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Passivation and Corrosion Behavior of P355 Carbon Steel in Simulated Concrete Pore Solution at pH 12.5 to 14

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The passivation by potentiostatic polarization and electrochemical behavior of P355 carbon steel in saturated Ca(OH)₂ solution (SCS) at pH 12.5 to 14 were investigated. The effects of polarization potential, pH, polarization time on the behavior of P355 carbon steel were evaluated. The results illustrated that the P355 carbon steel exhibits well passive behavior with a broad passive region. The time for polarization current to reach a steady state will be prolonged with the increase of pH and the decrease of polarization potential. The passive film displays the behavior of n-type semiconducting. The optimal passivation potential is 300 mV positive and 100 mV negative to the passive film E_{corr} , which is usually in the range of -100 mV to -600 mV. The threshold value of the chloride ions is 0.1 M. More than 0.5 M chloride ions will lead to the passivity breakdown and initiate serious corrosion.

Keywords: passivation; electrochemical impedance spectroscopy; corrosion; saturated Ca(OH)₂ solution; carbon steel

1. INTRODUCTION

Over the past decades, the passivation and corrosion behavior of the steel in concrete have been studied much [1, 2]. Several studies focused on the electrochemical behavior of traditional carbon steel, austenitic or duplex stainless steel types such as Q235 [3], 304 [4], 316 [5] or 2205 [6, 7] stainless steel in typical environment [8]. In the field of nuclear industry, the steel reinforcement is exposed to concrete pore solution over the pH range 12 to 14 in the anoxic environment even for hundreds of years [9]. In this high alkaline environment, a protective passive film will be formed spontaneously and maintained on the surface of the P355 carbon steel [10, 11]. The composition of the concrete pore solution has great influence on the passivation of the carbon steel [12, 13]. However, till now, few previous works have focused on the electrochemical behavior of the P355 carbon steel in

"high alkaline" and "super-anoxic" environment [14]. We believe that the investigation of the passive behavior in saturated $Ca(OH)_2$ solution (SCS) with different pH by addition of NaOH, which was used as simulated concrete pore solution (SCPS), will contribute to a better understanding of the corrosion behavior of the carbon steel in concrete.

Since the natural corrosion rate of the steel in concrete is very low, very long time is needed to evaluate the corrosion behavior which is impractical to achieve based on laboratory experiments [15]. Therefore, electrochemical method is often used for quick evaluation of steel corrosion [16, 17]. Till now, the electrochemical and passive films of P355 carbon steel combining in high alkaline (pH>12.5) and anoxic environment at more negative polarization(-1.0 V -0 V) potential are scarcely investigated [18-20]. So, it is very worth exploring the structure and properties of the passive film formed on P355 carbon steel in this condition [21, 22].

The aim of this work is to investigate the passive films formed by potentiostatic polarization on P355 carbon steel for better understanding its electrochemical behavior in different alkaline and anoxic environment at more negative potential by combining potentiodynamic measurements, electrochemical impedance spectroscopy (EIS) and Mott-Schottky approach. Potentiostatic polarization was used to accelerate the formation of the stable passive films. Then, the non-destructive electrochemical impedance spectroscopy was mainly employed to investigate the electrochemistry and corrosion behavior of the steel in the alkaline environment. Saturated calcium hydroxide solution with different pH by addition of sodium hydroxide has been employed as the high alkaline environment. The influence of chloride ion on the passive film was also investigated in SCS containing a different concentration of chloride.

2. EXPERIMENTAL

The nominal chemical composition of the P355 carbon steel is given in Table 1. The specimen was a cylinder of 1 cm diameter and 1.5 cm length. Then the specimen was cast in epoxy resin. The exposed area as the test surface is 0.785 cm^2 . The specimen was mechanically wet-grounded with successively finer silicon carbide papers down to a 1200 grit surface finish and rinsed with ethanol and double distilled water after which the electrode was immediately placed into the cell. A newly polished specimen was used for each run. The N₂ deaerated saturated Ca(OH)₂ solution at pH 12.5, 13.5, 14 were named SCS_{12.5}, SCS_{13.5}, and SCS₁₄. The solution which has been used for Tafel measurement was defined as "aged" solution to distinguish from fresh solution. All chemicals employed were of analytical reagent grade. All electrochemical experiments were performed in a three-electrode cell by a Solartron S1 1280B electrochemical workstation (Fig.1). The sample was used as the working electrode, a platinum film was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The tip of the luggin tube was placed about 0.5 cm from the specimen surface. All potential values reported in this work are expressed on the SCE.

The bath was purged for at least 20 min before and during each test with high purity N_2 gas. The potentiodynamic test was performed at 0.1667 mV/s. Several potentials, which is close to the cathodic end, were selected within the passive region as the passive film formation potentials (from - 800 mV to 0 mV with an interval of 100 mV) to accelerate passivation via potentiostatic polarization. At each passive potential, potentiostatic polarization was kept for 12 to 72 h to ensure an "operational" steady state of the system. EIS was performed after potentiostatic polarization in an identical test solution. An Experiment was firstly designed to evaluate the influence of chloride ions on the passive film. P355 carbon steel was polarized at -0.1 V for 18 h in SCS_{12.5}, Then potentiodynamic polarization was continuously performed in sequence at a sweep rate of 0.2, 0.5, 1, 2, 5, 10 mV/s from -0.75 V_{SCE} to 0.75 V_{SCE} in the SCS_{13.5} containing 0.025, 0.1, 0.5, 1 M NaCl, respectively.

С	Mn	Р	S	Si	Cu	Ni	Cr	Mo
0.15	0.98	0.005	0.0005	0.324	0.043	0.05	0.082	0.009
Al	Nb	Zr	V	Ti	Со	В	Η	Ν
0.034	0.006	0.001	0.001	0.001	0.005	0.0001	1.95	0.034

 Table 1 Chemical composition of the P355 carbon steel.



Figure 1. A schematic of the electrochemical measurement system.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization behavior of P355 carbon steel in SCS

The potentiodynamic polarization curves could provide important features concerning the electrochemical behaviors of P355 carbon steel [23]. Fig.2 is the potentiodynamic plots of P355 carbon steel in N_2 deaerated SCS at pH 12.5, 13.5 and 14. As observed in Fig.2, when the potential is swept in the positive direction, the polarization curve exhibits a stable and wide passive range (-0.75 V to 0.54 V vs. SCE) which indicates the passive ability of P355 carbon steel is strong in this SCS. The polarization curves pass through the active region, active-passive transition region, passive region and transpassive region with the increase of potential from free corrosion potential to anode direction [24]. In the cathodic part, there are no significant differences in the shape of the curves at different pH. An

important feature is the anodic oxidation peak near -0.75 V, which reveals that ferrous oxidation is taking place corresponding to the oxidation of Fe(OH)₂ to Fe₃O₄ or Fe₃O₄ to Fe₂O₃, respectively [25]. At potentials higher than 0.54 V vs. SCE, a sharp increase of the current density was observed, which is due to the onset of oxygen evolution reaction (4OH \rightarrow O₂ + 2H₂O + 4e⁻), although passivity breakdown may occur simultaneously [26]. In fact, the potential of passivity breakdown is usually negative than 0.54 V.

As can be seen in Fig.2, the passivation current density in $SCS_{12.5}$ is more stable and lower than that of $SCS_{13.5}$ and SCS_{14} . Moreover, the polarization current density is less than 7×10^{-6} A cm² for the curves (a) and (b) in Fig.2, which corresponds to the solution of $SCS_{12.5}$ and $SCS_{13.5}$, respectively. However, as shown in Fig.2(c) and (d), the passivation current density are both higher than 7×10^{-6} A cm² This indicated that the protective properties of the passive film decrease with the increase of pH from 12.5 to 14. Although the corrosion resistance of the passive layer is improved with the $E_{\rm corr}$ positively shift 70 mV (-0.98 V to -0.91 V) by polarization 24 h at -0.2 V, the protective ability of the passive films in SCS_{14} solution is still worse than that of $SCS_{12.5}$. This suggests that the corrosion resistance of the passive films would decrease due to the very high alkaline environment (above pH 13), which is deleterious to the protective properties of the passivity. More stable and better protective passive film will be formed in an appropriate alkaline solution (such as pH 12.5). Meanwhile, the E_{corr} of the P355 carbon steel in different alkaline solution is varied and it takes a long time to reach a steady state which will result in the deviation of the E_{corr} , especially for potentiodynamic polarization. In order to reduce the data deviation, we employed the consistent test conditions, such as the same pretreatment, measure time, electrode system and configuration. Based on the results of polarization test, the formation potentials (-800 mV to 0 mV with an interval of 100 mV) were selected for the potentiostatic polarization, covering the "lower" part of the passive region, in order to simulate the very negative corrosion potential of carbon steel in the alkaline and anoxic conditions.



Figure 2. Potentiodynamic plots of P355 carbon steel measured in (a) SCS_{12.5}, (b) SCS_{13.5}, (c) SCS₁₄ and (d) polarization 24 h at -0.2 V in SCS₁₄. The sweep rate is 0.1667 mV/s, 25°C.

3.2 Potentiostatic polarization behavior of P355 carbon steel in SCS

Potentiostatic polarization was employed to accelerate the formation of the passive film on P355 carbon steel. The steady state described here is an "operational" one and the real steady state of

the passive film takes considerably more time to achieve, which is impractical to achieve based on laboratory experiments [27]. For applied potentials -700 mV to 400 mV, the steady state current density should be positive, while for the lower applied potentials (-1000 mV to -800 mV), because they are below the E_{corr} , the steady current should be negative because of the dominance of the cathodic reaction of hydrogen evolution. This is exactly what is observed in the potentiostatic polarization, as shown in Fig.3. The passive film, which is the product of a series of anodic processes, might exist at a negative current density.

In addition, it should be pointed out that the E_{corr} of the passive steel increases with the increase of the passive film thickness, which will change the current density and direction. This is related to the formation of an oxide layer on the working electrode which has changed the surface state [28]. Due to the difference of the passive film in the passivation process, the E_{corr} measured in the different stage of the passivation process is corresponding to the different thickness of the passive films. It has been accepted that the polarization current reflects the formation, early growth, and repassivation of passive films [29]. Therefore, it is necessary to record the trace of the current in the potentiostatic polarization process as shown in Fig.3. It is observed in Fig.3 that as the applied potential increases, the net current density is found to be positively shifted. This is probably due to the thicker passive film generated at higher potentials and less perturbation brought about by the cathodic reaction. There are a number of short-period current spikes, which are due to the breakdown of the passive film followed immediately by repassivation, reflecting the nucleation, growth, and repair of the metastable passive films.



Figure 3. Traces of the polarization current of P355 carbon steel recorded at different applied potential for 24 h in SCS_{12.5} and SCS_{13.5}.

Fig.3 also shows that the time (T_s) for passivation reach an "operational" steady state will be prolonged when the pH increases from 12.5. It shows that the polarization current increased as the pH increases. In other words, in the more alkaline environment, the corrosion resistance of the passivation steel will decrease. Moreover, as can be seen in Fig.3, the T_s is short at high applied potential and is long at low applied potential. As is shown in Fig. 3, at pH 12.5, the T_s is very short, even less than 1 h, but it will extend to 3 h at pH 13.5. It revealed that the very alkaline environment (pH >13) can delay the formation of oxidation layer, in which process more time is needed for the current to reach a stable state.

3.3 Effects of polarization potential on EIS in different SCS

The effects of applied potential on electrochemical impedance spectra were measured to investigate the passivation behavior. Fig.4 presents Nyquist and Bode plots of P355 carbon steel after potentiostatic polarization at the different potential for 24 h in $SCS_{12.5}$, $SCS_{13.5}$ at 25°C. It is clearly observed that the Nyquist plots were characterized by a semicircle arc covering most the high-frequency region, which is attributed to charge transfer process related to the surface film property [30]. The high-frequency semicircles are generally associated with the charge transfer at the electrode/electrolyte interface. The increasing in the radius of the semicircle arc indicated an increase in the passive film stability and resistance. The appearance of the straight line indicates that the kinetics is limited by diffusion of the oxidation products [31].

In Fig.4, the diameters of capacitive loop decrease with the increase of pH from 12.5 to 13.5, indicating that the corrosion resistance decreased when pH above 13. The passivation of P355 carbon steel in the SCS_{12.5} is stable and the passive film has good corrosion resistance. However, this will be changed in stronger alkaline solution, like SCS_{13.5} and SCS₁₄. As can be seen in Fig. 4, the overall impedance shows higher values in SCS_{12.5}, revealing an enhancement of the protective properties of the passive film. The largest radius in SCS_{12.5} is more than $5 \times 10^4 \ \Omega \cdot \text{cm}^{-2}$. However, the radius decreases to $5 \times 10^3 \ \Omega \cdot \text{cm}^{-2}$ in SCS_{13.5} and then decrease to $2 \times 10^3 \ \Omega \cdot \text{cm}^{-2}$ in SCS₁₄ at pH 14. It indicated that with the increase of the SCS pH, the decrease in semicircle radius has demonstrated a decrease of the passive film resistance with low stability. This suggests that very alkaline environment have a deleterious effect on the passivation. It was found that the SCS_{12.5} with the medium-high pH value was the optimal solution for the passivation of the P355 steel, which could improve stability and corrosion resistance of the passive layer.

It can be seen in Fig.4 that when the applied potential is negative than -0.7 V, the radius of the capacitive semicircle arc is obviously smaller than other positive potentials. In general, the higher (above -0.7V) of the polarization potential, the larger of the radius of the semicircle arc, which signifies higher polarization resistance and better corrosion protection provided by the oxide film [32]. However, the highest applied potential is not corresponding to the highest impedance. The potential which is 300 mV positive and 100 mV negative to $E_{\rm corr}$ of the passive film is believed the optimal applied potential, which is usually in the range of -100 mV to -600 mV vs. SCE.

The Bode plots of passive film covered P355 carbon steel polarized 24 h at the different potential were shown in Fig.4. As shown in Fig.4b, with the sequential increase of polarization potential from -0.7 V to -0.1 V, the peak of the phase angle increases from -75.6° up to -82.5°. |Z| at 0.01 Hz is $1.1 \times 10^5 \ \Omega \text{cm}^2$. This indicates that more protective film was formed at more positive potential. As seen in Fig.4d, with the increase of the applied potential, the peak of phase angle increases from -80.6° up to -83.8°. In the low-frequency range (<1 Hz), there has a second time constant and the |Z| at 0.01 Hz is $2.95 \times 10^4 \ \Omega \text{cm}^2$ which is smaller than $1.1 \times 10^5 \ \Omega \text{cm}^2$ in Fig.4(b).

The P355 carbon steel displays the characteristic features of the passive materials. It was found that the modulus and phase angle of the impedance are strongly dependent on the pH value. The phase angle increases to around -82.5 $^{\circ}$ C over a wide range of frequencies (Fig.4b), indicating a pure

capacitive response, which is also a typical impedance spectra pattern when a passive film is formed. This feature affects the stability and electrical behavior of the protective passive film. This illustrates that the passive film behaves similarly to a pure capacitor with some leakage within intermediate and low frequency range. It was commonly acknowledged that additional capacitance character of the film could improve the protective capability of the passive layer because of the large transfer resistance which hinders substance transportation across the film [33]. The maximum phase angle of impedance in intermediate frequency is around -83°, indicating a stable passive film is formed on P355 steel. However, in the more alkaline solution, such as $SCS_{13.5}$, the stability of passive film can be decreased, which could lead to deteriorating of the corrosion resistance.



Figure 4. Nyquist (a, c) and Bode (b, d) plots of P355 carbon steel polarized 24 h at different potential at 25°C in (a) and (b) SCS_{12.5}, (c) and (d) SCS_{13.5}.

As for the polarization potential, the phase angle decreased when the potential is negative than -0.8 V vs. SCE. When the applied potential is in the range of -0.6 V to 0.2 V, the passive film has the protective capacitive properties with the phase angle up to -80°. The increase of the impedance modulus as the potential increases from -0.7 V is a result of the gradual thickening of the barrier layer and the development of the bilayer structure. The high impedance obtained is due to the passive film, and the reduction in impedance is consistent with a loss of protectiveness against corrosion. The transpassive dissolution of the oxide layer is closely related to the passive film breakdown [34]. These verified that the potential which is 300 mV positive and 100 mV negative to $E_{\rm corr}$ of the passive film is the optimal applied potential, which is usually in the range of -100 mV to -600 mV vs. SCE.

The electrical equivalent circuit (EEC) used for analysis and fitting the impedance data are shown in the Fig.5. As shown in Fig.5, a R_s connected in series with two RQ elements in parallel two

time constants $R_1[Q_1(R_2Q_2)]$. This model supposes that the passive film was already formed. It consists of a porous layer that is filled up with electrolyte. The passive film undergoes changes in the microstructural and electrical properties.



Figure 5. Electrical equivalent circuit (EEC) models for fitting the impedance spectra of the P355 carbon steel in SCS.

As depicted in Fig. 5, the first process (R_1Q_1) at higher frequencies has been associated with the redox processes taking place in the passive film, the parameter Q_1 represents the capacitive behavior of the formed passive film and R_1 stands for the resistance due to the ionic paths through a passive film. In the second detected process, Q_2 represents the double layer capacitance behavior at the interfaces and R_2 for the corresponding charge transfer process resistance. It assumes that the passive film can not be considered as a homogeneous layer but rather as a defective layer [35]. Here, CPE is used for the description of a non-ideal capacitance with varying *n*. The impedance of the CPE is given by:

$$CPE = Z(\omega) = Z_0 \cdot (i\omega)^{-n} \tag{1}$$

where Z_0 is the *CPE* constant. The factor *n* is an adjustable parameter that always lies from -1 to 1. When *n* =1, the *CPE* is an ideal capacitance (C), when *n* =-1, the *CPE* is an ideal inductor (L), When *n* = 0, *CPE* is resistance (R). For 0.5 < n < 1, the *CPE* represents the distribution of the dielectric relaxation times, *when n*= 0.5, *CPE* is a Warburg impedance (W).

Table 2 shows the fitting parameters at different polarization potentials for 24 h in SCS_{12.5} and SCS_{13.5} based on the equivalent circuit in Fig.5. It was found that the film resistance R_1 decreased sharply as the applied potential is lower than -0.7 V, which reflects the protective property of the film become worse. The R_1 decreased with the increase of the SCS pH. With the decrease of the applied potential, the R_1 decreases. The CPE₁, which represents the surface heterogeneity, increased with the decrease of formation potential indicating an increase of defects in the passive film. The values of the exponent *n* are between 0.53 and 0.68, which shows that the CPE₁ has an intermediate character between the capacitor and Warburg impedance, indicating a considerable homogeneity of the passive film surface. The CPE ₂ is very close to the typical double layer capacitance. In general, the CPE₂ decreases as the applied potential shift to negative. The R_2 obtained is much higher than $7 \times 10^4 \Omega \text{ cm}^2$, indicating that the passive film has good resistance to the charge transfer processes. The charge transfer resistance R_2 , which seems to be dependent on the E_{corr} of the passive films, varies with film formation potential, increasing significantly. This means that the passive film formed at near the E_{corr} of the passive films are more protective than that formed at other passive potentials.

	E/V	-0.1 V	-0.2 V	-0.3 V	-0.4 V	-0.5 V	-0.6 V	-0.7 V
SCS _{12.5}	$R_{\rm s}$	44.51	37.03	38.34	35.11	35.31	32.06	35.48
	CPE_1	1.3×10^{-5}	1.9×10^{-5}	2.5×10^{-5}	3.3×10^{-5}	3.7×10^{-5}	4.8×10^{-5}	6.7×10^{-5}
	n_1	0.95	0.94	0.94	0.94	0.93	0.92	0.89
	R_1	4.9×10^{4}	3.6×10^4	6.5×10^4	4.3×10^{4}	4.0×10^{4}	1.8×10^{4}	1.3×10^{4}
	CPE_2	3.9×10^{-5}	3.7×10^{-5}	7.9×10^{-5}	4.9×10^{-5}	7.2×10^{-5}	6.1×10^{-5}	8.1×10^{-5}
	n_2	0.61	0.56	0.68	0.55	0.62	0.550	0.53
	R_2	9.7×10^4	9.6×10^4	7.7×10^{4}	2.6×10^5	2.4×10^{5}	3.9×10^{5}	1.7×10^{5}
	$R_{\rm s}$	4.63	3.48	4.41	4.43	5.14	4.60	4.60
SCS _{13.5}	CPE_1	2.5×10^{-5}	6.6×10^{-5}	2.9×10^{-5}	2.4×10^{-5}	3.4×10^{-5}	4.4×10^{-5}	1.0×10^{-4}
	n_1	0.92	0.84	0.93	0.97	0.93	0.91	0.87
	R_1	2.4×10^4	1.5×10^{4}	2.5×10^4	80.1	1.9×10^{4}	79.1	19.7
	CPE_2	2.7×10^{-5}	2.6×10^{-5}	4.5	1.2×10^{-4}	4.5×10^{-5}	2.0×10^{-4}	4.4×10^{-4}
	n_2	0.61	0.61	0.65	0.75	0.60	0.42	0.52
	R_2	1.1×10^{5}	1.1×10^{5}	7.7×10^4	5.5×10^4	8.9×10^{4}	1×10^{20}	1×10^{20}

Table 2. Fitting parameters for EIS passivated 24 h at different potentials in $SCS_{12.5}$ and $SCS_{13.5}$.



Figure 6. R_p as a function of polarization potential in different SCS.

According to the ECC, R_p was calculated by $1/R_p = (1/R_1) + (1/R_2)$. The R_p as a function of applied potential as shown in Fig.6. It can be seen that the R_p of SCS_{13.5} is small than that of SCS_{12.5}. With the increase of the formation potential from -1.0 V to -0.1 V, R_p increases slowly within the range of -1.0 V to -0.8 V. Then, the R_p reach the maximum value in the region of -0.6 V to -0.4 V, which is also the E_{corr} range of the passive film. When the formation potential surpasses -0.4 V, the R_p decreases slowly and keep constant after -0.2 V. It needs to point out that many factors could affect R_p . Obviously, the R_p obtained in the SCS_{12.5} is stable and repeatable. However, as for the "aged" SCS_{12.5} and SCS_{13.5}, a large fluctuation can be found for R_p in the $R_p \sim V$ curves as shown in Fig.6. This shows that the R_p formed at pH 12.5 is larger than that of 13.5. It can be seen that passive film with better corrosion resistance will be formed when the applied potential is close to the E_{corr} of the stable passive layers, which is in the range -0.1 V to -0.5V.

3.4 Effects of polarization time on the passivation process

The P355 carbon steel was passivated by potentiostatic polarization at -0.2 V_{SCE} for a different time in SCS_{12.5}. As can be seen in Fig.7a, the current density will reach a steady state after 3 hours in the SCS_{12.5}. As seen in Fig.7b, the radius of the semicircle arc is small at 2 h. Then, for 10 h. the radius of the semicircle arc increases largely. Continue to increase the passivation time to 24 h, it can be seen that the radius is even bigger. Although the radius is still growing as the passivation time up to 48 h, the increment of the radius of the semicircle is very small. This indicated that the passive film has reached a steady state in which the thickness and corrosion resistance of the oxide layer are independent of time [36]. Therefore, it takes 24 h to obtain the steady state of the passivation in $SCS_{12.5}$. In the Bode plot Fig.7c, the |Z| defined a straight line with a zero slope and the phase angle (ϕ) remained at about -4° at high frequency (HF) indicating a resistive behaviour. This resistance was attributed to the electrolyte resistance (Rs). Bode plots showed a capacitive behavior at medium and low frequencies (MF and LF), characterized by a slanted |Z| and the ϕ defining a maximum value (- 82.7° , -79.7°). At LF the ϕ tended to -17° as the |Z| approached a resistance. With the passivation time increasing to 48 h, the peak of phase angle widens to low frequency as shown in Fig.7c. The |Z|parameter at 0.01 Hz for 48 h polarization is 90 k Ω cm⁻² and for 24 h is 89 k Ω cm² for the rest samples were between 34 and 50 k Ω cm². The |Z| of the samples which were polarized 24 h and 48 h are very close and exhibited higher corrosion resistance. The first time constant in MF region $(1-10^3 \text{ Hz})$ is related to the existence of passive film, and the second time constant in the LF region (<0.1 Hz) is associated with the corrosion process of carbon steel. It was observed in Fig.7d that the E_{corr} of the passive film in SCS_{12.5} was -0.403 V and -0.415 V which is more positive than that (-0.467V, -0.47V) in $SCS_{13.5}$, indicating that the passive films formed at pH 12.5 have high corrosion resistance. Compare the shape of the Tafel curve in Fig.2 and Fig.7d, the current density is much smaller than 1×10^{-5} A cm⁻² which is close to the initial pit corrosion current ($i_{p12.5}$). The current density is also smaller than that of P355 steel having no preformed passive film (Fig.2). It can be obtained from the above analysis that 24 h could get a steady state passive film and it has good corrosion resistance.

The Sat. $Ca(OH)_2$ solution by addition of NaOH at pH 13.5 (SCS_{13.5}) was also investigated for passivation of P335 steel as shown in Fig.7(e-h). It was found that the time for polarization current to reach a steady state is more than 6 h, which is longer than 3 h of SCS_{12.5}. At the same time, the polarization current increases and more current spikes appear compared to that of SCS_{12.5}. It indicates that higher pH than 12.5 has detrimental effects on the passivation and corrosion resistance of the steel [37, 38]. Firstly, higher pH can extend the incubation time to reach a steady state of the passivation. Secondly, in the very alkaline environment, the metastable pits can be developed easier, which can be seen by the fluctuation of the current spike in Fig.7e. The current spike is associated with the nucleation, growth, and repair of a metastable pit. The damaged region is prone to become a preferential site for subsequent metastable pits. So, it is difficult to obtain the steady state. As shown in



Figure 7. Influence of passive time on the electrochemical properties of P355 carbon steel (a, e) current traces of potentiostatic polarization at -0.2 V_{SCE} , (b, f) the Nyquist, (c, g) the Bode and (d, h) Tafel plots of passivated samples. (a-d) in SCS_{12.5}, (f-h) in SCS_{13.5}, 25°C.

Fig.7f, with the extended of the potentiostatic polarization time, the radius of the semicircle arc constantly increases. The radius of the semicircle arc of 48 h is much larger than that of 24 h. This

shows that it takes more than 24 h to reach a balanced state of the passivation. 48 h of polarization is necessary to obtain a steady state passive film with better corrosion resistance.

Fig.7g shows Bode plots for the P355 steel with two-time constants, the maximum ϕ is 83° at 63 Hz and a second maximum ϕ is -30° at 0.05 Hz. The |Z| modulus of P355 steel increased with the passivation time, indicating 48 h is necessary for the stability of the protective oxide layer. The time constant in the MF region is attributed to the passive film properties. In the LF region, it is related to the electrochemical properties of the corroding carbon steel. At the different passivation time, the ϕ in the MF region is almost constant, indicating the same capacitive properties of the oxide layer in contact with the electrolyte. On the other hand, the ϕ in the LF region increased and was displaced to lower frequencies as a consequence of the retard of the corrosion process. Moreover, the maximum of |Z| modulus in the Bode plots is $2.98 \times 10^4 \ \Omega \ cm^{-2}$. It was seen that the corrosion resistance decreased than that solution of $SCS_{12.5}$ which was $9 \times 10^4 \ \Omega \ cm^{-2}$. Fig.7h shows that in the $SCS_{13.5}$ solution, the polarization current partly exceeds 1×10^{-5} A cm⁻² and the breakdown current ($i_{p13.5}$, 3×10^{-5} A cm⁻²) of the passive film is higher than $i_{p12.5}$ (1×10⁻⁵ A cm⁻²). The corrosion potential is -0.467 V and -0.470 V corresponding to 24 h and 48 h respectively. With the passive film formed, the corrosion potential is more positive than the bare metal (between -0.6 V and -0.9 V), and is slightly negative than that in $SCS_{12.5}$. It can be concluded that higher pH (such as 13.5, 14) is not the ideal conditions for the formation of protective passive films. The saturated calcium hydroxide solution with pH 12.5 is a good choice for P355 steel passivation.

polarization time		2 h	10 h	24 h	48 h
	R _s	40.87	31.29	37.68	29.99
	CPE ₁	2.01×10^{-5}	2.03×10^{-5}	1.93×10^{-5}	2.48×10^{-5}
	n ₁	0.95	0.950	0.95	0.95
$SCS_{12.5}$	R_1	1.46×10^4	2.51×10^{4}	3.36×10^4	4.26×10^4
	CPE_2	1.12×10^{-4}	6.42×10^{-5}	3.34×10^{-5}	4.56×10^{-5}
	n_2	0.53	0.47	0.54	0.58
	R_2	3.80×10^4	6.19×10^{4}	1.02×10^{5}	9.19×10^{4}
	R _s	4.12	4.09	5.31	5.02
SCS _{13.5}	CPE ₁	1.89×10 ⁻⁵	2.03×10 ⁻⁵	2.11×10 ⁻⁵	2.11×10 ⁻⁵
	n ₁	0.96	0.96	0.96	0.96
	R_1	4.70×10^{3}	6.42×10^{3}	5.34×10^{3}	7.06×10^{3}
	CPE ₂	1.17×10^{-4}	9.75×10 ⁻⁵	1.03×10 ⁻⁴	9.16×10 ⁻⁵
	n_2	0.45	0.54	0.52	0.59
	R_2	2.44×10^{4}	2.89×10^{4}	2.67×10^4	3.47×10^4

Table 3. Fitting parameters extracted from the EIS plots in Fig.7.

Table 3 depicts the fitting parameters based on the equivalent circuit shown in Fig.5. It can be found that the passive film resistance R_1 increased from 1.46×10^4 to 4.26×10^4 as the passivation time increases from 2h to 48 h in SCS_{12.5} solution, which reflects that the protective properties of the passive film become strong. The CPE₁ only slightly increased from 2.01×10^{-5} to $2.48 \times 10^{-5} \mu \Omega^{-1} \text{cm}^{-2} \text{s}^{-n}$ when the time increased from 2 h to 48 h for SCS_{12.5}. This suggests that there is no obvious difference of the defects in the passive films. Comparing CPE₁ and CPE₂, it was found that CPE₁ are lower than

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CPE₂. This represents that the formed passive film is thin and the double layer at the interfaces has a high capacitive behavior. The R_2 obtained at pH 12.5 is higher than that of pH 13.5, indicating that the passive film has the higher resistance to the charge transfer process in this SCS_{12.5}. Moreover, it can be seen that R_1 is smaller than R_2 , which is probably associated with the porous properties of the outer oxide layer. The higher R_2 of pH 12.5 indicates the film has good charge transfer process resistance.

3.5 Electrochemical properties of the passive films

Fig.8 is the Tafel plot of the P355 carbon steel by potentiostatic polarization 24 h. As seen in Fig.8a, in the SCS_{12.5}, there was a broader passive range from about -0.6 V to 0.6 V. After 0.6 V, an sharp increase of the current was observed, which is due to the breakdown of the passive films and the formation of the corrosion pits [39, 40]. The formation potential also affects the corrosion potential of the passive films, which can be checked by the changes of the E_{corr} in Fig.8a. It was found that the E_{corr} shifts to more positive potential and the i_{corr} decreases with the increase of the applied potential. When the applied potential is -0.1 V to -0.2 V, the E_{corr} is -0.391 V and -0.403 V. With the decrease of the applied potential, the E_{corr} will be more negative as the following sequence: -0.477V, -0.607 V, -0.629 V, -0.728 V and -0.741 V, corresponding to the applied potential -0.3 V, -0.4 V, -0.5 V, -0.6 V and -0.7 V, respectively. Compared with SCS_{12.5} the breakdown potential of the passive films in SCS_{13.5} is decreased 40 mV from 0.6 V to 0.56 V as seen in Fig.8b. It was observed that the E_{corr} shifts more quickly to positive than that in SCS_{12.5} with the increase of the applied potential. The formation process of the passive film is a dynamic process with the passivation and dispassivation. Proper pH is necessary for the formation of the passive films with good protective capability.

In the cathode polarization process, corrosion products such as Fe^{2+} will be produced and their influence on the passivation could not be neglected. The solution could be contaminated by corrosion products which will greatly affect the reproducibility of the EIS data. This is usually accompanied by pit corrosion, transient current spikes, and unstable current density [41]. The corrosion product comes from the dissolution in the cathodic and the anodic transpassive region. The corrosion product includes Fe^{2+} , Fe^{3+} , Mo^{2+} ions and its hydroxides corresponding to the composition of the P355 steel in Table 1. It is necessary to further investigate the influence of corrosion products on the passivation process.



Figure 8. Tafel plots of P355 carbon steel polarized at different potential for 24 h at 0.1667 mV/s in (a) SCS_{12.5}, (b) SCS_{13.5}.

The electrochemical capacitance of the passive film/electrolyte interface was measured as a function of the applied potential to assess the semiconducting properties of the passive films formed on this steel. The relationship between capacitance and the applied potential is given by the Mott-Schottky equation, which describes the potential dependence of the space charge capacity, C, of a semiconductor electrode under depletion condition:

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

where the negative sign represents p-type and the positive sign represents n-type conductivity. e the electron charge, N charge carrier density, the donor density for n-type or the acceptor density for p-type semi- conductors, ε_0 the vacuum permittivity, ε the relative dielectric constant of the semiconductor, k Boltzmann's constant and T absolute temperature, E the applied electrode potential and E_{FB} the flat band potential.

The Mott-Schottky plots of P355 carbon steel in SCS is shown in Fig. 9. It displays the $C^2 vs$. *E* for the passive film formed on P355 steel at different potentials. The curve shows a straight line with a positive slope, and it demonstrates that the passive film displays the oxide behavior as the n-type semiconductor in this potential region. Moreover, the linear region slope becomes more positive with the applied potential increase from -1.0 V to -0.1 V. The decrease of capacitance with the applied potential is attributed to an increase in the thickness of the electron depleted layer and a diminishing number of charge carriers. This phenomenon indicates a modification in the electronic properties of the passive film and is related to an increase in the conductivity of the film due to the solid state oxidation.



Figure 9. Mott Schottky of P355 carbon steel at different applied potential to -1.0 V_{SCE} at a step rate of 25 mV/s, 5000 Hz, 25°C, in the solution (a) SCS_{12.5}, (b) SCS_{13.5}.

The values of N_D , N_A can be determined from the slope of the experimental C^{-2} vs. *E* assuming the dielectric constant of the passive film on the steel. According to equation (3), the slopes of the linear portion of the C^{-2} vs. *E* give the charge carrier density *N*, from the relation:

$$N = \frac{2}{m \cdot \varepsilon \cdot \varepsilon_0} \tag{3}$$

where *m* is the slope of the Mott-Schottky plot in the linear region of interest, *e* is the electron charge, ε the relative dielectric constant of the semiconductor, ε_0 the vacuum permittivity, the value is 8.85×10^{-12} F m⁻¹. According to the calculated results, the values of *N* are in the range of 10^{20} - 10^{22} cm⁻³, which matches the reported values for the passive film of the steels. Moreover, the values of N_D and

 N_A decrease with the increase of potentials. Thus, passive films formed at low passive potentials have more disordered structures and higher defect densities than those formed at higher passive potentials.

3.6 Effects of chloride ions on the passivation behavior

An experiment was firstly designed to evaluate the influence of chloride ions on the passive film of P355 carbon steel. Firstly, the P355 carbon steel was polarized at -0.1 V for 18 h in the N₂ deaerated Sat. Ca(OH)₂ solution (pH = 12.5, 25°C) to obtain the same passive films. Then potentiodynamic polarization was continuously performed in sequence at a sweep rate of 0.2, 0.5, 1, 2, 5, 10 mV/s from -0.75 V_{SCE} to 0.75 V_{SCE} in the SCS_{13.5} containing 0.025, 0.1, 0.5, 1 M NaCl, respectively, as shown in Fig.10. In Fig.10, for all the tested baths, no obvious pitting potential was observed, indicating that the excellent anticorrosion properties of the passive films. A rapid increase in the anodic current density (i_{corr}) at 550 to 600 mV vs. SCE potential was observed, which may be due to the oxidation of hydroxyl ions (4OH $\rightarrow O_2 + 2H_2O + 4e^-$) [42]. Sun [22] studied the pitting corrosion resistance of low-alloy steel and low-carbon steel at different chloride concentration. Macdonald [39] studied the effect of chloride ion concentration on pitting corrosion of carbon steel in saturated Ca(OH)₂ solution. Compare these similar literatures, it was found that the scanning rate and continuous sweep were not be considered which is different from this method.

In Fig.10, the $i_{a,-0.4V}$, $i_{a,-0.2V}$ was defined as the following formula:

$$\Delta i_{a,-0,4V} = i_{a,-0,4V}^{0.5} - i_{a,-0,4V}^{0.2}$$
(4)
$$\Delta i_{a,-0,2V} = i_{a,-0,2V}^{1} - i_{a,-0,2V}^{0.5}$$
(5)

where the a represent the SCS_{13.5} solution containing 0.025 M NaCl, which is used for Fig.10(a). Then b, c, d represent the SCS_{13.5} solution containing 0.1, 0.5 and 1 M NaCl respectively. As shown in Fig.10a, $i_{a,-0.4V}^{0.5}$ is the current density at the rate of 0.5 mV/s when the potential is -0.4 V in the 2nd curve. And similarly, $i_{a,-0.4V}^{0.2}$ is the current density at the rate of 0.2 mV/s when the potential is -0.4 V in the 1st curve. $i_{a,-0.2V}^{1}$, $i_{a,-0.2V}^{0.5}$ is the current density which the scanning rate is corresponding to 1 mV/s (3rd curve), 0.5 mV/s (2nd curve) when the potential is -0.2 V.

Table 4 sets out corrosion potential (E_{corr}) and current density (i_{corr}) extracted from the Tafel region (Fig.10). According to the results of Fig.10 and Table 4, it can be observed that the value of $\Delta i_{.04V}$ and $\Delta i_{.02V}$ followed the sequence: $\Delta i_{a, -0.4V} < \Delta i_{b, -0.4V} < \Delta i_{c, -0.4V} < \Delta i_{d, -0.4V}$, and $\Delta i_{a, -0.2V} \approx \Delta i_{b, -0.2V} < \Delta i_{c, -0.2V} < \langle \Delta i_{d, -0.2V} < \Delta i_{d, -0.2V}$. Therefore, it can be inferred that the chloride ion have no obvious influence on the corrosion resistance of the passive film in SCS when the concentration of chloride ion is less than 0.1 M. However, as shown in Fig.10c, when the concentration of chloride ions is up to 0.5 M, it is obvious that the polarization current density increases largely which can be confirmed by the value of $\Delta i_{c, -0.4V} >> \Delta i_{b, -0.4V}$. In addition, continue to sweep the third time at 1 mV/s, it seems that the resulting $\Delta i_{c, -0.2V}$ has not increased much which indicated the passive films still exist. However, it can be seen that the current density increases largely at the following "A" point in Fig.10c due to a serious corrosion being started. When the concentration of chloride ion is up to 1 M as shown in Fig.10d, large $\Delta i_{d, -0.4V}$ and $\Delta i_{d, -0.2V}$ was observed and very serious corrosion occurred with high corrosion current. At the same time, the shape of the Tafel plot has been changed much and the sample was obviously

corroded which can be seen by naked eyes. Surpass 1M is greatly beneficial to result in serious corrosion. Then, it can be seen from the above analysis that it is needed to restrain the concentration of chloride ions to 0.1 M, more than 0.5 M chloride ions will have a greatly destructive effect on the passive film.



Figure 10. Continuous potentiodynamic curves of P355 carbon steel at the sweep rate of 0.2, 0.5, 1, 2, 5, 10 mV/s in SCS_{13.5} containing 0.025, 0.1, 0.5, 1M NaCl respectively. The steel was polarized at -0.1 V for 18 h in the N₂ deaerated SCS_{12.5}.

Table 4 E_{corr} (V_{SCE}) and i_{corr} (μ A cm⁻²) extracted from Fig.10.

$\operatorname{Cl}^{-1}(\operatorname{mol} L^{-1})$	0.0	0.025		0.1		0.5		1	
$v (mV s^{-1})$	$E_{\rm corr}$	$i_{\rm corr,}$	$E_{\rm corr}$	i _{corr,}	$E_{\rm corr}$	i _{corr,}	$E_{\rm corr}$	$i_{\rm corr,}$	
0.2	-0.677	1.08	-0.692	0.12	-0.524	0.03	-0.673	0.23	
0.5	-0.596	1.22	-0.595	0.11	-0.708	0.27	-0.726	4.27	
1	-0.529	0.97	-0.498	0.17	-0.671	0.34	-0.71	7.44	
2	-0.500	1.07	-0.473	0.27	-0.649	0.82	-0.695	22.7	
5	-0.454	1.25	-0.416	0.44	-0.656	1.47	-0.664	25.2	
10	-0.433	0.82	-0.406	0.56	-0.561	1.56	-0.669	29.5	

The E_{corr} and i_{corr} change plots as a function of scanning rate in the continuous potentiodynamic scan from 0.2 to 10 mV/s in sequence can be seen in Fig.11. It was found that the E_{corr} increases with the increase of scanning rate when the concentration of chloride ions in the SCS_{13.5} solution is 0.025 M

and 0.1 M. However, when the concentration of chloride ions is 0.5 M, the E_{corr} decreases sharply, then increases slowly. The E_{corr} is more negative than that of 0.025 M and 0.1 M. When the chloride ions are up to 1 M, the lowest E_{corr} value was obtained, which shows the worst protective property of the passive film in this condition. Robert D [16] reported the similar results that in alkaline solutions, all high-strength stainless steels showed high corrosion resistance at Cl⁻ concentrations from zero to 0.25 M. When Cl⁻ concentrations is above 0.5 M, most of them exhibited low corrosion susceptibility, which certified the credibility of the findings of this study.



Figure 11. E_{corr} and i_{corr} change plot as a function of the scanning rate in the continuous potentiodynamic scan from 0.2 to 10 mV/s in sequence.

This could also be verified by the i_{corr} vs. v plots. It can be observed that i_{corr} of the SCS containing 0.5 M chloride ions is larger than the solution which contains 0.025, 0.1 M chloride ions. However, when the concentration of chloride ions is up to 1 M, the i_{corr} increases hugely by more than 20 times. This indicates that more than 0.5 M chloride ions will damage the corrosion resistance of the passive films, and more than 1 M chloride ions will completely destroy the passive film and greatly accelerate the corrosion process.

4. CONCLUSIONS

The electrochemical behavior and passive film properties of P355 carbon steel in simulated concrete pore solutions under an anoxic condition at different pH were evaluated by potentiodynamic measurements, EIS, Mott-Schottky methods. The main conclusions were obtained as follows: The P355 carbon steel exhibits well passive behavior in SCS with a broad passive region from -0.7 V to 0.5 V vs. SCE. The equivalent circuit $R_1[Q_1(R_2Q_2)]$ is suitable for the P355 in SCS. However, the formation and protective properties of the passive film are greatly influenced by the pH value and applied formation potential. Different from previous studies, which accept that the corrosion resistance of the passive film increases with the increase of the applied potential, in this experiment, it was found that the highest applied potential is not corresponding to the best impedance. The optimal formation potential for passivation of the P355 steel in SCS is usually in the range of -100 mV to -600 mV vs. SCE. The

passive film formed displays the behaviors of n-type semiconducting. The R_p formed in SCS_{12.5} is larger and less fluctuated than that of SCS_{13.5}. Moreover, the fresh SCS is beneficial to stable R_p . The threshold value of the chloride ions is 0.1 M, below which the passive film still have the protective ability of a barrier layer. It is needed to restrain the concentration of chloride ions to 0.1 M in SCS, more than 0.5 M chloride ions are greatly beneficial to initiate serious corrosion.

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References

- 1. F. Mao, C. Dong, D.D. Macdonald, Corros. Sci., 98 (2015) 192.
- 2. H. Luo, H. Su, C. Dong, X. Li, Appl. Surf. Sci., 400 (2017) 38.
- 3. X. Feng, X. Lu, Y. Zuo, D. Chen, Corros. Sci., 82 (2014) 347.
- 4. Y. Gao, J.A. Syed, H. Lu, X. Meng, Appl. Surf. Sci., 360 (2016) 389.
- J.C. Galván, M.T. Larrea, I. Braceras, M. Multigner, J.L. González-Carrasco, J. Alloys Compd., 676 (2016) 414.
- 6. W. Dec, M. Mosiałek, R.P. Socha, M. Jaworska-Kik, W. Simka, J. Michalska, *Electrochim. Acta*, 212 (2016) 225.
- 7. J. Lv, T. Liang, C. Wang, T. Guo, J. Alloys Compd., 658 (2016) 657.
- 8. H. Zheng, W. Li, F. Ma, Q. Kong, Cement Concrete Res., 55 (2014) 102.
- 9. Y.-M. Chen, M.E. Orazem, Corros. Sci., 104 (2016) 26.
- F. Tang, X. Cheng, G. Chen, R.K. Brow, J.S. Volz, M.L. Koenigstein, *Electrochim. Acta*, 92 (2013) 36.
- 11. F. Zhang, J. Pan, C. Lin, Corros. Sci., 51 (2009) 2130.
- 12. S.M. Abd El Haleem, S. Abd El Wanees, A. Bahgat, Corros. Sci., 75 (2013) 1.
- 13. R. Feng, J. Beck, M. Ziomek-Moroz, S.N. Lvov, Electrochim. Acta, 212 (2016) 998.
- 14. F. Mao, C. Dong, S. Sharifi-Asl, P. Lu, D.D. Macdonald, *Electrochim. Acta*, 144 (2014) 391.
- 15. L. Zhang, A. Ma, J. Jiang, D. Song, D. Yang, J. Chen, Surf. Coat. Technol., 232 (2013) 412-418.
- 16. R.D. Moser, P.M. Singh, L.F. Kahn, K.E. Kurtis, Corros. Sci., 57 (2012) 241.
- 17. Z. Ai, J. Jiang, W. Sun, D. Song, H. Ma, J. Zhang, D. Wang, Appl. Surf. Sci., 389 (2016) 1126.
- 18. X. Feng, Y. Zuo, Y. Tang, X. Zhao, X. Lu, Electrochim. Acta, 58 (2011) 258.
- 19. B. Huet, V. L'Hostis, F. Miserque, H. Idrissi, Electrochim. Acta, 51 (2005) 172.
- 20. G. Liu, Y. Zhang, Z. Ni, R. Huang, Constr. Build. Mater., 115 (2016) 1.
- 21. H.-S. Ryu, J.K. Singh, H.-S. Lee, M.A. Ismail, W.-J. Park, Constr. Build. Mater., 133 (2017) 387.
- 22. J. Shi, W. Sun, J. Jiang, Y. Zhang, Constr. Build. Mater., 111 (2016) 805.
- 23. B. Li, W. Zhang, W. Zhang, Y. Huan, J. Alloys Compd., 702 (2017) 38.
- 24. H. Luo, H. Su, C. Dong, K. Xiao, X. Li, Constr. Build. Mater., 96 (2015) 502.
- 25. J.M. Deus, B. Díaz, L. Freire, X.R. Nóvoa, Electrochim. Acta, 131 (2014) 106.
- 26. S. Sharifi-Asl, D.D. Macdonald, A. Almarzooqi, B. Kursten, G.R. Engelhardt, J. Electrochem. Soc., 160 (2013) C316.
- 27. P. Lu, B. Kursten, D.D. Macdonald, *Electrochim. Acta*, 143 (2014) 312.
- Y. Zhang, M. Urquidi-Macdonald, G.R. Engelhardt, D.D. Macdonald, *Electrochim. Acta*, 69 (2012) 1.
- 29. Y. Wang, Y. Zuo, X. Zhao, S. Zha, Appl. Surf. Sci., 379 (2016) 98.

- 30. M. Mohammadi, L. Choudhary, I.M. Gadala, A. Alfantazi, J. Electrochem. Soc., 163 (2016) C883.
- 31. M.S. Anwar, B. Fadillah, A. Nikitasari, S. Oediyani, E. Mabruri, Procedia Eng., 171 (2017) 517.
- 32. W. Kuang, J.A. Mathews, M.L. Taylor, D.D. Macdonald, Electrochim. Acta, 136 (2014) 493.
- 33. Y. Wang, Y. Zuo, Corros. Sci., 118 (2017) 24.
- 34. H. Liu, D. Xu, A.Q. Dao, G. Zhang, Y. Lv, H. Liu, Corros. Sci., 101 (2015) 84.
- 35. D.D. Macdonald, *Electrochim. Acta*, 56 (2011) 7411.
- 36. S. Sharifi-Asl, M.L. Taylor, Z. Lu, G.R. Engelhardt, B. Kursten, D.D. Macdonald, *Electrochim. Acta*, 102 (2013) 161.
- 37. D. Addari, B. Elsener, A. Rossi, *Electrochim. Acta*, 53 (2008) 8078.
- 38. M. Cabrini, S. Lorenzi, T. Pastore, Electrochim. Acta, 124 (2014) 156.
- 39. S. Sharifi-Asl, F. Mao, P. Lu, B. Kursten, D.D. Macdonald, Corros. Sci., 98 (2015) 708.
- 40. B. Li, W.W. Zhang, Int. J. Electrochem. Sci., 12 (2017) 7017.
- 41. S. Fajardo, D.M. Bastidas, M. Criado, J.M. Bastidas, Electrochim. Acta, 129 (2014) 160.
- 42. M. Criado, I. Sobrados, J. Sanz, J.M. Bastidas, Surf. Coat. Technol., 258 (2014) 485.

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