Electrochemical Behavior of 2205 Duplex Stainless Steel in a Chloride-Thiosulfate Environment

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The electrochemical behavior of 2205 duplex stainless steel in chloride-thiosulfate environment was investigated by various methods: potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and Mott-Schottky measurements. The chemical composition of the passive films was analyzed by X-ray photoelectron spectroscopy (XPS). The composition of the gases produced during the corrosion process was detected by a mass spectrometer. The results indicated that $S_2O_3^{2-}$ had a synergistic and detrimental effect on passive film breakdown and made it easier for Cl⁻ to initiate pitting by reducing to hydrogen sulfide which catalyzed the anodic dissolution. The selective dissolution of the ferrite phase was investigated on 2205 duplex stainless steel. The Cl⁻ and $S_2O_3^{2-}$ slightly deteriorated the passive films in the passive region at high anodic potentials, and $S_2O_3^{2-}$ facilitated the oxidation of Cr(III) to Cr(VI). The capacitance and XPS results revealed that the oxide films on 2205 duplex stainless steel consisted mainly of Cr oxide and Fe oxide, and in different passive regions, they exhibit different electrochemical and semiconductor properties.

Keywords: 2205 duplex stainless steel, electrochemical behavior, chloride-thiosulfate, passive film.

1. INTRODUCTION

Thiosulfate $(S_2O_3^{2-})$, one of the main sulfide oxidation products, as well as other reactive sulfur species, are well known for their deleterious effect on the resistance of highly alloyed sensitized stainless steel to localized corrosion [1-5]. Thiosulfate has been proven to that it act synergistically with other common ions, such as chlorides and sulfates, that are responsible for severe damage in various environments related to the petroleum, paper and pulp industries [6-10]. Thiosulfate pitting was reported to be most severe when the molar ratio of (chloride + sulfate) to thiosulfate is between 10 and 30 [7,10,11-13]. The effect of thiosulfate in chloride containing environments on localized corrosion has

been interpreted as occurring in two different ways: (1) thiosulfate is reduced to elementary sulfur (S^0), which adsorbs on the fresh bare metallic surface preventing passivation; or (2) thiosulfate is reduced to hydrogen sulfide (H₂S) which catalyzes the anodic dissolution of stainless steel [10,14-17].

Duplex stainless steels have been increasingly employed in industrial applications in recent years, due to their high strength and excellent corrosion resistance in many environments, such as those in desalination systems; in chemical plants; and in the petroleum, pulp and paper industries [18-21]. The composition, thickness and semiconductor characteristics of the passive films are critical to the corrosion behavior of the stainless steels [22,23]. Although a large number of studies have been devoted to the role of thiosulfate on the pitting corrosion of stainless steels, less attention has been paid to investigating the electrochemical characterization or structure of passive films on 2205 duplex stainless steel formed in chloride-thiosulfate environments. Thus, the localized corrosion behavior and electrochemical properties in that medium remain unclear.

The present study aims to investigate the corrosion behavior, composition, electrochemical properties and structure of films on 2205 duplex stainless steel in naturally aerated thiosulfate-chloride (the molar ratio of (chloride + sulfate) to thiosulfate is 15) solution. The corrosion behavior of the stainless steel in the tested environment was studied by potentiodynamic polarization, and the growth and electrochemical characterization of the films were investigated using electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis. The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS). The surface morphology was observed by a digital microscope KEYENCE VHX-5000 with a visible 3D microscopy system and scanning electron microscopy (SEM). A mass spectrometer was used to detect the composition of the gases produced during the corrosion process.

2. MATERIALS AND METHODS

The chemical composition (wt.%) of 2205 duplex stainless steel for the present study is shown in Table 1.

Element	С	Cr	Ni	Mo	S	Р	Cu	Mn	Si	Ν	Fe
Content	0.018	22.47	5.39	3.06	0.003	0.025	0.15	0.93	0.34	0.163	Balance

Table 1 Chemical compositions of 2205 duplex stainless steel (wt.%).

The measurements of the stainless steels were taken after they were solution annealed at 1050 °C for 2 hours, followed by water quenching. All surfaces of the sample needed the oxide layer to be removed. Specimens with a diameter of 11 mm and a thickness of 2 mm were connected with copper wire and covered with epoxy resin allowing a surface area of 1 cm² to be exposed to the solution medium. The working surfaces of the specimens were wet ground using a series of silicon carbide (SiC) papers

and finally polished with 1.0 and 0.5 μ m alumina polishing powder, rinsed, ultrasonically degreased with alcohol and dried in warm air.

Electrochemical measurements were performed in (a) 3.5% sodium chloride and (b) 3.5% sodium chloride + 0.05 M sodium thiosulfate solutions at room temperature. The test solutions were freshly prepared with distilled water for each electrochemical measurement. All measurements were run using a Princeton VersaSTAT 3 electrochemical system, which comprised a traditional corrosion cell with a three-electrode system. A saturated calomel reference electrode (SCE) was connected to the cell via a Luggin capillary filled with a salt bridge as reference electrode and a platinum plate was used as a counter electrode.

At the beginning of each electrochemical measurement, the specimens were pretreated with a cathodic reduction process at -0.8 VSCE for 30 minutes to remove the oxide film. The specimen was then able to corrode freely for 30 minutes and obtain a stable open circuit potential (OCP) for all tests. The potentiodynamic polarization curves started at -0.8 V_{SCE} to the transpassive potential and were recorded at a rate of 0.5 mV s⁻¹. EIS tests were performed at a steady state OCP and varied from 100 kHz to 10 mHz, with a frequency of 10 points per decade and at an amplitude of 10 mV ac as a sine function. ZView software was used for the measured EIS data analysis. Mott-Schottky measurements were scanned from -0.8V_{SCE} to 1.2V_{SCE} in the anodic direction at a step height of 15 mV and a frequency of 1 kHz. All the electrochemical measurements were repeated three times on separate specimens at room temperature (25 °C).

The chemical analysis of the passive films after potentiostatic polarization at different potentials for 8 hours was performed by XPS using a Thermo ESCALAB 250XI spectrometer with a pass energy of 20 eV and a monochromatic Al K α radiation source. The spectrum fitting was performed using XPSPEAK software which contains the Shirley background subtraction and Gaussian-Lorentzian tail function.

The composition of the gases produced during the corrosion process was measured by a mass spectrometer Pfeiffer Vacuum QMS 220. When a steady state anodic dissolution was obtained, the mass spectrometer was connected to the reaction to detect the composition of the gas prior to platform. The electrochemical experiment potential of the corrosion behavior selected for analysis was determined based on the potentiodynamic polarization curve.

3. RESULTS AND DISCUSSION

3.1. Polarization Measurements

A comparative plot of the potentiodynamic polarization curves for 3.5% NaCl solution with and without thiosulfate are shown in Figure 1, revealing multiple steps dissolution, prepassive, passive and transpassive. No significant differences were observed in the shape of the plots, suggesting that the kinetics of the corrosion processes are not substantially affected. It is clear that thiosulfate alone did not cause severe corrosion; however, the chloride caused the pitting potential to shift slightly toward the

negative direction, showing that $S_2O_3^{2-}$ had a detrimental effect on the passive film breakdown and made it easier for Cl⁻ to initiate pitting in the chloride-thiosulfate environment.

The morphology of the pitting in the specimens after the polarization measurements in the chloride and thiosulfate solution was different from that in chloride-only solution, as shown in Figure 2 and Figure 3. The number of pits in the thiosulfate containing solution was greater than that in the chloride-only solution, and the pits were typically deep and large in diameter. A possible explanation for this is that thiosulfate accelerated corrosion in pits that were already initiated, leading to rapid pitting propagation. Thiosulfate and chloride had a synergistic effect on the initiation of pitting corrosion. In addition, it should be noted that pits were found in the ferrite phase and at the ferrite side of the ferrite-austenite boundary, as demonstrated in Figure 4.



Figure 1. Potentiodynamic polarization of 2205 duplex stainless steel in (a) 0.05 M Na₂S₂O₃, (b) 3.5% NaCl, and (c) 3.5% NaCl + 0.05 M Na₂S₂O₃.



Figure 2. Corrosion morphology of 2205 duplex stainless steel after potentiodynamic measurements in (a) 3.5% NaCl and (b) 3.5% NaCl + 0.05 M Na₂S₂O₃ solution.



Figure 3. 3D visualization of pits on 2205 duplex stainless steel after potentiodynamic measurements in (a) 3.5% NaCl and (b) 3.5% NaCl + 0.05 M Na₂S₂O₃ solution.



Figure 4. Images of pits on 2205 duplex stainless steel after potentiodynamic measurements in 3.5% NaCl + 0.05 M Na₂S₂O₃ solution.

The selective dissolution of the ferrite phase was attributed to the higher corrosion resistance of austenitic phase due to the enrichment of N and Ni [24]. Selective dissolution of the ferrite phase in 2205 duplex stainless steel was reported in 10 wt.% FeCl₃ solution, and the phenomenon was argued to be due to the difference in chemical composition between the two phases. The differences in the austenite and ferrite phases might be affected by the presence of Cu in the austenite phase which can enhance the pitting resistance of the austenitic phase. In addition, the high levels of sulfur in the ferrite phase may reduce the pitting resistance. Similarly, the presence of phosphorus which is higher in the ferrite phase than in the austenite is also believed to have a detrimental effect. Therefore, this synergy between elements accounts for the improved pitting resistance of the austenite phase.

It can be clearly seen that H₂S was generated during the dissolution process at a high anodic potential, and even though it was limited, its generation indicated that the thiosulfate ion was reduced to hydrogen sulfide which would catalyze the anodic dissolution of the duplex stainless steel. The aggressive Cl⁻ ions in the solution attacked the passive films at high anodic potential, causing oxide film breakdown and metastable pitting initiation. Once the films were broken down, the adsorbed $S_2O_3^{2-}$ ions on the fresh bare metal surface could form FeS. The sequence is explained as follows [25-27]. At first $S_2O_3^{2-}$ was oxidized to form S:

$$\begin{split} & S_2 O_3^{2^-} + 6 H^+ + 4 e^- \rightarrow 2 S + 3 H_2 O \quad (1) \\ & S_2 O_3^{2^-} \text{ might also undergo a disproportionate reaction:} \\ & S_2 O_3^{2^-} + H^+ = S + H S O_3^- \quad (2) \\ & \text{The formed S incorporated with H}^+ \text{ by the following reaction:} \\ & S + 2 H^+ + 2 e^- = H_2 S \quad (3) \\ & \text{The formed H}_2 S \text{ eventually reacted accordingly:} \\ & M^{n+} + \frac{n}{2} H_2 S = M S n_{/2} + n H^+ \quad (4) \end{split}$$

where Mⁿ⁺ are the Fe, Cr or Ni ions that were dissolved by Cl⁻ pitting corrosion. On the one hand, this corrosion product, was cathodic to stainless steel, causing galvanic coupling corrosion, catalyzing the anodic dissolution and thus facilitating the corrosion process. On the other hand, the subsequent adsorption and electrochemical reduction resulted in blocking or retarding the passivation or repassivation and stabilizing the metastable pitting on the 2205 duplex stainless steel [28].

3.2. Electrochemical Impedance Spectroscopy



Figure 5. Nyquist plots of passive films for 2205 duplex stainless steel polarization at various formation potentials for 2 hours in 3.5% NaCl + 0.05 M Na₂S₂O₃ solution.



Figure 6. Equivalent circuit for the bilayer oxide film on 2205 duplex stainless steel in 3.5% NaCl + $0.05 \text{ M} \text{ Na}_2\text{S}_2\text{O}_3$ solution.

The electrochemical characteristics were measured by EIS to investigate the relative stability of the passive film on the 2205 duplex stainless steel. Figure 5 displays the typical Nyquist plots determined for 2205 stainless steel in 3.5% sodium chloride + 0.05 M sodium thiosulfate solution after immersion in an applied potential for 2 hours at room temperature. It is interesting to note that the impedance arc radius increased at first and then decreased with polarization potential. This trend revealed that the solution containing Cl⁻ and S₂O₃²⁻ slightly deteriorated the passive films in the passive region at high anodic potentials and contributed to the detrimental effect of the thiosulfate [29]. Thiosulfate ions appeared to influence the passivation behavior in a complicated manner.

Thiosulfate ions have been reported as potentially detrimental to the stability of passive films [30]. This differs from the reported results for the passive film on 2205 duplex stainless steel in sodium thiosulfate solution [31]. This is most likely due to the intricate interaction of Cl⁻ and $S_2O_3^{2-}$. The impedance had the highest value at 0.2 V_{SCE}, revealing excellent passive film resistance and protective behavior in the solution [32-34]. However, when the anodic potential was above 0.2 V_{SCE}, the oxide dissolution acceleration is observed even though the specimen is in a well-passivated state.

To reveal the impedance response of corrosion in 3.5% sodium chloride + 0.05M sodium thiosulfate environment, an electrical equivalent circuit with two time constant phase elements, $R_1(CPE_1)$ and $R_2(CPE_2)$, were proposed to account for the electrochemical behavior and determine quantitative aspects of the electrolyte/sample interface. Yoon and Lee [35] suggested that the corrosion resistance of the passive film decreased with the increasing of doping concentration. The CPE is defined in an impedance representation as follows:

$$Z_{\omega} = Z \cdot (j\omega)^{-n} \tag{5}$$

where Z is the CPE constant, ω is the angular frequency, $j^2 = -1$ is the imaginary number and *n* is the CPE exponent. The factor *n* is an adjustable parameter that ranges from 0 to 1. CPE can represent resistance (n = 0, Z = R), capacitance (n = 1, Z = C), or Warburg impedance (n = 0.5, Z = W).

The appropriate equivalent circuit is shown in Figure 6. Therefore, the physical interpretation used in the present study was as follows. R_s is the solution resistance and the high frequency time constant $R_1(CPE_1)$ is correlated with the areas covered with the passive film and is represented by the passive film admittance CPE_1 and the passive layer resistance R_1 . The low frequency time constant $R_2(CPE_2)$ is assigned to the active surface area, which is represented by the charge transfer resistance R_2 and the admittance associated with the double layer capacitance in the active areas [36].

The resistance curves as a function of potential are shown in Figure 7. After the values were deduced, C was calculated from Q using the following equation [37]:

$$C = \frac{(QR)^{1/n}}{R} \tag{6}$$

where R is the resistance of the passive film, Q is a constant phase element, and n is the index of Q. Then, C can be applied to estimate the thickness of the passive films, which is effective for the parallel plate capacitor model. The thickness of the passive layer was measured with impedance at the formation using the following relation [38]:

$$d = \frac{\varepsilon \cdot \varepsilon_0 \cdot A}{C}$$
(7)

where *d* is the passive layer thickness, ε is the dielectric constant with a usual value of 15.6 for stainless steel, ε_0 is the vacuum permittivity (8.85 × 10⁻¹⁴ F cm⁻¹), *A* is the valid area of specimen and *C* is the capacitance of passive film.



Figure 7. Resistance values of the passive film R₁ as a function of potential.

However, accurate values of the passive film thickness are difficult to obtain via capacitance analysis because the dielectric constant ε is generally not well known and may vary with the chemical

composition of the passive films. The estimated values of passive film thickness in the chloridethiosulfate solution at different potentials were shown in Table 2. The values of *d*, which were estimated, indicate that the films formed are generally a few nanometers thick at different formation potentials, reaching a maximum thickness of 2.83 nm at 0.2 V_{SCE} formed potential in the chloride-thiosulfate environment. This phenomenon is different from the results reported in the literature [31], which suggest that the values of a passive film thickness are proportional to the applied potentials within the whole passive region in the Na₂S₂O₃ solution. The phase angle in the low frequency region in the Bode diagram (not shown) decreased with increasing applied potential, indicating degradation of the passive film. Accordingly, it can be deduced that chloride and thiosulfate synergistically deteriorate the passive film slightly at high anodic potentials even in the passive region. It has been recognized that the detrimental effects of thiosulfate in chloride solutions depend on the electrode potential [39].

Table 2. The estimated values of passive film thickness on 2205 duplex stainless steel in the chloridethiosulfate solution at different potentials.

Potential (SCE)	-0.60	0.20	0.60
Thickness (nm)	0.80±0.09	2.83±0.13	1.44±0.11

3.3. Capacitance Measurements

The semiconductor characteristics of the passive films on 2205 duplex stainless steel formed in chloride solution containing thiosulfate at different potentials were investigated by electrochemical capacitance measurements. The relationship between capacitance behavior and the applied potential is provided by the classical Mott-Schottky theory, which indicates the potential dependence of the space charge capacitance, C, of a semiconductor electrode under depletion conditions [40]:

$$\frac{1}{C^2} = \pm \frac{2}{\epsilon \cdot \epsilon_0 \cdot e \cdot N} \left(E - E_{FB} - \frac{kT}{e} \right)$$
(8)

where the positive slope indicates an n-type semiconductor and negative slope indicates a p-type semiconductor, ε is the relative dielectric constant of the passive film that has a usual value of 15.6 for stainless steel, ε_0 is the vacuum permittivity with a value of 8.854×10^{-14} F cm⁻¹, e is the electron charge with a value of 1.6×10^{-19} C, N is charge carrier density, N_A is the electron donor density for an n-type semiconductor, N_D is the acceptor density for a p-type semiconductor, k is the Boltzmann constant with a value of 1.38×10^{-23} J K⁻¹, and T is the absolute temperature (K), E is the electrode applied potential and E_{FB} is the flatband potential. The donor density can be calculated from the slope of the linear plot C^2 vs E, and the flatband potential can be derived from extrapolation to C = 0. The interfacial capacitance C is acquired according to Sikora and Macdonald:

$$C = -\frac{1}{\omega \cdot Z_i} \tag{9}$$

where $\omega = 2\pi f$ is the angular frequency and Z_i is the imaginary component of the impedance.

Figure 8 displays the Mott-Schottky plots of the films on 2205 duplex stainless steel formed in 3.5% sodium chloride + 0.05 M sodium thiosulfate solution at different forming potentials. For duplex

stainless steels, it is supposed that the semiconductor properties exhibit the duplex character of the surface films, with an inner region mainly formed by Cr_2O_3 and an outer virtually consisting of Fe₂O₃. In the case where films on 2205 duplex stainless steel formed at various formation potentials, the plots C^{-2} vs. *E* (the applied potential) reveal the presence of four regions where a Mott-Schottky-type property can be detected.



Figure 8. Mott-Schottky approach for film formed on 2205 duplex stainless steel in 3.5% NaCl + 0.05 M Na₂S₂O₃ solution passivated at different potentials for 2 hours.

The first region, for potentials between -0.50 V_{SCE} and 0.25 V_{SCE} , is characteristic of n-type semiconductors with a positive slope. The negative slopes indicate a p-type semiconductor at a potential from 0.25 V_{SCE} to 0.6 V_{SCE} . The flat band potentials (*E_{FB}*) indicated the redox potentials of the electroactive ions in the electrolyte. The repeated variation of n-type to p-type occurs at potentials from 0.6 V_{SCE} to 0.85 V_{SCE} and 0.85 V_{SCE} to 1.0 V_{SCE} . This trend is possibly caused by the structure and composition of the passive films on stainless steel. Based on the polarization curve shown in Figure 1, it is generally understood that the semiconductor behavior reflects the bipolar character of the surface films for stainless steels and other Fe-Cr alloy materials. Additionally, it is worth noting that a fluctuation of the slopes occurred at approximately 0.4 V_{SCE} , which may be attributed to the dissolution of Cr oxides, where Cr(III) oxidized to form Cr(VI).

The values of donor density N_D can be calculated from the slope of the C^{-2} vs. *E* data assuming a dielectric constant of the passive film on the stainless steel [39]. The calculated N_D for the films on 2205 duplex stainless steel formed at various potentials in chloride solution containing thiosulfate are displayed in Table 3.

E/V _{SCE}	$N_d (10^{21} cm^{-3})$	E _{FB} (V/SCE)
-0.60	5.49±0.26	-0.62±0.08
0.00	1.82±0.38	-0.53±0.03
0.15	1.17±0.19	-0.54±0.06
0.20	0.98±0.13	-0.55±0.03
0.25	1.07±0.27	-0.50±0.07
0.60	5.12±0.15	-0.42±0.05

Table 3 Effect of passive potential on semiconducting properties of the films formed on duplex stainless steel in chloride-thiosulfate solution.

According to equation (8), the slopes of the linear portion of the C^{-2} vs. *E* plot provide the charge carrier density *N* according to the relation:

 $N = \frac{2}{e \cdot m \cdot \varepsilon_0 \cdot \varepsilon}$ (10)

where *e* is the electron charge, *m* is the slope of the Mott-Schottky plot in the linear portion, ε_0 is the vacuum permittivity, and ε is the relative dielectric constant of the semiconductor.

The point defect model (PDM) presumes that the cation interstitials and oxygen vacancies are generated at the metal/film interface, whereas cation vacancies are generated at the film/electrolyte interface [40]. In the PDM, the donor density N_D characterizes the dissolution cation vacancy concentration at the film/electrolyte interface. Therefore, the increase in N_D is related to the increased dissolution rate of the passive film, and the maximum value of doping density in the passive film is related to the worst corrosion resistance [34]. In other words, the film becomes thinner and reveals that the corrosion resistance of the passive layer is weakened. The E_{FB}, which determines the position of energy bands, is related to the redox potentials of electroactive ions in the electrolyte. The changes in E_{FB} are complicated and affected by various factors. As the polarization formation potential reached 0.6 V_{SCE}, E_{FB} sharply increased from -0.6 V_{SCE} to approximately -0.4 V_{SCE}. Tsuchiya and Cunha Belo [41] proposed that the results can be attributed to the transformed inner oxides.

3.4. XPS Analysis of Passive Films

The chemical composition may have a great effect on the stability and semiconductor characteristics of the passive film on steels. There are three different regions of anodic polarization with different electrochemical reactions and dynamic characteristics, causing different chemical compositions of the passive films. XPS measurements were done to analyze the chemical composition of passive films formed on specimens after electrochemical polarization at different potentials for 8 hours directly. Figures 9-12 illustrate the high-resolution spectra of Fe 2p_{3/2}, Cr 2p_{3/2}, Ni 2p_{3/2} and O 1s of the passive

films. These results reveal that the primary components of the passive films on 2205 duplex stainless steel in the chloride-thiosulfate solutions were Cr oxide and Fe oxide. After background subtraction according to Shirley [42], the XPS analyses were divided into different oxidation states by a fitting procedure that was studied in a previous study [40].



Figure 9. The XPS spectra of Cr 2p_{3/2} of the passive film formed on 2205 duplex stainless steel surface after passivation at -0.6 V_{SCE}, 0.2 V_{SCE}, 0.6 V_{SCE}.



Figure 10. The XPS spectra of Fe $2p_{3/2}$ of the passive film formed on 2205 duplex stainless steel surface after passivation at -0.6 V_{SCE}, 0.2 V_{SCE}, 0.6 V_{SCE}.



Figure 11. The XPS spectra of Ni 2p_{3/2} of the passive film formed on 2205 duplex stainless steel surface after passivation at -0.6 V_{SCE}, 0.2 V_{SCE}, 0.6 V_{SCE}.



Figure 12. The XPS spectra of O 1s of the passive film formed on 2205 duplex stainless steel surface after passivation at -0.6 V_{SCE}, 0.2 V_{SCE}, 0.6 V_{SCE}.



Figure 13. Evolution of Cr_2O_3 and Fe_2O_3 in the passive film formed on 2205 duplex stainless steel as a function of potential in 3.5% NaCl + 0.05 M Na₂S₂O₃ solution.

According to binding energies, the chromium profile revealed that there are mainly three constituent peaks representing the metallic state: Cr^0 (574.3 eV), Cr_2O_3 (576.3 eV) and $Cr(OH)_3$ (577.1 eV). The oxide species are the primary chemical component of the passive films on the stainless steel. The chromium in the oxide layer plays an important role in the corrosion resistance and the electrochemical behavior of the passive films. The spectra of Fe $2p_{3/2}$ show several constituent peaks corresponding to the metallic Fe⁰ (707.7 eV), Fe²⁺ and Fe³⁺ species. The relative peaks of FeO (709.4 eV) and Fe₂O₃ (710.9 eV) indicate that the Fe²⁺ and Fe³⁺ species were in the iron oxide in the passive films. Ni $2p_{3/2}$ spectra represented the metallic state Ni⁰ (852.8 eV), NiO (854.3 eV) and Ni(OH)₂ (855.6 eV). The oxygen species, O²⁻ and OH⁻, of the passive film act as metal ion connections. The O 1s signal indicated three different components as well. The peak at 530.2 eV was a result of an anhydrous oxide species, M-O (M being the alloy), whereas the peak at 531.8 eV was characteristic of the hydrated oxide species, M-OH. The final peak at 533 eV was due to residual water on the specimen surface. Additionally, the spectra for S 2p were also scanned, but no obvious peaks were detected in the passive films.

The applied passive potential increased from $0.2V_{SCE}$ to $0.6V_{SCE}$ leading to an increase in the content of metallic Fe and metallic Cr. The increasing metallic content revealed that the thickness of the passive film decreased due to the detrimental effect of thiosulfate. From the spectra of the passive films in the tested solution at $0.6 V_{SCE}$, a sufficient overpotential existed for chromium oxidation and dissolution, and the ratio of Fe₂O₃ to Cr₂O₃ in the passive film increased as the polarization potential increased, as shown in Figure 13. The values were normalized based on the composition of the survey san. The critical potential indicates the boundary between two types of passive films. At low potential, a Cr-rich passive film protected the surface, whereas above 0.2 V_{SCE}, Cr(III) oxidized to Cr(VI) and dissolved into the solution.

From thermodynamic considerations, when the potential was higher than 0.2 V_{SCE} , the outer passive film on 2205 duplex stainless steel was strongly affected by the applied formation potential, and the main carrier concentration increased rapidly with increasing formation potential. For the inner oxide layer, Cr(III) was initially oxidized to Cr(VI) and strongly dissolved at a higher potential, resulting in the reduction of Cr₂O₃ in the film, which was important for the corrosion resistance of the stainless steel. The deterioration of the passive film caused by the dissolution can be observed by the decrease of impedance and the increase of N_D . Figure 14 showed the schematic of the electrochemical behavior of 2205 duplex stainless steel in chloride-thiosulfate environment. In summary, the passivation process was dynamic rather than static; that is, the passive film was growing and dissolving simultaneously. In the passive state, both oxide formation and dissolution processes occurred on the specimen surface. The former thickens the passive film, whereas the latter leads to a reduction of the film thickness. When the passivation potential was higher than 0.2 V_{SCE} , the dissolution rate of the passive film was greater than the growth rate, the film became thinner, and the protection became worse. As the potentials continued to increase, the dissolution rate increased.



Figure 14. Schematic of the electrochemical behaviour of 2205 duplex stainless steel in chloridethiosulfate environment.

4. CONCLUSIONS

The electrochemical behavior of 2205 duplex stainless steel in 3.5% chloride solutions containing 0.05 M thiosulfate was investigated using potentiodynamic polarization, EIS, Mott-Schottky and XPS measurements. The main conclusions obtained are presented below:

The polarization results show that $S_2O_3^{2-}$ played a detrimental effect on pitting potential in the chloride containing 0.05 M thiosulfate solution. H₂S generated during the dissolution process at high anodic potential was detected indicating that the thiosulfate ion was reduced to hydrogen sulfide, which catalyzed anodic dissolution once the films were broken down. The selective dissolution of the ferrite phase was observed on 2205 duplex stainless steel.

The evolution of the impedance on the passive films indicated that the deterioration effect of $S_2O_3^{2-}$ on passive films was dependent on anodic potentials. The impedance showed the highest value at 0.2 V_{SCE}, revealing the most excellent passive film stability and the best protective behavior. However, when the anodic potential was above 0.2 V_{SCE}, the oxide dissolution acceleration was observed even though the specimen was in the well-passive state.

Mott-Schottky analysis revealed that the passive films on 2205 duplex stainless steel alternately conducted n-type and p-type properties at different potential ranges. The films formed in the chloride-thiosulfate environment presented a bilayer structure. The donor density of the films was in the range of 10^{20} - 10^{21} cm³, and the donor density varied with film formation potential. Additionally, as the polarization formation potential reached 0.6 V_{SCE}, *E_{FB}* increased from -0.6 V_{SCE} to approximately -0.4 V_{SCE}.

The passive films on 2205 duplex stainless steel formed in chloride solutions containing thiosulfate at different formation potentials, consisted mainly of Cr oxide and Fe oxide. At a potential of 0.6 V_{SCE}, the Cr(III) in films was initially oxidized to Cr(VI) and severely dissolved, resulting in a reduction in the content of Cr₂O₃, and the ratio of Fe₂O₃ to Cr₂O₃ in the passive film increased. Thiosulfate promoted the transformation of Cr(III) oxidized to Cr(VI). When the passivation potential was higher than 0.2 V_{SCE}, the dissolution rate of the passive film enhanced, and the film became thinner.

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