Influence of Cerium and Tungsten Addition on the Passive Behaviour of 444-type Ferritic Stainless Steels

Ming-yu Ma¹, Chun-lin He², Hou-long Liu¹, Li-qing Chen¹,*

¹ State Key Laboratory of Rolling and Automation, Northeastern University, Shenyang 110819, China
² College of Mechanical Engineering, Shenyang University, Shenyang 110044, China
*E-mail: lqchen@mail.neu.edu.cn

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The surface passivity properties of conventional 444-type ferritic stainless steel (FSS), Ce-containing 444-type FSS and W-Ce-containing 444-type FSS were studied in a 1.0 mol/L H₂SO₄+0.5 mol/L NaCl solution by employing electrochemical impedance spectroscopy (EIS) analysis, the potentiodynamic polarization test and capacitance measurement. The potentiodynamic polarization curves revealed that the Ce and/or W addition did not affect the pitting potential \( E_{p} \) and the corrosion potential \( E_{corr} \), whereas the corrosion current density \( i_{corr} \) and the passive current density \( i_{p} \) were decreased significantly. The morphological observation of the specimens after polarization suggested that alloying with Ce and W decreased the number of pitting sites and inhibited the active dissolution of pits. The Mott-Schottky analysis revealed that all the oxide layers formed on FSS behaved as n-type semiconductors at the potential range of 0.3–0.8 V SCE and that the donor concentration \( N_{D} \) in the passive film increased with Ce and W alloying. In addition, the diffusivity values of the donors in FSS passive films were calculated based on the combination of capacitance measurements and PDM theory. The EIS analysis showed that the Ce-W-containing stainless steel presented lower polarization resistance values.

Keywords: Ferritic stainless steel; Tungsten; Cerium; Passive film; Diffusivity.

1. INTRODUCTION

It is well known that the excellent anti-corrosion property of stainless steel is a result of the contribution of a stable passive film on the stainless steel surface. In the last decade, researchers proposed different models and theories to explain the surface passivation. The point defect model (PDM) established by Macdonald et al. was the most popular description [1,2]. PDM assumed that the passive film contained highly concentrated point defects. The protective film built on the passivated alloy is a mixture of metallic oxide layers, which should be an insulator with a perfect crystal structure. However, the point defects including oxygen vacancies, metal interstitials, and metal vacancies dope the passive
film, which makes it behave as a semiconductor. Moreover, according to the predominant point defects within the structure, the passive films are classified as p-type semiconductors and n-type semiconductors. Therefore, the type and the density of point defects are important to study the protective mechanism against corrosion [3-5].

Although PDM describes the passive film qualitatively, the capacitance measurement in the form of Mott-Schottky plots provides a microscopic quantitative calculation of the point defect concentration within the passive film. The Mott-Schottky plot has turned out to be a useful in situ method to study the semiconducting behaviour of oxide films [6,7]. The previous studies on the semiconducting behaviour of barrier layers formed on various materials have made a crucially important contribution to understanding the growth and breakdown of passive film [8-11]. It has been demonstrated that the semiconducting behaviour of the passive layer is affected by the alloy composition, solution temperature, pH value of solution, aggressive ion concentration and so on.

On the basis of PDM theory, the diffusion of charge carriers in passive film under the influence of an electrostatic field leads to the growth and breakdown of the passivated surface. Thus, the point defect diffusion process is a key factor in understanding the migration of charge carriers and the kinetics of the oxide layer growth. The Mott-Schottky analysis in conjunction with PDM was employed to evaluate the diffusivity of charge carriers within the oxide film on various materials [12, 13]. It is predicted that the diffusivity is affected by the alloy composition, environment of corrosion and microstructure of the matrix. The effect of grain size on the passivity of stainless steel is still keenly debated in the literature. Some researchers showed that nanocrystallized stainless steel exhibited a lower density and diffusivity of the donor [14, 15], while others reported the opposite effect of grain refinement on passivity [16]. The calculation of point defect diffusivity within the barrier layer formed on AISI316L stainless steel in different concentration H2SO4 solutions suggested that the donor density and diffusion flux increased with the solution concentration [17]. The point defect diffusivity of the donors within the passive film formed on AISI316L is one order of magnitude higher than that of AISI321 in H2SO4 [18].

The good mechanical properties, excellent anti-corrosion behaviour, and low cost of 444-type ferritic stainless steel make it meet the requirements of various industrial applications [19-22]. To achieve the goal of improving the properties of 444-type ferritic stainless steel in high-temperature situations, elemental cerium and tungsten were added to improve the high-temperature property and the oxidation resistance. As a fairly new alloy element in economy stainless steel, tungsten was alloyed in steel to enhance the mechanical properties of stainless steel under high temperature conditions [23, 24]. Furthermore, researchers also observed that during the high temperature oxidation process, rare earth addition is beneficial to the adhesion oxide scale. On the other hand, it has been demonstrated by previous researchers that alloying with rare earth metals (REMs) dramatically decreased the number of inclusions, which is detrimental to the alloy matrix pitting corrosion resistance. Therefore, this purification effect is responsible for improving the corrosion resistance by REM addition [25-27]. Tungsten is believed to exhibit similar chemical and electrical behaviours to those of molybdenum, considering the location in the periodic table of elements [28,29]. Thus, W is predicted to have a positive influence on the anti-corrosion ability in 19Cr2Mo ferritic stainless steel [30].

The passive behaviour of stainless steels is important for further understanding their fundamental properties and applications. However, until now, there has been no study on the concentration and
diffusion behaviour of charge carriers in passive film formed on 444-type ferritic stainless steel in acid solutions. In this study, the potentiodynamic polarization test, electrochemical impedance spectroscopy (EIS) and capacitance measurement of ferritic stainless steel were performed. The Mott-Schottky plot was used to model the experimental data in combination with PDM. The effect of the alloying element Ce and W on the passivity of the stainless steel surface was also discussed.

2. EXPERIMENTAL SECTION

The elemental composition of the 444-type FSSs is listed in Table 1. All received alloys were forged and then hot rolled at 1150°C to a thickness of 5 mm. The hot rolled plates were annealed for 10 min at 1000°C and cold rolled to 1 mm. Finally, the cold rolled steels were recrystallization annealed at 1000°C for 1 min. The heat-treated stainless steel sheets were cut into 10 mm×10 mm and mounted in a cold curing epoxy resin. The FSS samples were polished with SiC paper to 2000 grit and then cleaned with acetone and dried with hot air.

Table 1. Elemental composition of the received stainless steels (in wt%).

<table>
<thead>
<tr>
<th>Steel Code</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Nb</th>
<th>Ti</th>
<th>N</th>
<th>Mo</th>
<th>Ce</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSS1</td>
<td>0.006</td>
<td>0.54</td>
<td>0.33</td>
<td>0.006</td>
<td>0.006</td>
<td>19.7</td>
<td>0.436</td>
<td>0.174</td>
<td>0.072</td>
<td>2.09</td>
<td>–</td>
<td>–</td>
<td>Bal.</td>
</tr>
<tr>
<td>FSS2</td>
<td>0.009</td>
<td>0.52</td>
<td>0.32</td>
<td>0.008</td>
<td>0.008</td>
<td>19.5</td>
<td>0.450</td>
<td>0.155</td>
<td>0.072</td>
<td>1.97</td>
<td>0.048</td>
<td>–</td>
<td>Bal.</td>
</tr>
<tr>
<td>FSS3</td>
<td>0.007</td>
<td>0.50</td>
<td>0.32</td>
<td>0.010</td>
<td>0.009</td>
<td>19.1</td>
<td>0.441</td>
<td>0.137</td>
<td>0.071</td>
<td>1.95</td>
<td>0.056</td>
<td>0.58</td>
<td>Bal.</td>
</tr>
<tr>
<td>FSS4</td>
<td>0.010</td>
<td>0.53</td>
<td>0.35</td>
<td>0.008</td>
<td>0.010</td>
<td>19.9</td>
<td>0.443</td>
<td>0.113</td>
<td>0.071</td>
<td>2.03</td>
<td>0.053</td>
<td>1.12</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

All electrochemical tests were carried out with a PARSTAT 2273 electrochemical station in a 1.0 mol/L H₂SO₄+0.5 mol/L NaCl solution at 25±1°C. A traditional electrochemical cell equipped with a saturated calomel electrode as the reference electrode was applied. For the EIS tests, the specimens were scanned at frequencies ranging from 100 kHz to 10 mHz with the amplitude of 10 mV. The experimental data were analysed with the ZSimpWin software, from which the fitting model was selected. The potentiodynamic polarization tests were conducted in a potential range of −0.25 V_{OCP}–1.6 V_{SCE}, and the scanning rate was 0.5 mV/s. All FSS specimens were potentiostatically polarized at 0.1, 0.2, 0.3 and 0.4 V_{SCE} (within the steady passive potential range for all steels) for 1 h to form stable passive films before the capacitance measurements. The capacitance measurements of the oxide layer formed at various potentials were performed in a potential range of 0 to 1.0 V_{SCE} by applying a 50 mV step rate, 10 mV ac signal and 1 kHz fixed frequency. Prior to both potentiodynamic and potentiostatic polarization, the steel surface was cathodically polarized at −0.8 V_{SCE} for 180 s to completely remove
the oxides formed in air. The EIS tests were conducted after stabilization for 10 min at the open circuit potential. The potentiodynamically polarized specimens were cleaned in acetone, and a scanning electron microscope (SEM) was used to observe the pitting morphology.

3. RESULTS AND DISCUSSION

3.1 Pitting corrosion analysis

The potentiodynamic polarization curves of the FSSs are shown in Fig. 1, and the extracted electrochemical parameter values are summarized in Table 2. It can be seen from Fig. 1 that all specimens exhibit a transition from the active state to the passive state in the tested potential range. Apart from a slight reduction in critical passive potential ($E_c$), the decreases in corrosion current density ($i_{corr}$), critical passive current density ($i_c$) and stable passive current density ($i_p$) caused by Ce and/or W addition can be observed, as shown in Table 2. On the other hand, tungsten and cerium addition did not alter the corrosion potential ($E_{corr}$) or the pitting potential ($E_p$) significantly.

![Figure 1. Polarization curves of ferritic stainless steel in a 1.0 mol/L H$_2$SO$_4$+0.5 mol/L NaCl solution.](image)

<table>
<thead>
<tr>
<th>Steel Code</th>
<th>$E_c$ (mV)</th>
<th>$i_c$ (μA/cm$^2$)</th>
<th>$E_p$ (mV)</th>
<th>$i_p$ (μA/cm$^2$)</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSS1</td>
<td>−334</td>
<td>16</td>
<td>0.89</td>
<td>152</td>
<td>482</td>
<td>317</td>
</tr>
<tr>
<td>FSS2</td>
<td>−379</td>
<td>6</td>
<td>0.98</td>
<td>51.6</td>
<td>490</td>
<td>250</td>
</tr>
<tr>
<td>FSS3</td>
<td>−379</td>
<td>6</td>
<td>1.0</td>
<td>23.6</td>
<td>486</td>
<td>235</td>
</tr>
<tr>
<td>FSS4</td>
<td>−379</td>
<td>1</td>
<td>0.99</td>
<td>5.8</td>
<td>488</td>
<td>172</td>
</tr>
</tbody>
</table>

Actually, the decreasing $E_c$ and $i_c$ indicated that alloying with Ce and W promoted the initiation of film formation. Moreover, the decreasing corrosion current density revealed that alloying Ce and W
with 19Cr2Mo stainless steel decreased the dissolution rate of the unprotected matrix. All of these observations supported the beneficial impact of tungsten and cerium addition on the pitting corrosion resistance and passive film stability.

3.2 Corrosion morphology

Fig. 2 shows the SEM images of the ferritic stainless steels after the potentiodynamic polarization test in a 1.0 mol/L H₂SO₄+0.5 mol/L NaCl solution. As shown in Fig. 2, the pits grown on all stainless steel specimens are shaped like semi-ellipses and no visible metal lacy cover exists over the pit mouth. Compared with FSS1, FSS2 exhibited a lower number of pits. The decrease in pitting sites can be attributed to the formation of stable REM sulphide inclusions, which would not act as nucleation sites for pitting [31-33]. Therefore, it showed that the resistance to pitting corrosion of Ce-containing stainless steels was superior to that of the conventional 444-type ferritic stainless steel. Moreover, it can be observed clearly from the SEM images that the diameters of corrosion holes have been dramatically reduced with W alloying in the Ce-containing steel.

![Figure 2. SEM images of the ferritic stainless steel after potentiodynamic polarization in a 1.0 mol/L H₂SO₄+0.5 mol/L NaCl solution: (a) FSS1, (b) FSS2, (c) FSS3, and (d) FSS4.](image)

In general, the localized breakdown of the passive film results in the rapid dissolution of the bare alloy matrix in an aggressive solution. The potentiodynamic polarization analysis revealed that all of the passive films were broken down at a comparable potential. Thus, the decrease in dissolved alloy volume
resulted from the reduction in dissolution rate by alloying with W. In summary, Ce addition should inhibit the formation of stable pits and consequently make ferritic stainless steels less susceptible to pitting corrosion. Concerning W addition, this alloying element improves the pitting corrosion resistance of FSSs by reducing the corrosion rate.

3.3 Capacitance measurements

PDM suggested that the point defects present in the oxide layer are cation vacancies, oxygen vacancies, and cation interstitials. In addition, the electron acceptors within p-type semiconductors are cation vacancies, while anion vacancies and cation interstitials act as the electron donors for n-type semiconductors [34, 35]. It is expected that the elemental composition and the electronic structure of the barrier layer formed on an alloy should be more complicated than those for pure metals because the oxidation state difference between the alloying element cation and the bulk metal may affect the film electronic defect structure. For example, the barrier layers on stainless steels are n-type, whereas that on pure Cr is p-type, while all of them are described as “defective Cr$_2$O$_3$”. This deviation is because of the new alloy elements doping the barrier layer or the cation vacancy generation inhibition effect caused by anion vacancies and cation interstitials that is generated in the barrier layer on ferritic stainless steels [36, 37].

It has been proved by previous studies that a space charge layer exists in the oxide film outer layer and maintains a potential drop through the passive layer. The appearance of a gap between the Fermi level of the semiconductor located on the test surface and the redox potential of the electrolyte leads to the electron transfer between the alloy surface and the solution. To characterize the semiconducting behaviour of stainless steel, the Mott-Schottky measurement was conducted to study the capacitance of the electrode surface. In the Mott-Schottky theory, the most important assumption is that the dominant capacitance measured in the test is related to the space charge layer, whereas at a frequency of 1 kHz, the double layer capacitance at the steel surface/electrolyte should be neglected.

The functional relationship between the measured capacitance $C$ and the applied potential $E$ is described by the Mott-Schottky formula [38, 39]:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_D} (E - E_{fb} - \frac{kT}{e})$$

for p-type (1)

where $N_D$ is the donor concentration for n-type semiconducting behaviour; $T$ is the absolute temperature; $E_{fb}$ is the flat band potential; and $\varepsilon_0$, $\varepsilon$, $e$, and $k$ are the vacuum permittivity (8.854×10$^{-12}$ Fm$^{-1}$), dielectric constant (15.6), electron charge (1.602×10$^{-19}$ C) and Boltzmann constant, respectively.

Fig. 3 shows the Mott-Schottky diagrams for all FSS samples in a 1.0 mol/L H$_2$SO$_4$+0.5 mol/L NaCl solution. The plots for all specimens are qualitatively similar, which can infer the same electronic character for the passive films. In the range of approximately 0.3–0.7 V$_{SCE}$, the positive slopes of the linear part reveal that all the semiconductors formed on the ferritic stainless steels behave as n-type. For all specimens, the peaks that appeared in the Mott-Schottky plots indicate that the semiconducting behaviour of the films changes from n-type to p-type. Additionally, it should be noticed that the slope values increase with the applied potential for all ferritic stainless steels.
Figure 3. Mott-Schottky plots of the films formed at different potentials: (a) FSS1, (b) FSS2, (c) FSS3, and (d) FSS4.

By assuming the semiconductor dielectric constant, the slope of the Mott-Schottky plots in the range of 0.3–0.5 V\textsubscript{SCE} was fitted to calculate the donor density $N_D$ according to the following formula \cite{40, 41}:

$$N = \frac{2}{m \cdot \varepsilon \cdot \varepsilon_0 \cdot e} \quad (2)$$

where $m$ is the slope fitted from the linear part in the Mott-Schottky plots.

The calculated values of $N_D$ for the semiconductors formed on FSSs in a 1.0 mol/L H\textsubscript{2}SO\textsubscript{4}+0.5 mol/L NaCl solution at various potentials are presented in Fig. 4. It can be seen from Fig. 4 that significantly quantitative differences can be observed in the capacitance, although they have similar semiconducting behaviour. The alloying elements Ce and W increased the capacitance of the film, which results from an increase in the number of charge carriers and a reduction in the electron depleted layer. At the same film formation potential, Ce and W addition resulted in a slight increase in $N_D$. Generally, a higher donor concentration in the barrier layer means more non-stoichiometry defects in the oxide layer, which leads to a more disordered passive film structure.
Figure 4. Donor density of the passive films of the ferritic stainless steels formed in a 1.0 mol/L H₂SO₄+0.5 mol/L NaCl solution at different formation potentials: (a) FSS1, (b) FSS2, (c) FSS3, and (d) FSS4.

As mentioned earlier, other elements alloyed in stainless steels result in the new alloying element doping of the barrier layer. In summary, the harmful influence of alloying with Ce and W on the passive film could be attributed to the new cation that dopes the semiconductor, which neutralizes the dopant, thereby making the steel surface less protective to the penetration of insidious ions.

3.4 Donor diffusivity calculation

PDM assumes that in the film growth process, the transfer of metal interstitials and/or oxygen vacancies is required [42]. As mentioned above, the main point defects in n-type semiconductors formed on ferritic stainless steels are oxygen vacancies and metal interstitials; however, the contribution of vacancies and interstitials on the diffusivity is impossible to separate. Thus, the calculated diffusivity involves the synergistic effect of these two types of point defects. The relationship between the semiconductor formation potential $E_f$ and the donor density $N_D$ within a semiconductor has been given as the following formula [43-45]:

$$N_D = \omega_1 \exp(-bE) + \omega_2$$  \hspace{1cm} (3)

where $\omega_1$ and $\omega_2$ are constants obtained from the fitting curves. Fig. 5 shows the exponential fitting curves of the experimental data. The uncertain constants related to the donor diffusivity could be determined from the fitting parameters. $D_0$ could be demonstrated by the following equation [46]:

$$D_0 = -\frac{J_0}{2G\omega_2}$$  \hspace{1cm} (4)
where \( J_0 \) is the diffusion flux of the point defects at the passive state, and \( G \) is a constant related to the electric field strength and temperature. The relationship between the diffusion flux \( J_0 \) and the passive current \( i_p \) could be described by:

\[
J_0 = -\frac{i_p}{2e} \tag{5}
\]

\[
G = \frac{F \varepsilon}{RT} \tag{6}
\]

where \( F \) is the Faraday constant, \( \varepsilon_L \) (3.9×10\(^6\) V/cm) is the mean electric field strength of the space charge layer, \( T \) is the thermodynamic temperature, and \( R \) is the gas constant.

The combination of the capacitance measurement in the form of the point defect concentration analysis and PDM provides the diffusion properties of charge carriers in the oxide layer formed on the ferritic stainless steels in a 1.0 mol/L H\(_2\)SO\(_4\)+0.5 mol/L NaCl solution, and the obtained parameters are shown in Table 3. Taking into account the error caused by assuming the same value of \( \varepsilon_L \), the values of the diffusivity of the donors are estimated to be in the range of 10\(^{-17}\)–10\(^{-15}\) cm\(^2\)/s and decrease with Ce and W alloying.

### Table 3. Parameters fitted from Figure 4 and the calculated diffusion coefficient

<table>
<thead>
<tr>
<th>Steel Code</th>
<th>( \omega_1 ) (10(^{21}) cm(^{-3}))</th>
<th>( \omega_2 ) (10(^{21}) cm(^{-3}))</th>
<th>( b ) (V(^{-1}))</th>
<th>( i_p ) (µA/cm(^2))</th>
<th>( D_0 ) (10(^{-16}) cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSS1</td>
<td>4.66</td>
<td>1.52</td>
<td>11.8</td>
<td>152</td>
<td>10.3</td>
</tr>
<tr>
<td>FSS2</td>
<td>3.08</td>
<td>1.14</td>
<td>2.79</td>
<td>51.6</td>
<td>4.7</td>
</tr>
<tr>
<td>FSS3</td>
<td>2.30</td>
<td>3.0</td>
<td>14.84</td>
<td>23.6</td>
<td>0.82</td>
</tr>
<tr>
<td>FSS4</td>
<td>1.63</td>
<td>2.6</td>
<td>7.48</td>
<td>5.8</td>
<td>0.23</td>
</tr>
</tbody>
</table>

When the alloy is exposed to an aggressive environment, the semiconducting passive film with a bilayer structure will build at the alloy/electrolyte interface. The protectivity of the barrier layer involves the concentration and the diffusion coefficient of electron donors within passive film. The lower diffusivity of the passive film formed on Ce- and W-containing stainless steel reveals that alloying with Ce and W inhibits the reaction rate within the passive film. Therefore, the alloying elements, Ce and W, increase the stability of the passive film, although the donor density is increased.

### 3.5 Thickness analysis of passive film

Based on PDM, the passive films have a bilayer structure, where the defective barrier grows towards the alloy matrix and the outer layer forms via the precipitation of metallic oxides or oxyhydroxides. Generally, the thickness of the oxide layer on stainless steel could be calculated approximately from the expression [47, 48]:

\[
L_f = \frac{\alpha_0 A}{C_0} - \frac{\alpha_0 A}{C} \tag{7}
\]

Fig. 5 presents the thickness values of the film formed on FSSs and fitted as a function of \( E_t \). It is notable that the film thickness increased with the film formation potential. Moreover, the slope of the fitting line for the Ce- and/or W-containing specimens decreased.
It can be concluded that Ce and/or W addition decreased the growth rate of the film formed on ferritic stainless steel. The film growth process is controlled by the transportation of electronic carriers from the matrix/semiconductor interface to the semiconductor/electrolyte interface. As a result, the lower diffusivity value leads to a lower film growth rate.

3.6 EIS measurement

The EIS experiments were conducted on the passivated surface of type 444-type ferritic stainless steels to evaluate the influence of the alloying elements, cerium and tungsten, on the interfacial properties of the oxide layer formed on FSSs. On the basis of the polarization plots, the prepassivated potentials were 0.1, 0.2, 0.3 and 0.4 V_{SCE}, which were within the passive range for all specimens. The measured impedance responses are shown in Fig. 6 as Nyquist plots. All the specimens display similar capacitive features, which are characterized by the semicircle arc of the Nyquist plot. The presence of the capacitive surface can be attributed to the charge transfer process associated with the passive layer capacitance. In general, the corrosion resistance is proportional to the polarization resistance, which is characterized by the radius of the capacitance loop.
Based on the response character, the R(Q(R)) equivalent circuit, as shown in Fig. 6, was selected to characterize the charge transfer resistance. The fitting circuit consists of a solution resistance (Rs) between the stainless steel surface and the reference electrode, constant phase angle element (CPE), which is more suitable than a pure capacitor [49], and charge transfer resistance (Rct).

The impedance of Q is expressed by the formula [50]:

\[
Z_Q = \frac{1}{Y_0 (i\omega)^n}
\]  

(1)

where \( Y_0 \) is the admittance, \( \omega \) is the angular frequency, and \( n \) is the Q exponent, \( i^2 = -1 \).

![Figure 7. Equivalent circuit for fitting the EIS data.](image)

Table 4. Polarization resistance of the film in 1.0 mol/L H₂SO₄+0.5 mol/L NaCl (Ω·cm²)

<table>
<thead>
<tr>
<th>Steel Code</th>
<th>0.1 V_SCE</th>
<th>0.2 V_SCE</th>
<th>0.3 V_SCE</th>
<th>0.4 V_SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSS1</td>
<td>1.55×10⁵</td>
<td>1.26×10⁵</td>
<td>0.75×10⁵</td>
<td>1.36×10⁵</td>
</tr>
<tr>
<td>FSS2</td>
<td>1.35×10⁵</td>
<td>1.11×10⁵</td>
<td>0.68×10⁵</td>
<td>1.01×10⁵</td>
</tr>
<tr>
<td>FSS3</td>
<td>1.05×10⁵</td>
<td>1.08×10⁵</td>
<td>0.73×10⁵</td>
<td>0.85×10⁵</td>
</tr>
<tr>
<td>FSS4</td>
<td>0.77×10⁵</td>
<td>0.64×10⁵</td>
<td>0.51×10⁵</td>
<td>0.62×10⁵</td>
</tr>
</tbody>
</table>

The fitted polarization resistances of all specimens are shown in Table 4. It is observed that the polarization resistance of the Ce and W-containing ferritic stainless steel is lower than that of the conventional 444-type stainless steel. The polarization resistance (\( R_p \)) provides a key parameter of the corrosion reaction and relates to the corrosion resistance. The decrease in polarization resistance indicates that the addition of Ce and W could not improve the anti-corrosion property of the ferritic
stainless steel in a 1.0 mol/L H$_2$SO$_4$+0.5 mol/L NaCl solution.

4. CONCLUSIONS

The conventional 444-type ferritic stainless steel and the Ce- and/or W-containing 444-type ferritic stainless steels showed a comparable pitting potential in a 1.0 mol/L H$_2$SO$_4$+0.5 mol/L NaCl solution. The current density of the steady state passive film decreased with Ce and W addition, which suggested that the protectivity of the passive film was improved by alloying with Ce and W. Furthermore, alloying with Ce reduced the number of pitting sites, while W addition inhibited the active dissolution rate of pits. On the other hand, the alloying element Ce and W addition increased the donor density within the passive film but did not change the type of semiconductor of the passive film. Further analysis based on PDM revealed that the beneficial effect of alloying with Ce and W is related to the suppression of the transportation of the donor within the passive film. In other words, the essence of a more stable passive film lay on the decrease in diffusivity of point defects, which restrained the electrochemical reaction process within the passive film formed on the Ce and W-containing ferritic stainless steel.

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References

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