Localized corrosion behaviour of nickel-free high-nitrogen 19Cr-18Mn-0.69N austenitic stainless steel in 3.5-% NaCl

Corrosion behaviour of 19Cr-18Mn-0.69N austenitic stainless steel was studied by cyclic polarization technique in 3.5-% NaCl solution and was compared with that of other austenitic stainless steels having different compositions namely, AISI 316L and one with 14% Cr and 8% Mn, denoted 14Cr-8Mn in the following. The results showed that 19Cr-18Mn-0.69N austenitic stainless steel exhibits higher pitting resistance compared to that of other two alloys. SEM micrographs of 19Cr-18Mn-0.69N austenitic stainless steel after corrosion showed no pits at the alloy surface even when it was polarized beyond transpassive pitting potential. However, severe attack was seen at the araldite-metal interface. But, in case of AISI 316L and 14Cr-8Mn severe pitting attack was seen at the surface, whereas no attack was seen at the araldite-metal interface. Critical crevice temperature for the three stainless steels was determined. 19Cr-18Mn-0.69N austenitic stainless steel was found to have good crevice corrosion resistance compared to the other alloys investigated.

The ongoing research and development of stainless steel continues to produce new ideas for improving the mechanical properties and corrosion properties of this important class of engineering materials. Considerable emphasis has been placed on improving steel making practice with the intention of improving both the cost and performance of the final product [1; 2].

The development of austenitic steels with improved properties was initiated in 1960 and became widespread in the 1980s [3]. Generally, austenitic stainless steels contain nickel as an alloying element to stabilize the austenitic phase and to some extent provide corrosion resistance [4]. Earlier improvements were mostly related to increase chromium, molybdenum and nickel contents. Recently, much interest has focused the possibility of substituting nickel by manganese in ferrous materials [5]. Several studies were made to evaluate the potential of Fe-Cr-Mn austenitic stainless steels to act as substitutes for Fe-Cr-Ni austenitic stainless steels in many applications. In Fe-Cr-Ni austenitic stainless steels, nickel stabilizes austenite and resists corrosion to some extent. The primary drawback of nickel addition in austenitic stainless steel is that it increases susceptibility to stress corrosion cracking [6]. Further, it leads to increases the cost of the alloy. So, highest interest exists on substituting nickel in austenitic stainless steels by manganese [7].

Most recently, the addition of nitrogen to these steels has caused wide interest, leading to the development of high-nitrogen high-manganese nickel-free austenitic stainless steels [8]. The production of the low-nickel steels is made possible by the addition of manganese which increases the nitrogen solubility in the matrix [9]. Such a steel alloy shows good combination of strength, toughness and cold workability [10]. Most researchers discussed the pitting resistance of this type of alloy, but the crevice corrosion behaviour is still unknown. This was reason for the present authors to investigate the corrosion behaviour of one such stainless nickel-free high-nitrogen stainless steel, namely 18Cr-18Mn, in 3.5-% NaCl, and to compare it with two other austenitic stainless steels namely, AISI 316L and a high-manganese austenitic stainless steel. Critical crevice temperature for all the three alloys was found out.

**Experimental method**

**Materials and microstructures.** Electro-slag remelted (ESR) alloy 19Cr-18Mn-0.69N was cold rolled and solution annealed at 1150 °C for 1 h. The other two alloys namely, AISI 316L and 14Cr-8Mn, both commercially available were solution annealed at 1050 °C for 1 h. The chemical compositions of the alloys examined in this study are shown in table 1.

To examine the resistance of the alloys to intergranular attack (IGC - intergranular corrosion), specimens were electrolytically etched as per ASTM A 262 A [11] in a solution of 10 % oxalic acid at room temperature. Samples were etched for 90 s at a current of 1 A/cm² by keeping them as an anode and a platinum sheet as a cathode. After etching, the microstructures of the specimens were observed by using an optical microscope. As the samples exhibited step-structure, indicative of the alloys’ intergranular corrosion resistance, they were subjected to further studies.

**Table 1:** Chemical composition of the austenitic stainless steels (mass contents in %)

<table>
<thead>
<tr>
<th>Alloys</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Ni</th>
<th>N</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>19Cr-18Mn-0.69N</td>
<td>0.070</td>
<td>18.07</td>
<td>0.011</td>
<td>0.043</td>
<td>0.37</td>
<td>-</td>
<td>0.69</td>
<td>19.59</td>
<td>-</td>
</tr>
<tr>
<td>14Cr-8Mn</td>
<td>0.063</td>
<td>8.22</td>
<td>0.018</td>
<td>0.070</td>
<td>0.27</td>
<td>2.74</td>
<td>-</td>
<td>14.79</td>
<td>-</td>
</tr>
<tr>
<td>AISI 316L</td>
<td>0.025</td>
<td>1.52</td>
<td>0.010</td>
<td>0.026</td>
<td>0.49</td>
<td>11.6</td>
<td>-</td>
<td>17.81</td>
<td>2.65</td>
</tr>
</tbody>
</table>

**Polarization tests.** Electrochemical polarization behaviour of the alloys was studied using a set-up consisting of a potentiostat/galvanostat driven by an adequate software, and an electrochemical cell. The cell was a glass vessel similar to ASTM G5 with 1000 ml capacity. The cell consisted of a platinum sheet as counter electrode, a saturated calomel electrode (SCE) as reference electrode and the specimen as working electrode. 3.5-% NaCl solution was chosen as electrolyte. Samples of 1 cm² exposed surface area were hot mounted, and electrical connection was provided by drilling the backside of the mount and soldering the copper wire, finally closing the hole by cold cured resin. The samples were ground till 4/0 grade silicon carbide paper.
and finally wet polished using alumina powder. To avoid interference from crevice corrosion, the mount-sample interface was carefully coated with a thin epoxy sealant. A cyclic polarization experiment was carried out to study the repassivation behaviour of the alloy. The potential was scanned from -300 mV with respect of OCP (open circuit potential) to the potential at which current reaches 5 mA, and then the potential was reversed till it reaches OCP.

Ferric chloride test. The ferric chloride solution test based on the practice MTI-2 (Materials technology institute of the chemical process industry) [12] modified practice of ASTM G48 standard [13] was carried out. Therefore, specimens of 50 · 25 · 3 mm dimension with a 600 grit surface finish were used. Multiple crevice assembly device used in this study consisted of two serrated PTFE washers. Each of these washers providing 12 grooves was fastened to one side of the stainless-steel plate specimen, so as to form 12 crevice sites on each side of the specimen. The washers were initially secured at a specified torque of 0.28 Nm. The whole crevice assembly was immersed in 800 ml of 6 % ferric chloride (FeCl₃ · 6H₂O) solution for 24 h. The starting test temperature of the solution was calculated based on the following equation that relates the crevice corrosion temperature (CCT) to the alloy composition [13]:

\[
\text{CCT} = 3.2 \% \text{Cr} + 7.6 \% \text{ Mo} + 10.5 \% \text{ N} - 81.0
\]

Table 2: Electrochemical parameters of the alloys derived from the polarization curves obtained in 3.5 % NaCl

<table>
<thead>
<tr>
<th>Alloys</th>
<th>i-pass, A/cm² at 100 mV (vs SCE)</th>
<th>E-pit, mV (SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19Cr-18Mn-0.69N</td>
<td>4 · 10⁻⁷</td>
<td>1050</td>
</tr>
<tr>
<td>14Cr-8Mn</td>
<td>8 · 10⁻⁶</td>
<td>-80</td>
</tr>
<tr>
<td>AISI 316L</td>
<td>2 · 10⁻⁷</td>
<td>280</td>
</tr>
</tbody>
</table>

Subsequent tests were conducted either by lowering or raising the test solution temperatures in steps of 5 °C. Tests were continued to find the highest temperature at which specimens suffered an attack just lower than 25 μm. In accordance with ASTM standard, this value is defined as the minimum depth for crevice attack. The number of crevice sites observed on each of the alloys above CCT is also reported.

Results and discussion

Polarization test. Cyclic polarization curves of all the three alloys are compared in Fig. 1. The electrochemical kinetic parameters namely, corrosion potential (Ecorr), passive current density (i-pass), pitting potential (E-pit), and passive region (ΔE = E-pit - E-corr) for these alloys were obtained from the curves, and are summarized in Table 2. As there is no potential independent current region, the passive current density exhibited by the alloys at 100 mV (vs SCE) was compared. The following observations can be made on the basis of the data summarized in table 2. 19Cr-18Mn-0.69N shows a lower passive current density (i-pass) by an order of magnitude, compared to that of 14Cr-8Mn. But the former exhibits a higher E-pit than that of AISI 316L. Notably, 19Cr-18Mn-0.69N shows a significantly higher E-pit compared to both the other alloys. Thus, E-pit of 19Cr-18Mn-0.69N, AISI 316L and 14Cr-8Mn were found to be 1050, 280, and -80 mV (vs SCE) respectively. The polarization data was supported by the SEM micrographs, obtained after completion of polarization tests, Fig. 2. 19Cr-18Mn-0.69N does not show any attack, whereas the other two alloys suffered severe pitting attack.

The passivation tendency of 18Cr-18Mn-0.69N was not steady at the initial anodic potential as like that of higher anodic potential. This effect might be due to the formation of NH₄⁺ at lower potentials, as reported by Baba et al. [14]. At higher anodic potentials, due to the presence of higher amounts of nitrogen in steel, it forms a stable nitride namely, NO₃⁻ [15].

The higher passivity of the film19Cr-18Mn-0.69N is probably caused by the high concentration of chromium oxide film and/or by the existence of nitrates in the surface [16...18]. The increase in current of more than 1050 mV is probably due to the oxygen evolution reaction according to pH potential diagram [19]. From table 1 it can be clearly seen that the major difference in composition between 19Cr-18Mn-0.69N and 14Cr-8Mn is nitrogen, while there

![Fig. 1: Cyclic polarization curves of three austenitic stainless steels obtained in 3.5 % NaCl](image1)

![Fig. 2: SEM photographs of a) 19Cr-18Mn-0.69N, b) 14Cr-8Mn, and c) AISI 316L observed after the polarization test](image2)
is a marginal variation in chromium content. But AISI 316L has almost the same Cr content as 19Cr-18Mn-0.69N. So, comparing all three alloys, it can be said that N plays a decisive role in enhancing pitting and crevice corrosion resistance of 19Cr-18Mn-0.69N. Pitting resistance of an alloy is indexed using pitting resistance equivalent number (PREN). The relation between PREN and pitting potential was given by Sherir et al. [20], fig. 3, to show how effective N enhances pitting resistance of stainless steels. Since AISI 316L contains 17.81 % Cr, 2.65 % Mo 0.067 % N, PREN turns out to be 27.66. From the figure the corresponding pitting potential of 0.6 M (~3.5 %) NaCl solution is around 200 mV (SCE) for the above composition. This is in good agreement with the experimental results as shown in fig. 1, where a sudden jump in current density occurred at a potential of about 280 mV. For 14Cr-8Mn, the PREN value is around 14.96 and the corresponding pitting potential amounts to -70 mV which also is in good agreement with the results obtained. Similarly for 19Cr-18Mn-0.69N, the PREN value is around 30.46 and the corresponding pitting potential may lie between 0 to 1000 mV. From table 2, the pitting potential of 19Cr-18Mn-0.69N can clearly be identified as 1050.

Further examination of polarization curves of these alloys shows positive hysteresis. But, what is interesting is that 19Cr-18Mn-0.69N exhibits the largest hysteresis loop among the three alloys in spite of the fact that this alloy exhibits a far higher $E_{\text{pit}}$ than the remaining alloys. Further, AISI 316L and 14Cr-8Mn alloys possess $E_{\text{prot}}$ close to that of their $E_{\text{corr}}$-values. On the other hand, $E_{\text{prot}}$ of 19Cr-18Mn-0.69N alloy is below $E_{\text{corr}}$, although this alloy did not suffer from pitting during the polarization test (fig. 1). As this alloy was subjected to a far higher anodic potential than the other two alloys, such an effect may be due to the crevice corrosion attack on the alloy. Hence, edges of the alloys are examined. From SEM micrograph, fig. 4, it is obvious that 19Cr-18Mn-0.69N specimen indeed suffered from severe attack at the interface (araldite-metal interface), whereas no such attack was seen on AISI 316L and less attack was observed on 14Cr-8Mn specimens. While the above data suggests high susceptibility of 19Cr-18Mn-0.69N to crevice corrosion, it should, again, be pointed out that this alloy was subjected to a far higher anodic potential than the other two alloys. This could be one of the reasons, why the alloy suffered severe crevice corrosion.

Attempts to eliminate crevice attack on the alloy-mount interface were not fully successful. Hence, the following corrosion experiments were carried out to examine this aspect and to find true susceptibility of the alloy to crevice corrosion.

**Crevise corrosion test.** In order to evaluate the crevice corrosion resistance of 19Cr-18Mn-0.69N, the alloy was subjected to crevice corrosion test as per MTI-2 [12] (modified ASTM standard G48). The starting crevice temperature calculated by equation (1) was found to be -6 °C for AISI 316L, -32 °C for 14Cr-8Mn and -8 °C for 19Cr-18Mn-0.69N. As per the standard, the starting crevice test temperature was determined by using equation (1). Any- way, it does not seem to be applicable to the present condition, hence, tests were conducted over a wide temperature range. In doing so, the temperature of the solution was either lowered or raised in steps of 5 °C, until the highest temperature was found at which the specimens suffered an

<table>
<thead>
<tr>
<th>Materials</th>
<th>critical crevice temperature (°C)</th>
<th>depth of attack (μm)</th>
<th>No. of attack sites (depth &gt;25 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19Cr-18Mn-0.69N</td>
<td>-16 °C, -8 °C, 5 °C, 10 °C, 15 °C</td>
<td>no attack, 4, 15, &gt;50</td>
<td>0, 0, 0, 3,</td>
</tr>
<tr>
<td>14Cr-8Mn</td>
<td>-36 °C, -31 °C, -16 °C, -16 °C</td>
<td>15, &gt;50, &gt;50, 5</td>
<td>0, 6, 9, 0,</td>
</tr>
<tr>
<td>AISI 316L</td>
<td>-11 °C, -6 °C</td>
<td>&gt;50, &gt;50</td>
<td>6, 8</td>
</tr>
</tbody>
</table>

![Fig. 3: Pitting potential (0.6M (3.5 %) NaCl at 25 °C) versus PREN for stainless steel used in this study.](image)

![Fig. 4: SEM photographs of the interface of a) 19Cr-18Mn-0.69N, b) 14Cr-8Mn, and c) AISI 316L after polarization test.](image)
attack of just below 25 μm (depth). A few typical photographs of the samples subjected to the crevice corrosion test are shown in fig. 4, and the depth of attack is summarized in table 3. The CCT for AISI 316L, corresponding to 5 μm deep attack, was found to be -16 °C. At -16 °C the depth of attack for all the alloys is compared (table 3) to evaluate the relative performance of AISI 316L with the other two alloys. At this temperature 14Cr-8Mn suffered crevice attack of 50 μm at 9 sites, while AISI 316L suffered 5 μm crevice attack and no attack was found with 19Cr-18Mn-0.69N, fig. 5. The CCT for 19Cr-18Mn-0.69N was found to be 10 °C and for 14Cr-8Mn at about -36 °C. Hence, from this study it can be said that 19Cr-18Mn-0.69N has higher crevice corrosion resistance than the other two alloys.

Reversal at different potentials. 19Cr-18Mn-0.69N was subjected to cyclic polarization with lower apex potentials than $E_{\text{pit}}$ reported earlier. Cyclic polarization curves obtained for a few scans reversed at 300, 600 and 800 mV (vs SCE) apex potentials are shown in fig. 6. As can be seen, all the reverse scans exhibit lower passive current density than the forward scans. Even though all these cyclic polarization curves obtained up to 800 mV (vs SCE) as apex potential show a negative hysteresis loop, indicating stable passivity, microscopic examination, fig. 7, of the polarized specimen reveals crevice attack on those samples scanned with apex potential of 600 mV (vs SCE) and above. The apex potential below which the alloy was found to be resistant to crevice corrosion (500 mV vs SCE) happens to be higher than $E_{\text{pit}}$ values of the other two alloys. Thus, the alloy seems to have reasonable resistance to crevice corrosion.

Conclusion

The 19Cr-18Mn-0.69N showed higher passivity compared to 316L and 14Cr-8Mn in 3.5 % NaCl. Critical crevice temperature of 19Cr-18Mn-0.69N was higher compared to that of other two materials, suggesting better crevice resistance compared to the two other materials. Reversal at different potentials in the passive region and subsequent SEM micrograph studies confirm that attack on araldite-metal interface of 19Cr-18Mn-0.69N was due to the reason that the sample was subject to a higher potential.

References
