Abstract

The effect of partial replacement of nickel with nitrogen on the mechanism of localized corrosion resistance and repassivation for nitrogen-bearing stainless steel was investigated using anodic potentiodynamic polarization technique. The solutions used for this study contained 0.0, 0.05 and 0.33 M Fe$^{3+}$ for solutions I, II and III respectively, in a total Cl$^{-}$ ion concentration 1 M. The pitting attack was found to be retarded by nitrogen addition and the samples were able to passivate as the nitrogen increase. Addition of nitrogen allows decreasing the % of Ni, but to a certain limit. Nitrogen adsorb on the interface of the metal oxide and results in repulsion of Cl$^{-}$ ions. Moreover, it reacts with H$^{+}$ ions in the solution leading to higher pH, which explains the retardation effect of nitrogen to corrosion.

Keywords: localized corrosion – pitting corrosion – anodic polarization – nitrogen stainless steel.
Introduction

Nitrogen is considered an important alloying addition to austenitic stainless steel in terms of corrosion resistance. It promotes passivity, widens the passive range in which pitting is less probable, and improves stress corrosion cracking resistance in some media, and enhances the resistance to intergranular corrosion. Moreover, nitrogen dissolved in austenitic stainless steel was found to increase its strength. The following mechanisms have been suggested to explain how nitrogen operates: (1) nitrogen in solid solution is dissolved and produces NH$_4^+$, depressing oxidation inside a pit; (2) concentrated nitrogen at the passive film/alloy surface stabilizes the film, and prevents attack of anions (Cl$^-$); (3) produced nitrate ions improve the resistance to pitting corrosion; (4) nitrogen addition stabilizes the austenitic phase; and (5) nitrogen blocks the kink, and controls the increase of electric current for pit production.

In order to develop a resources-saving stainless steel with excellent localized corrosion resistance, 2 key technologies were adopted. The first key is high nitrogen alloying. Nitrogen enrichment improves pitting and crevice corrosion resistance without increasing chromium or molybdenum content. Therefore, adding nitrogen may contribute to reduce necessary chromium and molybdenum content. Moreover, as nitrogen is austenite former, adding nitrogen lowers the nickel content required for forming a single austenitic phase. Lowering the nickel in stainless steel lowers the costs of production. The aim of this paper is to study the effect of partial replacement of nickel with nitrogen on the pitting corrosion behavior of austenitic stainless steel.

Experimental

The chemical composition of the samples is described in Table 1. The samples were prepared, cold worked and normalized by Steel laboratory (CMRDI). Austenitic stainless steel (sample 1) was used as the blank material for all the samples. In samples 2-5 the nitrogen content was gradually increased while the nickel content was gradually decreased.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>W</th>
<th>Ni</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.42</td>
<td>3.07</td>
<td>1.61</td>
<td>19.22</td>
<td>1.70</td>
<td>8.56</td>
<td>0.00</td>
<td>bal.</td>
</tr>
<tr>
<td>2</td>
<td>0.41</td>
<td>3.07</td>
<td>1.61</td>
<td>19.22</td>
<td>1.70</td>
<td>7.06</td>
<td>0.256</td>
<td>bal.</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>3.07</td>
<td>1.61</td>
<td>19.22</td>
<td>1.70</td>
<td>5.13</td>
<td>0.321</td>
<td>bal.</td>
</tr>
<tr>
<td>4</td>
<td>0.39</td>
<td>3.07</td>
<td>1.61</td>
<td>19.22</td>
<td>1.70</td>
<td>3.71</td>
<td>0.373</td>
<td>bal.</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>3.07</td>
<td>1.61</td>
<td>19.22</td>
<td>1.70</td>
<td>0.13</td>
<td>0.45</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Electrochemical measurements

Experiments were designed to investigate the role of partial replacement of nickel by nitrogen on the corrosion behavior of austenitic stainless steel. The solutions used in this investigation were solution I 1 M NaCl, solution II 0.85 M NaCl + 0.05 M FeCl$_3$ and
solution III 0.01 M NaCl + 0.33 M FeCl₃. The overall chloride concentration was maintained constant. Potentiodynamic polarization curves were used to test corrosion behavior of the samples in different solutions at 25°C. PGSTAT30, Autolab computerized potentiostat was used for testing. The current was measured as a function of the potential, which changed with scan rate 0.5 mV/s. The electrode potentials were measured with respect to Silver/silver chloride reference electrode in a saturated KCl solution. The counter electrode was a platinum wire, while the sample was used as the working electrode.

**Results and discussion**

*Corrosion in 1 M NaCl*

Figure 1 shows potentiodynamic polarization curves for different samples of nitrogen stainless steel in 1 M NaCl solution at 25°C. Sample 1, where there is no nitrogen and the nickel is 8.56, the curve indicates anodic dissolution, the Cl⁻ ions prevent passivation to occur. In other samples 2-5, where some percentages of nitrogen are added at the same time the percentages of nickel are decreased, there is a general tendency for passivation. The break in the current as the potential increases explains this passivation. The current for passivation decreases as the fraction of nitrogen to nickel increase but to a certain limit. This indicates that nitrogen promotes passivation of nitrogen stainless steel and the passivation requires a certain proportion of nickel to be present, i.e. the passivation due to nitrogen is supported by a presence of a critical percentage of nickel.

The initiation of pitting is clearly retarded by the presence of nitrogen, the incubation time being prolonged, so that the extent of attack is greatly decreased. However, it may be noted that the current oscillations (specially in sample 3) indicating pit formation and repassivation. These experiments strongly suggest the important role of nitrogen for repassivation. Not so much the pit initiation is retarded by nitrogen, but the stable pit growth is suppressed by immediate repassivation. The hypothesize about the effect of the negatively charged N⁻δ segregated beneath the passive film on the adsorption mechanism (17) of pit initiation. The accelerated dissolution rate of the passive film at the spot, where the aggressive anions are adsorbed, causes thinning of the film and approaching of the segregated N⁺δ and the adsorbed anions (Cl⁻). Upon breakthrough of the passive film, the repulsive interaction of segregated N⁺δ and adsorbed Cl⁻ certainly will lead to desorption of the Cl⁻, since the segregated species cannot move away rapidly. Moreover, the N⁺δ will be further enriched by anodic segregation. The removal of the aggressive anions may be the reason for the fast repassivation of the pits in a wide range of potentials.
Corrosion in FeCl₃ solution

Figures 2 and 3 show potentiodynamic polarization curves for the samples corroded in presence 0.05 and 0.33 Fe³⁺ ions respectively. The total Cl⁻ ions content was adjusted to 1 M by adding corresponding amounts of NaCl to the FeCl₃ solution. Generally, samples 1 and 2 showed no passivation. Samples 3, 4 and 5 showed passivation as indicated by the break in the current in the anodic region. It is noteworthy to observe that the mode of passivation in sample 3 where there is a medium addition of nitrogen and nickel, is different from that for sample 5 where the nitrogen is greatest and the nickel is almost non. In sample 3, the anodic current is almost the lowest and the passivation takes place over a wider range of potential. In sample 5, the current decreases greatly with increasing the potential and the breakdown of passivation occurs rapidly.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current Density (A cm⁻²)</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10⁻¹</td>
<td>-0.1</td>
</tr>
<tr>
<td>2</td>
<td>10⁻⁰</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>10⁻⁻¹</td>
<td>-0.2</td>
</tr>
<tr>
<td>4</td>
<td>10⁻⁻²</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>10⁻⁻³</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

Fig. 1 Potentiodynamic polarization curves for different samples of nitrogen stainless steel in 1 M NaCl solution.
Fig. 2 Potentiodynamic polarization curves for different samples of nitrogen stainless steel in 0.05 M FeCl₃ solution, the total Cl⁻ 1 M.

Fig. 3 Potentiodynamic polarization curves for different samples of nitrogen stainless steel in 0.33 M FeCl₃ solution, the total Cl⁻ 1 M.
Few Authors have tried to analyze the solution after corrosion test of nitrogen steel. Their results suggest that upon dissolution of the steels mainly $\text{NH}_4^+$ is formed from the dissolved nitrogen. Most probably nitrogen from the metal surface, segregated in a negatively charged state, is directly converted according to the chemical reaction:

$$\text{N}_3^- + 4 \text{H}^+ \rightarrow \text{NH}_4^+ \qquad \text{(1)}$$

The negatively charged segregated state of nitrogen on iron was well established by AES, LEED and XPS. The enriched N can be found at the oxide/metal interface and at the top of the passive layer.

The stability of a corroding pit depends on the potential drop, the composition of the pit electrolyte and the pH drop. pH shifts have often served to explain the stability of a corroding pit. Especially in non-buffered solutions the hydrolysis of metal ions leads to acidification according to:

$$\text{Me}^{2+} + \text{H}_2\text{O} = \text{MeOH}(\varepsilon + 1) + \text{H}^+ \qquad \text{(2)}$$

The presence of hydrolysable cations whether as corrosion products or in the electrolyte may lower the pH to a value reaching down to 2.8. The precipitation of a hydroxide would be prevented, but passivation should still be possible. The pH shift of the pitting potential

$$E_p = E^\circ_p - 0.059 \times \text{pH} \quad \text{for iron} \quad E^\circ_p = 0.58 \text{ V} \qquad \text{(3)}$$

is generally much too small to shift the pitting potential above the potentiostatically applied value. So the metal surface cannot reach the active range of the polarization curve, except when the potential is set very close to the pitting potential, a case which may often occur in technical corrosion cases.

The effect of nitrogen in the steel on the chemistry in a growing pit can be mainly by raising the pH. This can be explained in terms of reaction (1) i.e. the formation of ammonium ion $\text{NH}_4^+$, which buffers pH in its formation. However, in the cases that the hydrolysis reactions deliver much more H$^+$ ions to the solution the nitrogen can tie up:

$$\text{Fe} \rightarrow \text{Fe}^{2+} \rightarrow \text{FeOOH} + 3\text{H}^+ \qquad \text{(4)}$$

$$\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{HCl} \qquad \text{(5)}$$

So the effect of N in a growing pit is rather limited.

Figure 4 shows the effect of partial replacement of the nickel by nitrogen on the general corrosion rate, mm/year, estimated from the polarization data. The figure clearly reveals that the corrosion rate is independent of the partial replacement of Ni by N in the solution containing only 1 M NaCl. However, the solution containing FeCl$_3$ showed noteworthy results. As the nitrogen content is increased and the nickel is decreased, the corrosion rate decreases to a minimum critical value. Beyond this critical value, the corrosion rate starts to increase again regardless of increasing the % of nitrogen with the decrease of the percentage of nickel. This suggest a combined effect of both nitrogen and nickel on passivation of the stainless steel. This requires further study to investigate the exact mechanism behind this behavior.
**Conclusions**

1. The pitting attack was found to be retarded by nitrogen addition and the samples were able to passivate as the nitrogen content is increased.

2. Nitrogen adsorbs on the interface of the metal oxide and results in repulsion of Cl\textsuperscript{-} ions. Moreover, it reacts with H\textsuperscript{+} ions in the solution leading to higher pH, which explains the retardation effect of nitrogen to corrosion.

3. Addition of nitrogen allows decreasing the % of Ni, but to a certain limit.

**Acknowledgment**

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References