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Passivity and Pitting Corrosion of 316L in Simulated Concrete Pore Solutions under Marine Environment

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In this study, the passivity and pitting corrosion of 316L in simulated concrete pore solutions were investigated through polarization curve, electrochemical impedance spectroscopy (EIS), and Mott–Schottky (M-S) analyses. In solutions with different pH levels and Cl⁻ concentrations, the corrosion resistance of 316L decreases with decreasing pH and increasing Cl⁻ concentration. The breakdown potential (E_b) is linearly related to the logarithm of Cl⁻ concentration under weak alkaline solutions. The undissolved corrosion product outflow from the corrosion pit would damage the passive film covered by the precipitates. In EIS results, the passive film resistance of 316L in pH 13 is higher than those in pH 9 and 11. In the XPS spectra, the ratios of Cr/(Fe+Cr+Ni) and Fe³⁺/ Fe²⁺ increase because of the selective dissolution effect on solutions with high Cl⁻ concentration and pH. In M-S data, the passive films under all test solutions are identified as n-type semiconductor. Concrete carbonation and Cl⁻ enrichment can reduce the stability of passive films and increase the corrosion tendency in marine environments.

Keywords: 316L; simulated concrete pore solution; Mott-Schottky; XPS; passive film

1. INTRODUCTION

Steel rebars embedded in concrete are readily passivated due to the high pH of the electrolyte inside the concrete pores [1,2]. However, the carbonation and the Cl^- permeation were the main failure reasons for the reinforced concrete structure. Especially in marine environment, the Cl^- enrichment cause for the seawater intrusion and evaporation would make severe corrosion on steel rebars [3,4]. The applications of stainless steel are one of the most reliable solutions to guarantee the durability and

service life of reinforced concrete structure in highly aggressive environments [5,6]. Owing to the dense passive film, 316L has higher corrosion resistance in reinforced concrete structure.

Under the effect of carbonization, the pH of concrete pore electrolyte would decrease continuously. It causes the change of components in the passive film and reduces the corrosion resistance [7,8]. In recent decades, the studies on the failure of reinforced concrete structure in marine environment are mainly focused on the carbon steel. Meantime, the influence of Cl^- on the corrosion behavior of metals has been widely researched for a long time [1,2,9]. However, the properties of passive films and the corrosion resistance of stainless steel in concrete pore solutions under marine environment are still less systematically studied.

In this paper, the stability of 316L stainless steel in simulated concrete pore solutions of marine environment was studied by cyclic polarization curves, EIS, M-S techniques and X-ray photoelectron spectroscopy (XPS). Some important influences of the change of pH and Cl⁻ concentration on the corrosion behavior and passive film properties of 316L were discussed.

2. EXPERIMENTAL

2.1 Test solution

Under the capillary action of concrete pore and transpiration of sun light, the Cl⁻ concentration can rise rapidly. To simulate Cl⁻ enrichment and different periods of carbonation process, suitable amount of NaOH and NaCl were adding into saturated Ca(OH)₂ to prepare simulate concrete pores solutions [7,10]. The pHs of simulated solution in different carbonization periods was 9,10,11,12,13. The Cl⁻ concentrations were 5 M, 0.5 M and 0.05 M. All the solution pHs were carefully detected by a pH meter.

2.2 Sample

The substrate stainless steel rebar was 316L, which presents the main alloy elements (w%): C: 0.03, Cr: 16.86, Ni: 10.19 Mo: 2.09 Mn: 0.64 Si: 0.33, P: 0.04, S: 0.004, Fe: bal. Metal sheets were cut from rebars and embedded in cold curing epoxy resin. The exposed area of metal was 1 cm². To avoid crevice corrosion, the passivating treatment was used 85 °C water bath in H₃P0₄(3 wt.%) and K₂Cr₂O₇(5 wt.%) solution for 30 minutes before embedding.

The samples were ground with wet SC abrasive paper of decreasing grit size up to 2000 and polished with diamond metallographic polishing agent up to 0.5 μ m. After polishing, the samples were degreased with anhydrous alcohol, rinsed with distilled water and dried with cold air stream just before immersion.

2.3 Electrochemical measurements

The electrochemical measurement was using a conventional three electrode system. The working electrode (WE) was 316L samples, reference electrode (RE) was a saturated calomel electrode

(SCE) and counter electrode (CE) was a 10*10mm² platinum electrode. All electrochemical tests processes were under 25 °C air conditioning environments.

The cyclic polarization curve measurements were using a scan rate of 0.5 mV/s starting from - 150 mV vs. OCP, reverse at $J=1 \text{ mA/cm}^2$ (50 mA/cm² for pH=13 and 0.5 M Cl⁻ environments) and end with the intersection of anode polarized and reversed curves. To ensure the initially stable of passive film, 2 h immersion was applied before the cyclic polarization curve measurements. After the cyclic polarization measurements, a VHX-2000 (KEYENCE) optical morphology was used in observing the pits morphology.

EIS measurements were performed at 168 h of immersion in the test solutions. The frequency was swept from 10 kHz down to 10 mHz with a sinusoidal signal of 10 mV. All the measurements results were fitted and simulated with Zsimpwin software.

M-S tests were scanned from low to high potential with a stepping interval of 50 mV. AC signal with frequency of 1000 Hz and amplitude of 10 mV was superimposed on the potential. For a semiconducting oxide/electrolyte interface, the Helmholtz double layer capacitance ($C_{\rm H}$) is much larger than the space charge capacitance ($C_{\rm SC}$) of semiconductor. Therefore, the reciprocal of measured capacitance (1/C) can be treated as the reciprocal of space charge capacitance ($1/C_{\rm SC}$) and the $C_{\rm H}$ can be ignored as equation (1) [11].

The relationship between measurement capacitance and applied potential under depletion condition can be described by Mott-Schottky equation (2) [12,13].

 $\frac{1/C_{SC}}{1/C^2} \approx \frac{1/C}{E_{fb}} = \frac{1/C_{SC}}{kT/e} + \frac{1/C_H}{\epsilon \epsilon_0 eN}$ Equation (1) Equation (2)

Where *E* is applied potential, $E_{\rm fb}$ is Flat band potential (The $E_{\rm fb}$ is the intersection of fitting line and the potential axis.), *e* is the elementary charge of electrons ($e = 1.602*10^{-19}$ C), ε is dielectric coefficient of the oxide, usually for 12 [14,15], ε_0 is the permittivity of vacuum($\varepsilon_0 = 8.854 \times 10^{-14}$ F/cm), *k* is the Boltzmann constant ($k = 1.38*10^{-23}$ JK⁻¹), *N* is defect concentration ($N_{\rm D}$ is the donor density and $N_{\rm P}$ is the acceptor density), *T* is the absolute temperature.

The surface elements of the passive film were characterized by X-ray photoelectron spectroscopy (XPS; ESCALAB 250 XI), in which Al K-alpha radiation was operated at 150 W and the detection spot was a diameter of 0.5 mm. Photoelectron spectra were fitted by XPS Peak. The C1s peak from contaminant carbon at 284.8 eV was used as a reference for charge correction.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization studies

Cyclic polarization curves provide important features related to the electrochemical behavior of 316L in solutions with different pH levels and Cl^{-} concentrations. Fig. 1(a–c) illustrates the experimental results.



Figure 1. Cyclic polarization curves of 316L under different pH and Cl^- concentration solutions. (a):0.05 M; (b):0.5 M; (c):5 M; (d): relationship between E_b and different solutions.

Fig. 1(a–c) shows the cyclic polarization curves of 316L in test solutions. Inherent laws under different solutions can be clearly presented by electrochemical parameters. Hence, the E_b and E_{corr} values decrease with decreasing pH in each Cl⁻ concentration. The relationship of E_{corr} to pH is mainly caused by the change in the oxidation–reduction potential of solutions [12].

 $E_{OR}(S) = constant E_0 - 0.0592 pH$ (Equation 3)

Where constant E_0 is the potential of pH=0.

Equation 3 describes the effect of solution pH on E_{OR} . Although the E_{OR} linearly decreases with decreasing pH, the E_{corr} does not entirely follow this linear relationship. At the ideal interface between the metal and the solution, all compositions and structures are constant with pH change. The electrode potential exhibits a linear relationship to solution pH. However, the selective dissolution of metals and the structure and thickness of passive film will change upon immersion in solutions with different pH levels. The state of the passive film is far from reaching the thermodynamic stability considering its short immersion time in the solutions.

It is worth to mention that the higher current steppings occur above 600 mV vs. SCE are not the breakdown of passive films. An additional reaction can start at this potential under alkaline solutions. The reaction (4) was the oxygen evolution reaction (OER) [16].

 $40H^- \rightarrow 2H_20 + O_2 \uparrow + 4e^-$ (Reaction 4)

The current density in 0.5 M solution with pH 13 easily reached 1 mA/cm^2 because of the OER interference and reverse scan before damage to the passive film. A high reverse current density value (50 mA/cm²) was applied to obtain correct breakdown potential.

In solutions with pH 13, the current peaks near 300 mV versus SCE reveal that the valence of chromium changed during high anodic polarizations. In reaction (5), dissolution of chromium oxide shifted to high valence [17,18].

 $Cr_2O_3 + 100H^- \rightarrow 5H_2O + 2Cr_2O_4^{2-} + 6e^-$ (Reaction 5)

The E_b value in the anodic polarization curves of the self-passive system represents the breakdown of the passive film. At high E_b value, the stability of the passive film and the corrosion resistance of the metal are high. Moreover, in concrete pore solutions with high pH, the corrosion resistance of 316L rebars is high. All E_b values were analyzed [Fig. 1(a–c)], and the drawn curve (Fig. 1d) indicates their relationship to Cl⁻ concentration. A good linear relationship was also found between E_b and logc(Cl⁻) in solutions with pH 9–11. In 0.05 M solutions with pH 12, the OER may reduce the E_b value. Under the OER interference, the OH⁻ activity of the passive film surface can be reduced to a low level. The interference can reduce the passive film stability and decrease the E_b value because the passive film of stainless steel is stable in solutions with high pH. Furthermore, when the applied potential exceeds the OER potential, the OER interference on E_b is large. Therefore, E_b values of 11 at 0.05 M and 12 at 0.5 M measurements are less affected by OER and can be considered accurate.

pH&c(Cl ⁻)	$E_{\rm corr}$ (mV vs. SCE)	$E_{\rm b}$ (mV vs. SCE)	$E_{\rm prot}$ (mV vs. SCE)	Area (Q/C)
9-0.05 M	-205	646	158	5.231E-4
9-0.5 M	-185	364	-6	7.223E-4
9-5 M	-201	145	-225	16.35E-4
10-0.05 M	-226	689	195	7.812E-4
10-0.5 M	-207	454	-90	8.489E-4
10-5 M	-244	238	-253	21.87E-4
11-0.05 M	-301	889	143	14.38E-4
11-0.5 M	-282	578	42	16.62E-4
11-5 M	-303	281	-366	31.77E-4
12-0.05 M	-289	1045	120	11.48E-4
12-0.5 M	-344	828	-60	27.29E-4
12-5 M	-391	325	-75	50.58E-4
13-0.05 M	-402	none	none	none
13-0.5 M	-383	1108	-74	171.7E-4
13-5 M	-413	418	-123	291.0E-4

Table 1. Pitting and passivation values of 316L under different pH and Cl⁻ concentration solutions.

Table 1 summarizes E_{corr} , E_b , protection potential (E_{prot}), and area between the anodic polarization and hysteresis curves of 316L in solutions with different pH levels and Cl⁻ concentrations. According to thermodynamics, the potential relationship between E_{corr} and E_{prot} determines the level of self-passivity after the breakdown of the passive films in the test environments. Environments with low pH levels and 5 M Cl⁻ cannot be self-passivated because Cl⁻ intrusion and enrichment process occur

earlier than carbonation. Therefore, using 316L rebars in marine concrete environment can maintain the passivation before the end of carbonation.



Figure 2. The corrosion morphologies of 316L after cyclic polarization measurements in different pH and Cl⁻ concentration solutions. (a) 9-0.05 M, (b) 11-0.05 M, (c) 9-5 M, (d) 11-5 M and (e) 13-5 M.

Fig. 2 shows the corrosion morphologies of 316L after cyclic polarization measurements. In Fig. 2(a, b), similar shaped pits were found on the samples tested with pH = 9-11 and 0.05 M Cl⁻ concentration. A slice of lacy cover was covered on the pits, and large pits may increase the applied potential in solutions with high pH levels. In addition, the hysteresis curves and E_{prot} showed the same trend in Fig. 1(a, b). The lacy cover can block the migration of ions inside and outside of the pits. In general, the repassivation potential depends on the chemical property of the solution in the pits. Hence, the solution composition can be considered similar to that inside the pits. As shown in Fig. 1 under the same Cl⁻ concentrations, the same hysteresis curve trend represents the same solution pH in the pits formed in different pH levels.

In Fig. 2(c–e), samples with high Cl^- concentration exhibit different morphologies and mechanisms of corrosion. The waterfall-shaped corrosion morphologies are wider under higher Cl^- concentrations and pH levels because of the hydrolysis of metal cations. For example, in iron hydrolysis (6–7) [22], many undissolved hydroxide particles would precipitate both inside and outside of the pits.

 $Fe \rightarrow Fe^{2+} + 2e^{-}$ (Reaction 6) $Fe^{2+} + 30H^{-} \rightarrow Fe(OH)_{3} \downarrow +e^{-}$ (Reaction 7)

 Cl^{-} acts as catalyst for reaction (6). This reaction was maintained at a fast rate in metal dissolution because of high Cl^{-} concentration. At high pH and Cl^{-} concentrations, the sediment

corrosion product can flow out from the pits and flow downward toward the gravity position, leading to the formation of waterfall-shaped corrosion morphologies [23]. Furthermore, at high pH, the applied anode potentials increased after the passive film breakdown. The downward flowing sediment corrosion product would reduce the stability of the passive film because of the hydrolysis reaction. All passive films covered with the sediment corrosion product were broken, and the formed corrosion morphologies are shown in Fig. 2.

3.2. EIS studies

For figuring out the passive film properties of 316L under simulated solutions, EIS, M-S and XPS analysis were using to explore the relationship between the corrosion resistance and the properties of the passive film. The EIS results were showed in Fig.3.



Figure 3. EIS results of 316L in different pHs with different Cl⁻ concentration solutions after 168 h immersion: (a) Cl⁻=0.05 M, (b) Cl⁻=5 M.



Figure 4. Equivalent electric circuit with two hierarchically distributed time constants.

The fitting of EIS results was using a two hierarchically distributed time constants equivalent electric circuit (-R(Q(R(QR)))-) [24,25] to model the electrochemical behavior of metal/film/solution system as Fig.4. The corresponding impedance, $Z(\omega)$, is given by equation 8.

 $Z(\omega) = R_1 + \frac{R_1}{(j\omega R_1 C_1)^{\alpha_1} + \left(\frac{R_1}{R_1 + Z_2}\right)}; \text{ where } Z_2 = \frac{R_2}{1 + (j\omega R_2 C_2)^{\alpha_2}} \text{ Equation (8)}$

Where the R_s represents the electrolyte resistance; R_1 and Q_1 are considered as the parameters connection with the defect reactions taking place in the passive film; Q_2 is assigned to the double electrode layer capacitance; R_2 is related to the polarization resistance. n_1 and n_2 is dispersion coefficient of two-time constants.

pН	C(Cl ⁻)	R _s	Q_1	n_1	R_1	Q_2	n ₂	R_2	$\chi^2 (10^{-3})$
		(Ωcm^2)	$(F/cm^2s^{\alpha 1})$		(Ωcm^2)	$(F/cm^2s^{\alpha 2})$		(Ωcm^2)	
9	0.05 M	29.90	8.993E-6	1	254.2	1.346E-5	0.896	8.296E6	0.5126
	5 M	1.584	1.484E-5	0.9502	38.91	9.567E-6	0.8946	2.544E6	6.717
11	0.05 M	62.43	1.191E-5	1	472.8	1.737E-5	0.8637	1.591E7	0.2655
	5 M	1.431	1.341E-5	1	62.48	1.516E-5	0.8166	1.161E7	5.104
13	0.05 M	9.984	2.259E-5	0.9527	8.196E4	8.431E-6	0.906	9.295E6	1.174
	5 M	1.646	1.964E-5	0.9506	2919	9.639E-6	0.8101	8.479E6	3.084

Table 2. Passive parameters from the fitting using the equivalent circuit in Figure 4 under different solutions after 168 h immersion.

Table 2 summarizes parameters obtained by fitting with the equivalent circuit in Fig. 4. All tests showed the same order of magnitude for R_2 values. Comparison of 0.05 and 5 M plots showed that the R_2 values decrease with increasing Cl⁻ concentration because of the effects of Cl⁻ on the dissolution rate of the passive film. The R_1 values increase with increasing pH and decreasing Cl⁻ concentration. This relationship can be interpreted as the effect of Cl⁻ and OH⁻ on the passive film. According to the point defect model (PDM), the defect reaction of Cl⁻ on the passive film can be described as reaction (9) [26,27].

 $\begin{array}{ll} V_{0}^{``}+Cl^{-}\rightarrow Cl_{0}^{``} & \text{Reaction (9)} \\ m\rightarrow M_{M}+\left(\frac{n}{2}\right)V_{0}^{``}+ne^{-} & \text{Reaction (10)} \end{array}$

Where $V_{\ddot{o}}$ represents oxygen (anion) vacancy on the film/solution interface, which come from the interface of metal/film interface as reaction (10); $Cl_{\dot{o}}$ represents Cl^{-} occupy the oxygen (anion) site; M_{M} represents metal cation in the cation site.

In solution containing Cl^- , this ion would be absorbed at the interface of oxide film/solution, and the density of oxygen vacancy will be reduced by the replacement of Cl^- , as shown in reaction (9). This process can also influence the inward (toward metal/oxide interface) diffusion of oxygen ions. Through a series of defect reactions and diffusion, the oxygen vacancy will be concentrated, and vacancy condensates will form on the inner side of the passive film, resulting in decreased density and resistance of the passive film.

In (-R(Q(R(QR))))-) equivalent electric circuit, R_2 is related to polarization resistance. In the EIS theory of dynamic fitting and single-time constant equivalent electric circuit fitting, R_2 is related to the dissolution rate of the passive film [12,28]. The dissolution rate of the passive film is typically determined by its stability. The process of low-time constant should decrease with increasing stability of the passive film. Moreover, the oxidation–reduction potential of solutions decreases with increasing pH. The potential drops in the metal/oxide/electrolyte system can be illustrated as follows [29,30]:



Figure 5. Illustration of potential drop in metal/oxide/electrolyte system.

Fig.5 shows a model of potential drop in metal/oxide/electrolyte system and where E_f is the Fermi energy of the metal, L is the thickness of passive film, M_M stands cation in the cation sublattice, O_o stands oxide ion in the anion sublattice, V_o stands oxygen (anion) vacancy and $V_M^{n'}$ stands cation vacancy. An obviously numerical relationship can be inferred from as equation (11).

 $\Delta V = \phi_{m/f} + \phi_f + \phi_{f/s} \qquad (equation 11)$

Where $\phi_{m/f}$ is the potential drop on the metal/film interface; ϕ_f is the potential drop in the film and the $\phi_{f/s}$ is the potential drop on the film/solution interface

A good Ohmic contact is formed at the metal/oxide film interface, and the value of $\emptyset_{m/f}$ can be considered zero because the concentration of defects in the passive film is sufficiently high $(>10^{15} \text{ cm}^{-3})$ [30]. In Equations (3, 11), the value of \emptyset_f and $\emptyset_{f/s}$ increase with anodic polarization and solution pH [27]. Hence, the electric field intensity in the passive film increases, whereas the oxidation–reduction potential decreases with increasing pH [28]. The diffusion coefficient and the dissolution rate of the passive films increase. Hence, the minimum value of R_2 may obtained at a modest pH value (pH = 11).

The selective dissolution of metals in solutions of different pH levels can intensely change the stability of the passive film due to the effect of OH^- on the film.

3.3 M-S analysis



Figure 6. Mott-Schottky results of 316L in different phis with different Cl⁻ concentration solutions.

The M-S plots were established for 316L after passivation at free corrosion potential for 168 h (7 d) in solutions with different pH levels and Cl⁻ concentrations (Fig. 6). The composition and microstructure of passive films are easily changed by prolonged cathodic or anodic polarization; as such, the linear parts of the M-S plots containing the corrosion potential can accurately describe the semiconductor properties of the passive film. By calculating the linear parts in Fig. 6, the positive slope of the fitting lines represents the dependence of the semiconductor properties of the passive films of p-type semiconductor are generally related to defects with metal ions and excessive cation vacancies. In general, n-type semiconductors are responsible for the diffusion of cation interstitial transport and anion vacancies [31].



Figure 7. The semiconductor properties of passive film formed on 316L after 168 h immersion in different pHs with different Cl⁻ concentration solutions.

Fig. 7 shows the donor defects of passive films formed in different test solutions. The defect density of the passive film increases with increasing concentrations of OH^- and CI^- . According to PDM, the density of oxygen vacancies can be increased by reaction (9) [27]. The donor defects are mainly provided by the oxygen vacancies of the n-type semiconductor [11]. Therefore, the density of the passive films decreases rapidly, and the donor defects increase with increasing intensity of CI^- on attacking the passive film.

Some studies suggested that different compositions of metallic oxides (Fe_2O_3 - Cr_2O_3 -NiO) are correlated with semiconductor properties [32,33]. Therefore, the Fe/Cr/Ni ratio in solutions with different pH levels is a critical evidence for explaining the semiconductor properties and the stability of passive films.

3.4 XPS analysis of passive films



Figure 8. The XPS detailed spectra for the passive film of 316L formed in pH=13 with 5 M Cl⁻ concentration solution. (a) the whole survey spectra, (b) iron, (c) chromium and (d) nickel.

The passive films of 316L formed after 168 h of immersion in different pHs with different Cl⁻ concentration solutions were examined by XPS. The results of the spectra for Fe, Cr and Ni are presented in Fig.8. Fig.8a shows the whole XPS survey spectra of passive film. Fe, Ni, Cr, O and C are the main elements in the passive film. C is possible come from the contaminant in the air. It is worth mentioning that the Cl element peak is not found near 200 eV. Fig.8b shows the detail spectra for the $Fe(2p_{3/2})$ spectrum. The peak at 707.1 eV represents the iron in the metallic state. According to this peak, the detection depth can be considered to reach the metal matrix and most of the elements of different depth in the passive films are detected. The peaks at 711.5 eV and 710.2 eV in Fig.8c can be attributed to the iron(III) oxide and iron(II) oxide components. The chromium spectrum shows two disrupt orbital and sublevel. The peaks at 576.9 eV and 574.2 eV can be ascribed to the orbital level of chromium(III) oxide and metallic chromium components. The peaks at 586.7 eV and 583.5 eV are the sublevel. Because of the peak intensity of 2p level are follow the 2:1 relationship between the $2p_{3/2}$ and 2p_{1/2} levels. The peak intensity of sublevel in Table 3 are omitted. Fig.8d shows nickel(II) oxide components at 852.8 eV and 855.4 eV. The peak of $Ni^{2+}(2p_{3/2sat})$ can be considered as photoelectron satellite line. By fitting and calculating all the peak intensity of 316L passive films, the area of all the peaks was recorded in Table 3.

Samples	$Fe^{3+}(2p_{3/2})$	$Fe^{2+}(2p_{3/2})$	$Fe^{0}(2p_{3/2})$	$Ni^{2+}(2p_{3/2})$	$Ni^{2+}(2p_{3/2sat.})$	$Cr^{3+}(2p_{3/2})$	$Cr^{0}(2p_{2/3})$
9-0.05 M	11760	14427	3003	1445	363	4712	239
11-0.05 M	15872	15109	1451	1606	305	6437	234
13-0.05 M	17973	15152	4528	3600	2005	11116	612
9-5 M	14119	12715	2576	1830	705	5004	1035
11-5 M	16302	15414	2999	1517	479	7579	452
13-5 M	19591	15537	5372	3966	1613	17621	373

Table 3. The XPS peak intensity of metal elements observed on the passive film formed in simulated solutions.

The ratio of $\text{Fe}^{3+}(2p_{3/2})/\text{Fe}^{2+}(2p_{3/2})$ gradually increases with increasing pH and Cl⁻ concentration (Table 3). Combined with the M-S results, the XPS data indicated that the proportion of the different valence states of iron (II-III) oxide may change the concentration of donor defects in the passive film. In passive oxide films, n-type defects are related to iron(III) oxide (Fe₂O₃ and FeOOH), and p-type defects are related to iron(II) oxide (FeO and FeCr₂O₄) [33-35]. Therefore, the higher ratio of iron (III) caused by changes in iron proportion can increase the concentration of n-type defects in passive films.



Figure 9. The XPS peak intensity ratio of metal elements observed on the passive film formed in simulated solutions. (a) Fe/(Fe+Cr+Ni) and (b) Cr/(Fe+Cr+Ni).

The proportion of metal elements in 316L passive film after 168 h of immersion in solutions with different pH levels and Cl⁻ concentrations can be qualitatively confirmed by comparing the ratios of Fe/(Fe+Cr+Ni) and Cr/(Fe+Cr+Ni). The selective dissolution in solution with high pH and Cl⁻ concentration can increase the chromium content and reduce the proportion of iron. Under similar Cl⁻ concentrations, the high proportion of chromium ions led to the high stability of the passive film. However, the effect of changes in the concentration of aggressive ions may not be simple. Furthermore, other factors may affect the mechanism of Cl⁻ on chromium enrichment in the passive film. Passive films can achieve thermodynamic stability within a short time because of the accelerated dissolution mechanism of Cl⁻. Therefore, the proportion of chromium in passive films formed in 5 M Cl⁻ solutions is higher than those formed in the other solutions. Moreover, chromium enrichment in passive films will not increase the concentration of donor defects because of the p-type semiconductor properties of the film made of chromium oxides [33].

4. CONCLUSIONS

1. The corrosion resistance and the resistance of the passive film of 316L in simulated concrete pore solutions decrease with increasing Cl⁻ concentration and decreasing pH. E_b follows the linear relationship between E_b and logc(Cl⁻) in weak alkaline solutions.

2. The hydrolysis of corrosion products decreases the solution pH solution and reduces the stability of all passive films in regions covered by the precipitates.

3. The element ratios of Fe/(Fe+Cr+Ni) in passive films decrease with increasing Cl⁻ concentration and pH levels. The ratios of Cr/(Fe+Cr+Ni) and Fe³⁺/ Fe²⁺ in passive films show opposite trends.

4. The dominant semiconductor properties of the passive films are donor defect in all tests. The donor defect density increases with increasing Fe^{3+}/Fe^{2+} ratio.

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