Influence of Oxygen Content on the Inclusion Formation and Pitting Corrosion Resistance of Hyper Duplex Stainless Steels

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To determine the influence of oxygen content on the formation of inclusion in 27Cr-7Ni hyper duplex stainless steel, samples were analyzed by scanning electron microscopy. Electrochemical tests were also conducted, which revealed that an increase in oxygen content reduces the resistance to pitting corrosion of the alloys. This was attributed to the formation of numerous inclusions, as well as an increase in the area of micro-crevices that occur between the inclusion and metallic matrix, and which act as initiation sites for corrosion pits.

Keywords: duplex stainless steel, pitting corrosion, inclusion, oxygen, polarization

1. Introduction

Super duplex stainless steels (SDSSs) are increasingly being used in a variety of applications in power plants, desalination facilities, and chemical plants due to their high resistance to pitting and crevice corrosion, excellent mechanical properties and relatively low cost when compared with other high-performance materials such as super austenitic stainless steels (SASSs).1–3 However, when used in shell and tube exchangers, the corrosion resistance of SDSSs is insufficient to allow high temperature operation or ensure a long service life. This has consequently led to the development of hyper duplex stainless steels (HDSSs), which combine a high pitting corrosion resistance with improved mechanical properties.

It is well known that meta-stable corrosion pits form at potentials far below the pitting potential of stainless steels,4–6 with pit nucleation, propagation and termination occurring through localized breakdown of the passive film. Meta-stable pit growth has become a well-documented feature of the pitting corrosion of stainless steel in chloride solutions.7–9

Stewart and William stated that inclusions dominate as pit nucleation site, and that the lifetime of a meta-stable pit is therefore directly related to the size of these inclusions. They also reported that laser melting of the surface of stainless steel improves its resistance to pitting corrosion by reducing the nucleation frequency and lifetime of micro-pits, as well as the size of any inclusions.10

Ke and Alkire demonstrated that pits do not initiate at MnS inclusions smaller than 0.7 µm, as such inclusion exhibit a high diffusion rate that is highly effective in dispersing MnS dissolution products.11,12

Suter and Böhni13 confirmed that the pitting potential depends on the size of inclusions, and that this size has to be kept well below 1 µm in order to substantially improve the pitting resistance of stainless steels. This assumption is in good agreement with the observations reported many years ago by Osozawa et al.,14 in which stable pitting corrosion pit growth was not observed in stainless steels with inclusions of no more than 2.5 µm in size.

Many studies have investigated the effect of alloying elements on the resistance to pitting corrosion of stainless steel. Pardo et al.15 suggested that Mn has a detrimental effect on the pitting corrosion resistance due to the formation of electrochemically unstable MnS inclusions that tend to dissolve and initiate electrochemical attack at the inclusion/matrix interface. The addition of Cu to HDSS also reduces the pitting corrosion resistance, but through an increase in activity of Cr that subsequently leads to an increase in the number of Cr oxides and oxy-sulfide acting as pitting initiators.16 Other researchers have shown that the addition of rare earth metals (REM) improves the pitting and crevice corrosion resistance of stainless steels,17–19 whereas the addition of S addition reduces the pitting corrosion resistance through the formation of numerous MnS and MnOS inclusions that increase the available area suitable for pit initiation.20

However, despite all these past efforts, the effect of oxygen content on the formation of inclusions and the precise mechanism of corrosion pit initiation and propagation has not yet been investigated. In addition, there have been only very few studies that were focused on HDSSs. This study therefore presents a guideline for the further development of improved duplex stainless steels (DSSs).

In this study, to elucidate the influences of oxygen content on the inclusion formation and pitting corrosion resistance of the alloys, potentiodynamic anodic polarization tests, potentiostatic tests, image analyses and scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) analyses were also performed.

2. Experimental Procedures

Ingots weighing 50 kg with dimensions 150 by 150 by 300 mm (width by length by height) were manufactured using a high frequency vacuum induction furnace. After these ingots were hot rolled in the range of 1333 to 1523 K, plates of 6 mm
thickness were manufactured. The chemical compositions of the alloys are presented in Table 1. The experimental alloys were cut and solution heat-treated for 5 min per 1 mm thickness at 1373 K and then quenched in water.

To observe the back-scattered electron (BSE) images of the alloys, the alloys were ground to 2000 grit using SiC abrasive papers, polished with diamond paste. The sample was ultrasonic cleaned in acetone and distilled water to remove any impurities from the polished surface of the sample. The various inclusions were observed using a SEM in BSE. In addition, the chemical composition of various inclusions were analyzed using a SEM and an EDS attached to a SEM. The SEM was used to observe the pitting sites on the specimen after taking the potentiostatic tests and potentiodynamic anodic polarization tests in a deaerated 4 M NaCl solution at 348 K.

The influence of oxygen content on the pitting corrosion resistance of the alloys was investigated using a potentiodynamic anodic polarization tests. The corrosion potential ($E_{corr}$), the pitting potential ($E_{pul}$), the passive region ($\Delta E_p$), the passivation current density ($I_p$) and the corrosion current density ($I_{corr}$) were obtained from the potentiodynamic polarization curves. The corrosion current density ($I_{corr}$) was commonly obtained by the extrapolation of the cathodic and anodic curve between 50 and 100 mV away from the corrosion potential. The pitting potential marked the end of the passive potential region and the transition from passive to transpassive behavior. The potentiodynamic anodic polarization tests were conducted in a deaerated 4 M NaCl solution at 348 K according to the ASTM G 5.21) Test specimens were joined with copper wire through soldering (95 mass% Sn-5 mass% Sb), and then mounted with an epoxy resin. One side of the sample was ground to 600 grit using SiC abrasion paper. After defining the exposed area of the test specimen as $0.5 \times 10^{-4} \text{m}^2$, the remainder was painted with a transparent lacquer. The test was conducted at a potential range of $-0.65 \text{V} \text{to} +1.1 \text{V}$ vs. SCE (saturated calomel electrode) and at a scanning rate of $1 \times 10^{-3} \text{Vs}^{-1}$, using the SCE. The current transients through the potentiostatic tests were measured in deaerated 4 M NaCl solution at 348 K with an applied potential of 0 V vs. SCE in the passive region of the potentiodynamic anodic polarization curves at which metastable pitting can occur.22,23) The current transients were recorded for the duration of 3600 s.

3. Results and Discussion

3.1 Microstructural analysis

The SEM-BSE images in Fig. 1 show the microstructure of the solution heat-treated alloys, in which the globular black particles represent sulfide and oxy-sulfide inclusions. No secondary sigma ($\sigma$) or chi ($\chi$) phases are evident in any of the samples; however, it is clear from this that the number and total area of inclusions increase with oxygen content.

Figure 2 depicts the influence of oxygen content on the number and area of inclusions per frame area in each

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>W</th>
<th>Si</th>
<th>Mn</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Fe</th>
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</thead>
<tbody>
<tr>
<td>HDSS-1</td>
<td>0.02</td>
<td>27.01</td>
<td>7.00</td>
<td>2.52</td>
<td>3.28</td>
<td>0.35</td>
<td>0.88</td>
<td>0.35</td>
<td>0.003</td>
<td>0.011</td>
<td>Bal.</td>
</tr>
<tr>
<td>HDSS-2</td>
<td>0.02</td>
<td>26.91</td>
<td>7.11</td>
<td>2.59</td>
<td>3.38</td>
<td>0.33</td>
<td>0.94</td>
<td>0.33</td>
<td>0.004</td>
<td>0.018</td>
<td>Bal.</td>
</tr>
<tr>
<td>HDSS-3</td>
<td>0.02</td>
<td>26.91</td>
<td>7.00</td>
<td>2.66</td>
<td>3.24</td>
<td>0.35</td>
<td>0.94</td>
<td>0.35</td>
<td>0.003</td>
<td>0.032</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 1 Chemical composition of the experimental alloys (mass%).
experimental alloy, showing a clear increase in the number and the total area of inclusions with increasing oxygen. Thus, the number of inclusions in the frame area of the HDSS-3 alloy represents an increase of 1.6 times that of the HDSS-1 alloy (Fig. 2 (a)). Similarly, area of inclusions in the frame area of the HDSS-3 alloy is a 2.8 times increase over the HDSS-1 alloy (Fig. 2 (a)). The increase in the oxygen content of the alloy also increased the number of inclusions, which varied in size from fine to coarse (Fig. 2 (b)).

In order to measure and calculate the interface between the inclusions and metallic matrix for a given frame area, the inclusions were assumed to be two dimensional circles and their circumference \( (2\pi r) \) was used to produce distribution maps classifying the inclusions of each measured area by size. As shown in Fig. 3, the increase in the number and area of inclusions that accompanies an increase in the oxygen content of the alloy also increases the area of interface between the inclusions and the matrix. As a result, the interface area of the HDSS-3 alloy was increased by 4.1 times when compared with that of the HDSS-1 alloy.

Figure 4 shows BSE images of the inclusions in the alloys, the chemical compositions of which were analyzed using SEM-EDS. As presented in Fig. 4 (a), the inclusions in the HDSS-1 alloy comprised mostly of (Cr, Mn, Al) oxides and (Cr, Mn, Fe, Al) oxides, and were therefore very similar in chemical composition to the inclusions in the HDSS-3 alloy, as shown in Fig. 4 (b).

### 3.2 Influence of oxygen content on the pitting corrosion resistance

Figure 5 shows the influence of oxygen content on the potentiodynamic polarization behavior of the alloys in a deaerated 4 M NaCl solution at 348 K, in accordance with ASTM G 5. The pitting potential \( (E_{\text{pit}}) \) is generally defined as being the breakdown potential required to destroy the passive film; and thus, as the \( E_{\text{pit}} \) of an alloy increases, its resistance to pitting corrosion also increases. This means that the decrease in \( E_{\text{pit}} \) that is evident in Table 2 as the oxygen
content of the alloys is increased is indicative of an accompanying reduction in pitting corrosion resistance. Thus, the pitting corrosion resistance of the HDSS-3 alloy is inferior to that of the HDSS-1 alloy, as the pitting potential of the HDSS-1 alloy ($E_{\text{pit}} + 735 \text{ mV}_{\text{SCE}}$) is much higher than that of the HDSS-3 alloy ($E_{\text{pit}} + 76 \text{ mV}_{\text{SCE}}$). The fact that the passivation behavior appears to be made more unstable with increasing oxygen content can be explained by the current transients of the HDSS-3 alloy in the passive region being much more frequent than those of the HDSS-1 alloy.

The potentiostatic polarization behavior (i.e., the current transient behavior) of each of the alloys in a deaerated 4 M NaCl solution at 348 K is shown in Fig. 6 for an applied potential of 0 V$_{\text{SCE}}$. This potentiostatic test was conducted to observe both the initiation of pitting corrosion and the repassivation of meta-stable pits; the number of current spikes corresponding to the initiation of pitting corrosion and the repassivation of the meta-stable pits being 23 for the HDSS-1 alloy, but increasing to 83 with the HDSS-3 alloy (Table 3). Two distinct processes are therefore assumed to occur prior to the stable formation of pits: namely, pit nucleation and the growth of meta-stable pits.

![Fig. 5 The potentiodynamic anodic polarization tests of the alloys in deaerated 4 M NaCl solution at 348 K according to ASTM G 5.](image)

![Fig. 6 The potentiostatic polarization tests at an applied potential of 0 V$_{\text{SCE}}$ of the alloys in a deaerated 4 M NaCl solution at 348 K according to ASTM G 5: (a) HDSS-1 alloy, (b) HDSS-2 alloy and (c) HDSS-3 alloy.](image)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$E_{\text{pit}}$, E/mV$_{\text{SCE}}$</th>
<th>$\Delta E_{p}$, E/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDSS-1</td>
<td>735</td>
<td>1072</td>
</tr>
<tr>
<td>HDSS-2</td>
<td>432</td>
<td>779</td>
</tr>
<tr>
<td>HDSS-3</td>
<td>76</td>
<td>430</td>
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</table>

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Number of current spike</th>
<th>Maximum peak height of current density, $I/\mu$A·cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDSS-1</td>
<td>23</td>
<td>9.7</td>
</tr>
<tr>
<td>HDSS-2</td>
<td>34</td>
<td>19.2</td>
</tr>
<tr>
<td>HDSS-3</td>
<td>83</td>
<td>55.4</td>
</tr>
</tbody>
</table>
3.3 Mechanism by which oxygen content influence pitting corrosion resistance

Figure 7 shows SEM images of the inclusions in the alloys after potentiostatic testing at an applied potential of 0 mV_{SCE} in a deaerated 4 M NaCl solution at 348 K. In this, we see that pitting corrosion is preferentially initiated at the interface area between the matrix and inclusions such as (Cr, Mn, Al) oxides and (Cr, Mn, Fe, Al) oxides, as the micro-crevices formed in this area allow chloride ions to more easily penetrate the metal. These micro-crevices are well-known to form at the boundaries between inclusions and the metal matrix due to differences in their respective coefficients of thermal expansion. 

Szummer et al. also reported to have found that inclusions on the surface of stainless steel can lead to the formation of weak spots in the passive film through direct exposure of the boundary between the inclusion and matrix to an aggressive external environment. Furthermore, as pitting corrosion clearly propagates from micro-crevices to inclusions, inclusions such as (Cr, Mn, Al) and (Cr, Mn, Fe, Al) oxides have a lower resistance to pitting corrosion than the metallic matrix.

SEM images of the inclusions in the alloys after potentiodynamic anodic polarization testing in a deaerated 4 M NaCl solution at 348 K according to ASTM G 5 are given in Fig. 8, and confirm that pitting corrosion in HDSS-1 and HDSS-3 alloy propagates from micro-crevices to inclusions, rather than the matrix. This again also indicates that inclusions such as (Cr, Mn, Al) and (Cr, Mn, Fe, Al) oxides have a lower resistance to pitting corrosion than the metallic matrix. Krawiec et al. showed that Cr-enriched inclusions (30 to 40 mass% Cr) in stainless steels do not undergo dissolution under open circuit potential (~150 mV_{SCE}) in 1 M NaCl solution; however, they did find that some areas containing Cr-enriched inclusions exhibit stable pitting at a potential of around 100 mV_{SCE} in 1 M NaCl solution. Vignal et al. reported the electrochemical dissolution of Cr-enriched inclusions (about 31 mass% Cr) in austenite stainless steels (ASSs) at potentials of around 450 mV_{SCE} in 1 M NaCl solution, with stable pitting of these inclusions above 600 mV_{SCE} confirming that the large amount of Cr in these heterogeneities prevents their dissolution. In this study, the increase in pitting corrosion initiation sites with increasing oxygen content means that the pitting corrosion resistance of HDSS-3 alloy is inferior to that of HDSS-1 alloy.

The decrease in the resistance to pitting corrosion with increasing oxygen content is the result of two important
factors: the increase in oxygen content increases the number and area of inclusions, which in turn increases the area of micro-crevices that act as pit initiation sites. The size of the inclusions has quite a pronounced effect on the frequency and lifetime of meta-stable pits; small inclusions (< 0.5 µm³) being too small to nucleate a damaging pit,10,13) while large inclusions (> 1 µm) generally induce large and long lasting current transients that directly correlate to the size of the dissolved inclusion.

4. Conclusions

(1) Increasing the oxygen content of 27Cr-7Ni hyper duplex stainless steel reduces its pitting corrosion resistance due to the formation of numerous (Cr, Mn, Fe, Al) oxide and (Cr, Mn, Al) oxide inclusions. This increases the total area of micro-crevices between these inclusions and the metal matrix, which act as pit initiation sites.

(2) In a deaerated 4 M NaCl solution at 348 K, pitting corrosion of 27Cr-7Ni hyper duplex stainless steel is initiated at micro-crevices and propagates toward the inclusions rather than the metallic matrix of the alloy.

Acknowledgements

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REFERENCES

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