Effects of Sulfur Addition on the Formation of Inclusions and the Corrosion Behavior of Super Duplex Stainless Steels in Chloride Solutions of Different pH

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Effects of sulfur addition on the formation of inclusions and the corrosion behavior of super duplex stainless steels in chloride solutions of different pH were investigated using potentiodynamic and potentiostatic polarization techniques. As sulfur content increased, the corrosion resistance decreased due to the formation of numerous manganese sul-

fides adhering to the tool surface. (feeding rate of 0.3 mm/rev., cutting depth of 1 mm and no cutting fluid).

1. Introduction

Super duplex stainless steels have been increasingly used for various applications such as desalination facilities and chemical plants due to the high resistance to pitting, crevice corrosion and stress corrosion cracking and good mechanical properties.1–3)

Manganese sulfide (MnS) is well known to provide inclusions favorable for machining. Given adequate conditions, such inclusions build a protective layer on the tool surface, termed a built-up layer (BUL), which promotes wear reduction of the tool.4–6) The manganese sulfide inclusions generate good results with respect to costs and productivity, motivating constant studies aimed at machinability improvements.7)

As referred to Fig. 1, Jeon and Kim elucidated that the tool life for an alloy with 0.053 mass% S was about 3 times longer than that of an alloy with 0.001 mass% S at a cutting speed of 100 m min⁻¹, due to the lubricating films of manganese sulfides adhering to the tool surface.

However, the intentional formation of sulfide inclusions such as MnS for the purpose of improving machinability, can lead to a deterioration of the resistance of the steels to pitting corrosion.8,9) In general, MnS in commercial stainless steels has been known to act as the initiation site of pitting corrosion in environments exposed to chloride ions.10–14) While the detrimental role of MnS has been recognized, the exact mechanisms of the pitting corrosion related to its presence have not been elucidated. In spite of a decrease in corrosion resistance due to addition of sulfur, in consideration of the machining cost and productivity, it is certainly worthwhile for industrial aspects if the machinability can be improved through optimizing alloy design by the addition of sulfur to super duplex stainless steels.

The corrosion behavior of duplex stainless steel is greatly affected by the difference in chemical composition between ferrite (α) and austenite (γ) phases. In general, Cr and Mo contents are higher in the α-phase whereas Ni and N are much higher in the γ-phase. Nitrogen (N) is a strong γ-stabilizer, and it increases the temperature at which the transformation of the α-phase to γ-phase occurs.15–17)

Accordingly, by controlling such alloying elements to achieve a balance of corrosion resistance between the α-phase and γ-phase, excellent corrosion resistance can be achieved. The pitting resistance equivalent number (PREN) has been introduced to estimate the relative pitting corrosion resistance in chromium (Cr), molybdenum (Mo), tungsten (W) and nitrogen (N) concentrations. Lorenz and Medawar found the following relationship between the PREN and nitrogen (N) concentrations.18) They reported that the PREN of stainless steels, a criterion for the resistance to pitting corrosion, is defined by the following experimental equation and is calculated according to the chemical compositions (mass%) of the major alloying elements such as Cr, Mo and

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The coefficient for the N content; however, it is reasonable to nearly double PREN and the alloying content of DSS is more complex stainless steels. N, which greatly affect the resistance to pitting corrosion of stainless steels.

\[
\text{PREN} = \left[ \text{mass}\% \text{ Cr} + 3.3(\text{mass}\% \text{ Mo}) + 0.5(\text{mass}\% \text{ W}) + 16(\text{mass}\% \text{ N}) \right]
\]

However, Bernhardsson et al.\(^{19}\) reported that while the formula is relevant for austenitic stainless steels (ASS) and the austenitic phase in duplex stainless steel (DSS), it is not valid for DSS for the following reasons. First, nitrogen is nearly completely solutionized in the austenite phase in DSS whereas it is rarely solutionized in the ferrite phase in DSS. The solubility of nitrogen in the ferrite phase in DSS has a maximum 0.05 mass\%. Second, the addition of nitrogen changes the partitioning coefficients for chromium and molybdenum.\(^{20}\) Therefore, the relationship between the PREN and the alloying content of DSS is more complex than that of ASS. However, it is reasonable to nearly double the coefficients for the N content;

\[
\text{PREN} = \left[ \text{mass}\% \text{ Cr} + 3.3(\text{mass}\% \text{ Mo}) + 0.5(\text{mass}\% \text{ W}) + 30(\text{mass}\% \text{ N}) \right]
\]

The PREN formula in eq. (2) for DSS has been used by several researchers to investigate DSS’s resistance to localized corrosion.\(^{21,22}\) However, the reasonable nitrogen factor in the PREN equation is still disputed. In particular, it is necessary to quantitatively verify the mechanisms of the initiation and propagation of pitting corrosion due to the PREN differences (PREN\(_y\) – PREN\(_\alpha\)) between the \(\gamma\)-phase and \(\alpha\)-phase in duplex stainless steels and the pitting corrosion behavior in chloride solutions of different pH.

To elucidate the effects of sulfur addition on the formation of inclusions and the corrosion behavior of super duplex stainless steels in chloride solutions of different pH and the reasonable nitrogen factor in the PREN equation, a metallographic examination, potentiodynamic & potentiostatic polarization tests, scanning electron microscope and energy dispersive spectroscopy (SEM-EDS) analyses of inclusion and austenite (\(\gamma\)) phase and ferrite (\(\alpha\)) phase, a scanning Auger multi-probes (SAM) analysis of two phases, and a thermodynamic calculation using Thermo-Calc software were conducted.

2. Experimental Procedures

2.1 Material and heat treatment

The experimental alloys were prepared by atmospheric melting in a high frequency induction furnace. For the raw material, commercial high-grade pure iron, chromium (Cr), molybdenum (Mo), nickel (Ni), ferro-chromium nitride of Fe–57.5 mass\% Cr–6.5 mass\% N, and ferro-sulfide of Fe–45 mass\% S were used. Table 1 shows the chemical composition of the experimental alloys designated as BASE and DXSS. The alloys were solution heat-treated for 30 min at 1403 K and then cooled in furnace to 1353 K, and then quenched in water.

2.2 Thermodynamic equilibrium calculation

To predict the phase diagram and PREN values of ferrite and austenite phases in experimental alloy, thermodynamic calculation using Thermo-Calc software was conducted. The steel database TCFE5 available with the Thermo-Calc software was used to perform the calculation and it should be stressed that such calculation give the equilibrium state of system.

2.3 Corrosion tests

Effects of sulfur addition on the corrosion behavior of super duplex stainless steels in chloride solutions of different pH were investigated using a potentiodynamic anodic polarization technique. The corrosion potential (\(E_{\text{corr}}\)), the pitting potential (\(E_{\text{p}}\)), the passive region (\(\Delta E_p\)), the passivation current density (\(I_p\)) and the corrosion current density (\(I_{\text{corr}}\)) were obtained from the potentiodynamic polarization curves. The corrosion current density (\(I_{\text{corr}}\)) 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 test was conducted in a deaerated 3.0 M NaCl of pH 7 and a deaerated 0.5 M HCl + 2.5 M NaCl of pH 1 at 338 K according to the ASTM G 5.\(^{23}\) The pH value was regularly checked using a Mettler pH meter.

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\(^{-4}\) m\(^2\), the remainder was painted with a transparent lacquer. The test was conducted at a potential range of \(-0.65\) to +1.1 V vs. SCE (saturated calomel electrode) and at a scanning rate of \(1 \times 10^{-3}\) V s\(^{-1}\), using a SCE. The current transients through the potentiostatic test were measured in deaerated 3.0 M NaCl and deaerated 0.5 M HCl + 2.5 M NaCl solution at 338 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.\(^{24,25}\) The current transients were recorded for a duration of 3600 s.

A SEM-EDS was used to observe the pitting sites on the specimen after taking the potentiodynamic tests in deaerated 3.0 M NaCl and deaerated 0.5 M HCl + 2.5 M NaCl solutions at 338 K.

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>N</th>
<th>Fe</th>
<th>PREN*</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE</td>
<td>0.015</td>
<td>24.36</td>
<td>7.09</td>
<td>3.98</td>
<td>0.52</td>
<td>0.82</td>
<td>0.001</td>
<td>0.29</td>
<td>Bal.</td>
<td>46.19</td>
</tr>
<tr>
<td>DXSS</td>
<td>0.016</td>
<td>24.74</td>
<td>7.12</td>
<td>3.99</td>
<td>0.50</td>
<td>0.91</td>
<td>0.053</td>
<td>0.28</td>
<td>Bal.</td>
<td>46.30</td>
</tr>
</tbody>
</table>

*PREN (Pitting Resistance Equivalent Number) = \text{mass}\% \text{ Cr} + 3.3 \times \text{mass}\% \text{ Mo} + 30 \times \text{mass}\% \text{ N}
2.4 Micro-structural characterization

To observe the optical microstructures of the alloys, the alloys were ground to 2000 grit using SiC abrasive papers, polished with diamond paste, and then electrolytically etched using 10 mass% KOH. The chemical compositions of various inclusions, γ-phase and α-phase were analyzed using a scanning electron microscope and energy dispersive spectroscope (SEM-EDS). The nitrogen content was analyzed using a scanning Auger multi-probes (SAM).

3. Results and Discussion

3.1 Effect of sulfur addition on the distribution of inclusions

Figure 2 shows the SEM microstructures of the alloys which were solution heat treated. It seemed that the globular particles in black shade are inclusions like sulfides and oxy-sulfides. No secondary phases such as sigma (σ) and chi (χ) were observed in the alloys. As S content in the alloy increased, the number and the areas of inclusions increased (Fig. 2).

Figure 3 presents the effect of the sulfur addition on the distribution of inclusions per frame area in the alloys. As S content in the alloy increased, the number and the total areas of inclusions per frame area increased (Figs. 3(a) and 3(b)). The number of inclusions per frame area in the alloy-DX5S was increased by 3.1 times, compared with that of the alloy-BASE. As S content in the alloy increased, the number of inclusions of various sizes ranging from fine inclusions to coarse inclusions increased (Fig. 3(c)).

Figure 4 shows back-scattered electron (BSE) images of the inclusions in the experimental alloys. The chemical composition and morphology for the inclusions were analyzed using a SEM-EDS. As presented in Fig. 4(a), the inclusions in the alloy-BASE were composed of the main type of (Mn, Cr) sulfides and (Mn, Cr, Fe, Al) oxides and the
mixed type of (Mn, Cr, Fe) oxy-sulfides and (Mn, Cr, Fe, Al) oxy-sulfides. As presented in Fig. 4(b), the inclusions in the S added alloy-DX5S were composed of the main type of (Mn, Cr) sulfides and (Mn, Cr, Al) oxy-sulfides and the mixed type of (Mn, Cr, Fe, Al) sulfides and (Mn, Cr, Fe, Al) oxy-sulfides. The chemical compositions of inclusions in the S added alloy-DX5S were similar to those in the alloy-BASE.

### 3.2 Effect of sulfur addition on the resistance to pitting corrosion

Figure 5(a) shows the effect of sulfur addition on the potentiodynamic polarization behavior of the experimental alloys in a deaerated 3.0 M NaCl solution at 338 K according to ASTM G 5. In general, the pitting potential ($E_p$) is defined as the breakdown potential destroying a passive film. As the $E_p$ of an alloy increases, the resistance to pitting corrosion of the alloy increases. As S content in the experimental alloys increased, the resistance to pitting corrosion decreased due to a decrease in the $E_p$ (Table 2). The passivation behavior appeared unstable with an increase in S content because the current transients of the S added alloys in the passive region are much more frequent than those of the base alloy.

The reasons that the resistance to pitting corrosion with an increase in S content decrease are as follows: the deterioration in the resistance to pitting corrosion as a result of the S addition seems to be associated with the inclusions in the alloy. In particular, the pitting potential of the alloy decreased with an increase in the area of inclusions per frame area. That is, as the interface areas between the inclusion and the matrix in the S added alloy-DX5S increased compared to those in the alloy-BASE (Fig. 3), the preferential sites for the initiation of pitting corrosion in alloy-DX5S increased compared to those in the alloy-BASE. The interface area between the inclusion and the metallic matrix appears to affect the resistance to pitting corrosion by supplying the preferential area as a role of pit initiation site. In this way, the resistance to pitting corrosion of the S added alloy was decreased.

Figure 5(b) presents the potentiostatic polarization behavior (the current transient behavior) for the experimental alloys in a deaerated 3.0 M NaCl solution at 338 K with an applied potential of 0 V vs. SCE in the passive region according to ASTM G 5. The potentiostatic test was conducted to observe the formation and the repassivation of meta-stable pits. As S content in the experimental alloys increased, the current spikes for the formation and the repassivation of the meta-stable pits increased.

The number of the current spikes corresponding to the initiation of pitting corrosion and the repassivation of the meta-stable pits of the alloy-DX5S was 46 whereas that of the
alloy-BASE was 11. It was assumed that there are two distinct processes before stable pit formation occurs: pit nucleation and growth of the metastable pit. As presented in Fig. 5(b), the degree of metastable pit growth in the S added alloy-DX5S seemed to increase compared to those in the alloy-BASE.

Figure 6(a) shows the effect of sulfur addition on the potentiodynamic polarization behavior of the experimental alloys in a deaerated 0.5 M HCl + 2.5 M NaCl solution at 338 K according to ASTM G 5. The resistance to pitting corrosion of the alloy-DX5S was inferior to that of the alloy-BASE because the $E_{\text{pit}}$ (0.05 V vs. SCE) of the alloy-DX5S is lower than that of the alloy-BASE and the critical passive current density of the alloy-DX5S was higher than that of the alloy-BASE in active region (Table 2).

Figure 6(b) presents the potentiostatic polarization behavior (the current transient behavior) for the experimental alloys in a deaerated 0.5 M HCl + 2.5 M NaCl solution at 338 K with an applied potential of 0 V vs. SCE. As S content in the experimental alloys increased, the current spikes for the formation and the repassivation of the metastable pits increased.

The corrosion potential ($E_{\text{corr}}$), the pitting potential ($E_{\text{pit}}$), the passive region ($\Delta E_p$), the passivation current density ($I_p$) and the corrosion current density ($I_{\text{corr}}$) were obtained from the anodic polarization curves for experimental alloys. The values of the pitting potential ($E_{\text{pit}}$), the corrosion potential ($E_{\text{corr}}$), the passive region ($\Delta E_p$), the passivation current density ($I_p$) and the corrosion current density ($I_{\text{corr}}$) for the experimental alloys are listed in Table 2.

Table 2 Electrochemical parameters for the experimental alloys in chloride solutions of the different pH obtained from the potentiodynamic anodic polarization curves.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Solution</th>
<th>Cl$^-$ concentration (M)</th>
<th>pH</th>
<th>$E_{\text{pit}}$ (mV vs. SCE)</th>
<th>$E_{\text{corr}}$ (mV vs. SCE)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$I_p$ (µA/cm$^2$)</th>
<th>$I_{\text{corr}}$ (µA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE</td>
<td>NaCl</td>
<td>3.0</td>
<td>7</td>
<td>943</td>
<td>-261</td>
<td>1011</td>
<td>1.4</td>
<td>0.28</td>
</tr>
<tr>
<td>DX5S</td>
<td>NaCl</td>
<td>3.0</td>
<td>7</td>
<td>247</td>
<td>-270</td>
<td>389</td>
<td>2.0</td>
<td>0.39</td>
</tr>
<tr>
<td>BASE</td>
<td>+ HCl</td>
<td>3.0</td>
<td>1</td>
<td>183</td>
<td>-353</td>
<td>394</td>
<td>1007.3</td>
<td>628.53</td>
</tr>
<tr>
<td>DX5S</td>
<td>+ HCl</td>
<td>3.0</td>
<td>1</td>
<td>54</td>
<td>-358</td>
<td>245</td>
<td>1528.5</td>
<td>935.87</td>
</tr>
</tbody>
</table>

Figure 6(b) illustrates the evolution of current density and potential with time for the experimental alloys in the passive region. The values of the pitting potential ($E_{\text{pit}}$), the corrosion potential ($E_{\text{corr}}$), the passive region ($\Delta E_p$), the passivation current density ($I_p$) and the corrosion current density ($I_{\text{corr}}$) for the experimental alloys are listed in Table 2. The $E_{\text{pit}}$, $E_{\text{corr}}$ and

Fig. 5 Effects of sulfur addition on potentiodynamic and potentiostatic polarization behavior of the alloys in deaerated 3.0 M NaCl solution at 338 K: (a) potentiodynamic polarization behavior and (b) potentiostatic polarization behavior at an applied potential of 0 V vs. SCE.

Fig. 6 Effects of sulfur addition on potentiodynamic and potentiostatic polarization behavior of the alloys in deaerated 0.5 M HCl + 2.5 M NaCl solution at 338 K: (a) potentiodynamic polarization behavior and (b) potentiostatic polarization behavior at an applied potential of 0 V vs. SCE.
\( \Delta E_p \) decrease with the increase of the acidity of chloride solution. The passivation current density \( (I_p) \) and corrosion current density \( (I_{corr}) \) increases when the acidity of chloride solution increases. It can be stated that a higher acidity (lower pH) imply lower \( E_{pit} \) and more difficult repassivation process. As the acidity increased, the intersecting point of the anodic and cathodic curve \( (E_{corr}) \) shifted to more negative potential and larger current density. The change in slope of the cathodic curve is due to the increase of hydrogen ion concentration equivalent to a change in pH of the solution. Acidity of solution normally influences the corrosion behavior of iron and its alloys by changing the stability of the oxide film, as predicted by the Pourbaix diagram.28)

### 3.3 Mechanism on the effects of sulfur addition on the pitting or uniform corrosion behavior in chloride solutions of different pH

Figure 7 presents scattered electron images (SEI) and optical microstructure in the alloys after the potentiodynamic polarization test in a deaerated 3.0 M NaCl at 338 K. The corrosion behavior is dominated by the pitting corrosion in NaCl solution. In the case of the 3.0 M NaCl solution, chloride ions \( (Cl^-) \) had a deleterious effect on the pitting corrosion. Chloride ions \( (Cl^-) \) penetrate the passive film and attack the exposed bare metal. As S content in the experimental alloys increased, the sites of pitting corrosion increased. The pitting corrosion of the base alloy and the S added alloy was initiated at the interface areas between inclusions and the matrix, and propagated to the inclusions, and then propagated to the \( \gamma \)-phases, and finally propagated to the \( \gamma \)-phases, based upon the not pitted \( \gamma \)-phases which existed at the edge of the large pit. It is necessary to verify the mechanism of propagation of pitting corrosion for high performance duplex stainless steel.

As presented in Table 3, to clarify the difference in the resistance to pitting corrosion between the \( \gamma \)-phase and \( \alpha \)-phase, the content of Cr and Mo in the \( \gamma \)-phase and the \( \alpha \)-phase in the alloys was quantitatively measured using a SEM-EDS and the N content was measured using a SAM. Then, the pitting resistance equivalent number (PREN) values of the \( \gamma \)-phase and \( \alpha \)-phase by the formula (1) and (2) using a nitrogen factor of 16 and 30 were calculated. When the PREN values are calculated by the formula (1) using a nitrogen factor of 16, the PREN differences \( (PREN_{\gamma} - PREN_{\alpha}) \) show negative values; thus, the PREN values of the \( \alpha \)-phases are higher than those of the \( \gamma \)-phases.
that in HCl solution, a synergetic interaction exists between dissolution of most metals and alloys, and the entire process involves the oxidation of the metal and formation of soluble Fe\(^{2+}\) ions according to equation as follows.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-
\]  

(3)

While the partial cathodic reaction involves the evolution of hydrogen gas.

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

(4)

It is generally accepted that in acidic chloride media, the corrosion rate is mainly controlled by the partial cathodic reaction.\(^{39}\) The overall surface of alloys in 0.5 M HCl + 2.5 M NaCl was strongly corroded due to active hydrogen ions (H\(^+\)). The ferrite phases were uniformly corroded much more than the austenite phases due to the difference of corrosion resistance between two phases. With the progress of uniform corrosion, the pitting corrosion was initiated at the interface areas between inclusions and the matrix, and propagated to the inclusions, and then propagated to the \(\alpha\)-phases, and finally propagated to the \(\gamma\)-phases.

In summary, the effects of solution of different pH on the corrosion behavior of the experimental alloys are schematically presented in Fig. 10. The corrosion behavior is dominated by the pitting corrosion in NaCl solution of pH 7. In the case of the NaCl solution of pH 7, chloride ions...
(Cl\(^-\)) had a deleterious effect on the pitting corrosion. Chloride ions (Cl\(^-\)) penetrate the passive film and attack the exposed bare metal. The pitting corrosion was initiated at the interface areas between inclusions and the matrix, and propagated to the inclusions, and then propagated to the \(\alpha\)-phases, and finally propagated to the \(\gamma\)-phases.

However, the corrosion behavior is dominated by the pitting corrosion and uniform corrosion in NaCl + HCl solution of pH 1. In the case of the HCl + NaCl of pH 1, both chloride ions (Cl\(^-\)) and hydrogen ions (H\(^+\)) had deleterious effects on the pitting and uniform corrosion. Hydrogen ions accelerated corrosion process due to increases of acidity. The overall surface of alloys in HCl + NaCl was strongly corroded due to active hydrogen ions. The ferrite phases were uniformly corroded much more than the austenite phases due to the difference of corrosion resistances between two phases. With the progress of uniform corrosion, the pitting corrosion was initiated at the interface areas between inclusions and the matrix, and propagated to the inclusions, and then propagated to the \(\alpha\)-phases, and finally propagated to the \(\gamma\)-phases.

The effects of sulfur addition on the formation of inclusions and resistance to pitting corrosion of the

<table>
<thead>
<tr>
<th>Alloys</th>
<th>BASE</th>
<th>DXSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>SEM</td>
<td></td>
</tr>
</tbody>
</table>

(Step 1) Uniform corrosion & initiation of pitting corrosion

OM

OM

(Step 2) Uniform corrosion & propagation of pitting corrosion

OM

OM

Fig. 9 SEM micrograph and optical microstructures of the alloys after the potentiodynamic polarization test in deaerated 0.5M HCl + 2.5M NaCl of pH 1 at 338 K.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>NaCl solution of pH 7</th>
<th>HCl + NaCl solution of pH 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step 1</td>
<td>Pitting corrosion at inclusions</td>
<td>Uniform corrosion at two phases</td>
</tr>
<tr>
<td></td>
<td>(\gamma) (\alpha) (\gamma) (\alpha) (\gamma)</td>
<td>(\gamma) (\alpha) (\gamma) (\alpha) (\gamma)</td>
</tr>
<tr>
<td>Step 2</td>
<td>Pit propagation from inclusions to ferrite phases</td>
<td>Uniform corrosion at two phases</td>
</tr>
<tr>
<td></td>
<td>(\gamma) (\alpha) (\gamma) (\alpha) (\gamma)</td>
<td>(\gamma) (\alpha) (\gamma) (\alpha) (\gamma)</td>
</tr>
</tbody>
</table>

Fig. 10 Schematic of the effects of pH on the corrosion behavior of the alloys in deaerated chloride solutions of different pH.
Experimental alloys are schematically presented in Fig. 11. Compared to the base alloy, as the interface areas between the inclusions and the matrix in the sulfur added alloy increase, the preferential sites for the initiation of pitting corrosion in the sulfur added alloys also increase. Hence, as sulfur content increased, the resistance to pitting corrosion decreased due to the formation of numerous manganese sulfides deteriorating the corrosion resistance. The pitting corrosion of the alloy was initiated at the interface areas between inclusions and the matrix, and then propagated to the \( \gamma \)-phases, and finally propagated to the \( \alpha \)-phases.

4. Conclusions

To elucidate the effects of sulfur addition on the formation of inclusions and the corrosion behavior of super duplex stainless steels in chloride solutions of different pH and the reasonable nitrogen factor in the PREN equation, a metallographic examination, potentiodynamic & potentiostatic polarization tests, scanning electron microscope and energy dispersive spectroscopy (SEM-EDS) analyses of inclusion and austenite (\( \gamma \)) phase and ferrite (\( \alpha \)) phase, a scanning Auger multi-probes (SAM) analysis of two phases, and a thermodynamic calculation using Thermo-Calc software were conducted. These various tests led to the following conclusions.

1. As sulfur content in the alloys increased, the pitting corrosion resistance decreased due to the formation of numerous manganese sulfides and manganese oxy-sulfides deteriorating the corrosion resistance and an increase in the areas of preferential interfaces for the initiation of the pitting corrosion.

2. The corrosion behavior is dominated by the pitting corrosion in neutral chloride solution and by the pitting corrosion and uniform corrosion in acidic chloride solution. In the case of the NaCl solution of pH 7, chloride ions (\( \text{Cl}^- \)) had a deleterious effect on the pitting corrosion. The pitting corrosion was initiated at almost all types of inclusions of MnS sulfides, MnOS oxy-sulfides and MnO oxides deteriorating the corrosion resistance, and then propagated to the \( \alpha \)-phases, and finally propagated to the \( \gamma \)-phases. However, in the case of the HCl + NaCl solution of pH 1, both chloride ions (\( \text{Cl}^- \)) and hydrogen ions (\( \text{H}^+ \)) had deleterious effects on the pitting and uniform corrosion. The ferrite phases were uniformly corroded more than the austenite phases due to the difference of corrosion resistances between two phases.

3. The resistance to pitting corrosion of the tested super duplex stainless steel was affected by the preferential interface areas between inclusions and the matrix, and the PREN difference between the \( \gamma \)-phase and the \( \alpha \)-phase for the initiation and propagation of the pitting corrosion. It is reasonable to explain the difference of pitting corrosion resistance between these two phases in tested super duplex stainless steels through the PREN values calculated using a nitrogen factor of 30 in this study.

REFERENCES