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Passivation and Depassivation of HPB335 Carbon Steel in Simulated Concrete Pore Solution

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In order to study the corrosion mechanism of carbon steel, the passive film characteristics, critical chloride threshold and depassivation of HPB335 carbon steel in different solutions were studied. This study mainly used Mott–Schottky analysis, open-circuit potential, linear polarization resistance and point defect model (PDM) to study the passive film characteristics and depassivation mechanism of carbon steel. The experimental results show that the passive film quality and aggressive ions threshold of carbon steel in highly alkaline solutions are mainly related to pH. In the characteristics of the passive film, the correlation between the resistance and the chloride threshold is relatively large. In addition, PDM was used to study the depassivation mechanism of carbon steel. This study demonstrates the effectiveness of PDM for passivation and depassivation of carbon steel in highly alkaline solutions.

Keywords: carbon steel, passive film, chloride threshold, depassivation, PDM

1. INTRODUCTION

It is well known that carbon steel forms a dense passive film in concrete due to the high alkaline environment [1]. This passive film protects the carbon steel, making it less susceptible to corrosion [2]. However, due to the carbonation of the concrete and the invasion of chloride ions, the passive film of the carbon steel will be damaged [3,4]. Pitting corrosion occurs in the carbon steel after depassivation [5]. At present, the researchers believe that carbonation and aggressive ions (such as chloride ions) are the main reasons for the depassivation and pitting corrosion of carbon steel. In comparison with carbonation, invasion of chloride ions is a major factor in inducing steel corrosion. But there is still no clear chloride threshold for the initiation of steel corrosion. A specific chloride threshold is affected by many factors, such as the surface roughness of the carbon steel [6], the distribution of steel impurities and grains, the solution environment (mainly aggressive ions and inhibitive ions) [7–9]. It is important to specify the chloride threshold in a particular situation, as researchers cannot give a general expression to describe the critical value of chloride under different environment. By controlling the factors that affect the chloride threshold, describing the chloride threshold in a certain situation will be greatly helpful for the study of the chloride threshold under multiple factors.

Concrete is a heterogeneous material, and the environment around the carbon steel in concrete is actually very complicated. It is difficult to measure the corrosion ratio of carbon steel in concrete using electrochemical theory. Recently, many researchers have performed electrochemical measurements on carbon steel in an environment that simulates pore solutions. Although the simulated pore solution cannot totally represent mortar or concrete, but it is still a good choice until better technology emerged [10–14]. Alonso studied the chloride threshold in mortar using electrochemical techniques [15]. The results indicate that when the $[Cl^-]/[OH^-]$ ratio is 1.17~3.98, the carbon steel starts depassivation and pitting. Generally, researchers use the ratio between aggressive ions and inhibitive ions to describe the threshold of carbon steel pitting. Shishir studied the chloride threshold in simulated pore solutions of alkali-activated concretes [16]. Some researchers modified the chloride threshold based on electrochemical method to describe the depassivation of carbon steel, such as $[Cl^{-}]/[OH^{-}]^{3}$ [16]. In addition, more researchers studied the influential parameters on chloride threshold, such as carbon steel surface treatments, sample sizes, simulated pore solutions, and mix proportions of mortar and concrete [1,6,16–22]. While there is still rare attention being paid to the investigation on the relationship between depassivation mechanism and chloride threshold of carbon steel by now. The chloride threshold of carbon steel is determined by the external environment, and different environments will induce the characteristics change of the passive film, which will cause the chloride threshold variation of carbon steel. Most scholars studied chloride thresholds in different situations, and different chloride thresholds were obtained accordingly. Furthermore, the chloride threshold will show a slight vibration even in a stable environment. As a result, the chloride threshold given by some scholars is within a certain range [15,20]. Therefore, exploring the mechanism of depassivation, rather than influence of the environment, is of great significance to the study of chloride threshold. In this study, the relationship between the passive film characteristics and chloride threshold is discussed.

There are several electrochemical techniques to study the chloride threshold of carbon steel and the characteristics of passive film formation and destruction. The passive film of carbon steel is usually an N-type semiconductor in high alkaline environment, and Mott–Schottky (M-S) analysis is considered to be an important method to study the semiconductor properties of the passive film [14,23,24]. The open-circuit potential (OCP) can identify whether the carbon steel is in a passive state or a corrosion state. The linear polarization resistance (LPR) method determines the state of the carbon steel by measuring the resistance [1,16,20]. The point defect model (PDM) are generally used to describe the growth and annihilation of metal passive film. This model was proposed by Digby D. Macdonald and has been verified by many researchers [25–29].

The purpose of this work was to investigate the chloride threshold and the phenomenon of passivation and depassivation of carbon steel under different pH and chlorides environments. Next, the relationship between the chloride threshold and the passive film characteristics or the formation and

destruction mechanism will be discussed. M-S analysis was used to analyze the state of carbon steel when it was passivated. The OCP and LPR method were employed to describe the threshold and state of carbon steel depassivation. Finally, PDM was used to explore the principle of depassivation of carbon steel due to chloride ions. This study used several different electrochemical methods and theories to study the passivation and depassivation of carbon steel in simulated pore solution to achieve a comprehensive understanding of chloride threshold.

2. EXPERIMENT

2.1. Specimen preparation

HPB335 plain carbon steel rebar with the length of 50 mm and diameter of 10 mm was prepared. The chemical composition (wt.%) of the steel is listed in Table 1. The rust on the surface of steel rebar was removed and the carbon steel rebar was polished with 100# to 1200# silicon carbide (SiC) papers to smooth. The sample was rinsed with double distilled water and absolute ethanol, and then dried under flowing high purity N_2 gas. Then the steel rebar was sealed with epoxy resin except one end was left as working face. In order to prevent crevice corrosion, the working end was also rimmed with epoxy resin. After edge banding, a digital photo of working face was taken to perform an image processing on the actual working area of the steel carbon rebar.

Table 1. Chemical composition of carbon steel rebar

Element	С	Mn	Si	S	Р	Iron
Content (wt.%)	0.22	0.61	0.23	0.034	0.038	98.868

Carbon steel is easier to be measured using electrochemical means in simulated pore solutions than in mortar or concrete. This experiment used three synthetic solutions to simulate the concrete pore solutions. Each element and proportion in the simulated solution is like that measured in real concrete to better simulated the concrete pore solutions[30]. The chemical composition of simulated pore solutions is listed in Table 2. In order to adjust the pH value and the ionic species of the solution, NaHCO₃ was added into SPS1 and SPS2. The temperature of the solution maintained as $24\pm1^{\circ}$ C, and the pH of the solution was measured by PHS-3C pH meter.

Table 2. Chemical	composition	in simulated	pore solution
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Solution	NaOH (mol/L)	KOH (mol/L)	Ca(OH) ₂ (mol/L)	NaHCO ₃ (mol/L)	pН
SCPS	0.15	0.45	Sat.	-	13.6
SPS1	0.15	0.45	Sat.	0.01	13.5
SPS2	0.026	0.078	Sat.	0.03	12.9

2.2. Experimental procedure

All electrochemical measurements were conducted using the CHI660E electrochemical workstation. A three-electrode system was used in the experiment, in which the working electrode (WE), the counter electrode (CE), and the reference electrode (RE) were a carbon steel rebar, a platinum plate and Ag/AgCl (sat. KCl) electrode, respectively. To reduce the inhomogeneous distribution of potential and current, the reference electrode was connected through a Luggin probe. Luggin probe was about 5mm away from the surface of the working electrode.

2.2.1. OCP, LPR, M-S analysis

Polyethylene electrolytic cell was used for OCP, LPR test and M-S analysis. 500ml SCPS, SPS1, SPS2 solutions were poured into three electrolytic cells respectively. In each electrolytic cell, three prepared samples were installed to eliminate sampling and testing errors. The carbon steel samples were passivated for 9 days in the electrolytic cell. In order to analyze the depassivation of steel rebar, 0.1mol NaCl was added to SCPS and SPS1 every 24h, and 0.05mol NaCl was added every 24h to SPS2. During adding NaCl, NaCl was added to a medical needle, and then part of the solution was inhaled to dissolve all the NaCl. Adding NaCl every 24h would ensure a fully reaction between the carbon steel and chloride ions. To prevent evaporation and carbonation, the electrolytic cell was covered with a plastic plate during the experiment, except for the addition of NaCl solution and electrochemical testing.

Generally, carbon steel may be passivated in a highly alkaline solution in 8 days [13]. In this experiment, carbon steel was passivated for 9 days in solution and OCP data were measured every 24 hours during passivation. The OCP data on 0 day was measured after the sample was placed in the solution for 12 hours. M-S analysis was used to study carbon steel samples after passivating for 9 days. When the carbon steel was passivated, chloride ions were added to the solution. Before chloride ions were added, OCP and LPR measurements were performed.

During OCP monitoring, when the system reached a steady state (varying less than ± 1 mV/min), the OCP data was recorded. The scan rate of LPR test was 0.1667mV/s, and the scan ranged from -10mV to +10mV in relative to the open-circuit potential. M-S analysis was measured at a frequency of 1kHz and scanned in the range of -0.2V to 0.5V. In order to reduce the polarization time of the passive film and the non-linearity of the data, a voltage increment of 0.05V and a voltage amplitude of 10mV were applied [14].

2.2.2. PDM

A customized electrolytic cell was used for PDM test. Different molarity of NaCl was mixed to prepare four subtypes of SPS1. After configuration, the NaCl concentration in SPS1 were 0.5mol/L, 1.0mol/L, 1.5mol/L, 2.0mol/L. The solution was sprayed with ultrahigh-purity N_2 gas about 2h to eliminate the influence of oxygen before and during the experiment. The carbon steel sample was placed in the solution until the open-circuit potential of the sample was stable in performing a potentiodynamic polarization. At first, carbon steel samples were subjected to potentiodynamic polarization in solutions

with different chloride ions concentrations (0.5mol/L, 1.0mol/L, 1.5mol/L, 2.0mol/L) for 15 times under a scan rate of 0.1667mV/s to obtain the breakdown potential. Then the potentiodynamic experiments were performed in SPS1 (2.0mol/L NaCl) with scan rates of 0.1667 mV/s, 1.667 mV/s, 6.667 mV/s and 10 mV/s, respectively.

3. RESULTS AND DISCUSSION

3.1. OCP and Mott-Schottky analysis

Figure 1 shows the average open-circuit potentials of carbon steel rebar in relative to the Ag/AgCl reference electrode in three solutions. It can found from Figure 3 that the open-circuit potential increases gradually for all samples in solutions and it tends to be stable after 6d. The decline of gradual increment means that the carbon steel changes from an active state to a passive state in this highly alkaline environment. The open-circuit potential of carbon steel in SCPS and SPS1 are -245mV and -238mV respectively, and in SPS2 is -112mV at 0 day. From 6d, the passive potential of samples in SCPS and SPS1 narrowly ranges between -100mV and -120mV, and that in SPS2 slightly varies about -30mV. It can be concluded from Figure 3 that the open-circuit potential of carbon steel is determined by the pH value of the solution. As the pH value of SCPS is close to SPS1, the development of open-circuit potential of carbon steel for SCPS and SPS1 is nearly the same during the monitoring. The experiment results clearly indicate that the passive potential of carbon steel in SPS2 is higher than those in SPS2 and SCPS. It can also be obtained from Figure 1 that the passive potential is lower in the solution with higher pH.



Figure 1. Average open-circuit potential of turned-and-polished carbon steels in simulated concrete pore solutions

Mott–Schottky analysis is often used to study the semiconducting properties of passive films [14,23]. In order to study the electronic properties of the passive films formed on carbon steels in these three solutions, M-S analysis of carbon steel was taking from 10d. The M-S equation bridging the relationship between capacitance C and the applied potential is expressed as [31]:

$$\frac{1}{C^2} = \pm \frac{2}{\varepsilon \varepsilon_0 eN} \left(E - E_{\rm FB} - \frac{kT}{e} \right) \tag{1}$$

where *C* (F/cm²) is the capacitance; the negative sign yields p-type and the positive sign represents n-type conductivity, respectively; ε is the relative dielectric constant of the semiconductor, taken as 12 for carbon steel [32]; ε_0 (F/m) is the vacuum permittivity, taken as 8.854×10⁻¹²(F/m); *e* (C) is the electron charge; *N* (cm⁻³) is charge carrier density, i.e., the donor density for n-type or the acceptor density for p-type semiconductors; *E* (V) is the applied potential and *E*_{FB} (V) is the flat band potential; *k* (J/K) is Boltzmann's constant, taken as 1.381×10⁻²³ J/K; *T* (K) is absolute temperature.

The C^{-2} for the passive film of carbon steel formed in different solutions is plotted against *E* in Figure 2. The results show that the passive films of carbon steel after 10 days passivation time in three solutions exhibit n-type semiconductive behavior. It can infer from the variation of M-S data that C^{-2} generally increased with the *E*. Another feature is that the M-S curves in the three solutions are all obviously hump-like. If it is an n-type behavior with only a single donor state, the M-S plots will show a positive linear slope. The hump-like curve implies that the passive film has a double-layer structure, because it has two donor states, shallow and deep donor states. Generally, the passive film is firstly formed by an inner layer mainly composed of Fe^{II}-oxides, which is also a barrier layer. The barrier layer acts as a barrier to aggressive ions. After that, the inner layer gradually changes to the outer layer consisting Fe^{III}-oxides, and the outer layer is a loose and porous layer, which doesn't play a positive role in passivation [14,33].



Figure 2. Mott–Schottky plots for the formed passive film in simulated concrete pore solutions: (a) SCPS (pH=13.6, no CO₃²⁻), (b) SPS1 and SPS2 (pH=13.5, pH=12.9, both containing CO₃²⁻)

For a passive film with multiple n-type donor species, the shallow donor density N_{D1} and deep donor density could be given by following equation [34]:

$$N_{\rm D1} = \frac{2}{\varepsilon \varepsilon_0 e S_1}, N_{\rm D2} = \frac{2}{\varepsilon \varepsilon_0 e S_2} - N_{\rm D1}$$
⁽²⁾

Where S_1 (V) is the slope of the shallow donor region in the M-S plots (-0.25 to -0.1V); S_2 (V) is the slope of the deep donor region in the M-S plots (0.25 to 0.4V). The flat band potential can be calculated by Eq.(1). Taking the passive film as a parallel plate capacitor model of a homogeneous oxide layer, the thickness of the passive film *d*, can be calculated by Eq.(3):

$$d = \frac{\varepsilon \varepsilon_0 A}{C} \tag{3}$$

The electronic properties of the samples are shown in Table 3. The pH values in SCPS and SPS1 is similar, the difference between SCPS and SPS1 is that SPS1 contains a small amount of $CO_3^{2^-}$. SPS1 and SPS2 have the same ionic species, the difference is that SPS1 has a higher pH than SPS2. It can be summarized from Table 2 that $CO_3^{2^-}$ mainly affects the shallow donor density and pH mainly affects the deep donor density. Donor density is positively correlated with point defects in the passive film. The shallow donor density can characterize the inner layer of the passive film. And similarly, the deep donor density of sample pitting will be. So, the pitting probability ranking of the three solutions is SCPS<SPS1<SPS2. From the results, the correlation between the flat band potential and pH is relatively higher. And the flat band potential is not determined by the ionic species, it may be because there is less $CO_3^{2^-}$ in SPS1. It can be inferred from the thickness of the passive film that as the pH decreases, the thickness of the passive film also decreases. But the influence of $CO_3^{2^-}$ on the thickness of the passive film, it can be concluded that, among the three solutions, SCPS makes the carbon steel having a better passive film, followed by SPS1 and SPS2 in turn.

Table 3. Electronic properties of the carbon steels after passivation

	$N_{\rm D1}~(10^{21}{\rm cm}^{-3})$	$N_{\rm D2}~(10^{21}{\rm cm}^{-3})$	$E_{\mathrm{FB}}\left(\mathrm{V}\right)$	d (nm)
SCPS	1.107	1.033	-1.070	1.01~1.06
SPS1	4.811	1.679	-1.070	0.49~0.54
SPS2	3.576	4.712	-0.713	0.45~0.50

3.2. OCP and LPR

Figure 3 shows the OCP and LPR data measured daily before adding chloride ions. It can be seen from Figure 3 that the values of OCP and LPR have a significant decrease during the experiment. The decline is caused by pitting of carbon steel. As indicated by Figure 3(a), for the samples in SCPS, the OCP value slightly fluctuates after the addition of NaCl solution. But the OCP value decreases slowly afterwards. The value of LPR also decreases with the increase of chloride ions, and the change of LPR is synchronized with OCP. However, LPR value does not fluctuate, and the value mostly decreases slowly. When NaCl is added up to 2.8mol/L, the values of OCP and LPR decrease rapidly together. This means the chloride threshold of carbon steel in SCPS solution is about 2.8mol/L. For the samples in SPS1 (Figure 3(b)), the OCP value first increases a little, then decreases in fluctuations. The trend of

LPR value is similar to that of OCP, but there is little fluctuation. When NaCl is added to 1.4 mol/L, the values of OCP and LPR decrease sharply and then increase. This situation may be caused by the change of environment at that time, or it may be because the carbon steel goes through metastable pitting at first, and then depassivation latter. When NaCl is added up to 2.4~2.6mol/L, the values of OCP and LPR decrease rapidly and the carbon steel is pitting. Comparing the change of OCP and LPR of carbon steel in SCPS and SPS1, it can be found that the OCP and LPR values of carbon steel in SCPS are relatively more stable than in SPS1 before pitting. This may indicate that the carbon steel has better corrosion resistance in the SCPS solution, and the carbon steel is slightly less resistant to corrosion when slightly carbonation. Some scholars believe that slight carbonation will reduce the corrosion resistance, and when carbonation reaches a certain level, it will enhance the corrosion resistance of carbon steel [37].





Figure 3. OCP and LPR of carbon steels in three solutions change with increasing Cl⁻

For the samples in SPS2 (Figure 3(c)), the OCP and LPR values are very stable once NaCl is added. When the NaCl is up to 0.6mol/L, the values of OCP and LPR decrease rapidly, indicating that they start pitting at this moment.

The critical chloride threshold of carbon steel in these three solutions can be obtained from Figure 3. The OCP monitoring and LPR testing can well observe the transition point of carbon steel from passive state to active state. It can be concluded from the experimental results that carbon steel has higher corrosion resistance in SCPS and lower corrosion resistance in SPS2. Although the critical chloride threshold of carbon steel can be seen from the OCP and LPR test results, the corresponding corrosion resistance cannot be derived from the characteristics of the carbon steel passive film, such as film thickness and resistance. The thickness of the passive films of carbon steel in SCPS, SPS1, SPS2 estimated by M-S analysis are 1.06nm, 0.54nm and 0.50nm. But the chloride threshold of carbon steel in SPS1 is only a little smaller than in SCPS. The relative difference of chloride threshold is not so obvious as the thickness of the passive film. Although the passive film thickness of SPS1 is similar to that of SPS2, the chloride thresholds are quite different. In respect of the passive film resistance, it also has the similar performance. The resistance of passive film formed in SCPS, SPS1, SPS2 are 279k $\Omega \cdot cm^2$, 286k $\Omega \cdot cm^2$, 709k $\Omega \cdot cm^2$, but the chloride threshold of carbon steel in SCPS, SPS1, SPS2 are 2.8mol/L, 2.6mol/L. It seems that the resistance has an inverse relationship with the chloride threshold.

3.3. PDM

The potentiodynamic polarization repeated 15 times in SPS1 with an addition of 0.5mol/L NaCl solution is shown in Figure 4. When the potential was swept in the positive direction, the current remained unchanged and then increase rapidly. The area where the current remained unchanged is a clear passive region, and where the current increases rapidly is the Tafel region. The increase of the

current meant that the sample began to lose depassivation and reached the critical pitting potential. The potential at this inflection point is the breakdown potential (E_b). The 15-time potentiodynamic polarization measurements display good reproducibility. In the passive region, some short-term current spikes can be observed, the current first increases and then returns to its original state very quickly. This phenomenon can be attributed to the short-term metastable pitting of carbon steel. Generally speaking, from passivation to pitting, the corrosion of metal experiences two stages. The first one is metastable pitting and the second is depassivation or development of steady-state pitting. In most cases, the steady-state pitting will develop from metastable pitting [38]. While there exists a certain possibility that the corrosion will return back to passivation from metastable pitting, which causes the current spikes as shown in Figure 4.



Figure 4. Replication (15 times) of the potentiodynamic polarization curves for carbon steel in SPS1 with 0.5 mol/L NaCl (pH=13.5)

For the polarization curve with obvious current inflection point, the potential at the inflection point is taken as the breakdown potential. For the curve with no clear inflection point, the tangent of the curve of the Tafel region and the passive region is taken as the breakdown potential. Figure 5 shows the statistical distribution of E_b for all 15 measurements. The distribution of breakdown potential is in a narrow range between 0.55V and 0.60V. It can be seen from Figure 5 that the distribution of breakdown potential apparently follows normal distribution which is consistent with the proposal given by the PDM model. This phenomenon can be attributed to the fact that the cation vacancy diffusion of carbon steel is normal [27].



Figure 5. Statistical distribution of E_b of carbon steel in SPS1(pH=13.5) with 0.5mol/L NaCl

The potentiodynamic polarization curves for carbon steel in SPS1 with different chloride concentrations are demonstrated in Figure 6. As the chloride concentration increases, the breakdown potential of carbon steel decreases. In addition, in four solutions with different chloride ions concentration, it can be observed that the potential increases smoothly when the potential is greater than the breakdown potential for addition of 0.5mol/L NaCl. While for other cases, the potential remains unchanged after depassivation. The difference may be caused by an oxygen evolution reaction during passivation breakdown.



Figure 6. Potentiodynamic polarization curves for carbon steel in SPS1 (pH=13.5) with different concentration of of NaCl (0.5mol/L, 1.0mol/L, 1.5mol/L, 2.0mol/L)

The relationship between the chloride concentration and the breakdown potential (E_b) has been studied by many scholars, and most of them think that the breakdown potential and the chloride concentration have a logarithmic relationship [28,39]. The point defect model also considers that the chloride (aggressive ions) concentration is logarithmically related with the breakdown potential in a more detailed expression as:

$$E_{\rm b} = \frac{4.606 \text{R}T}{\chi \alpha \text{F}} \log(\frac{b}{D}) - \frac{2.303 \text{R}T}{\alpha \text{F}} \log(a_{\rm cl^{-}}) \tag{4}$$

Where

$$b = \frac{\mathrm{R}TJ_{\mathrm{m}}\Omega}{F\chi\varepsilon N_{\mathrm{A}}} \exp\left(\frac{\Delta G_{s}^{0} + (\chi/2)\Delta G_{A}^{0} - (\chi/2)F\phi_{f/s}^{0} - (\chi/2)\beta\mathrm{FpH}}{\mathrm{R}T}\right)$$
(5)

$$\phi_{f/s} = \phi_{f/s}^0 + \alpha V + \beta p H \tag{6}$$

$$\omega = \Delta G_s^0 + \frac{\chi}{2} \Delta G_A^0 - \frac{\chi}{2} F \phi_{f/s}^0$$
⁽⁷⁾

Where α and β are the dependencies of the potential drop across the film/solution interface ($\phi_{f/s}$) on the applied potential V and pH; F (96485.3C/mol) is Faraday constant; χ is oxide stoichiometry (MO_{$\chi/2$}, assuming that the barrier layer is composed of FeO by Section 3.1); ε is the electric field strength within the barrier layer; Ω is the volume per mole of cation in the film; a_{cl} is the chloride ions activity [40]; *D* is the diffusivity of the cation vacancy in the barrier layer; ΔG_s^0 and ΔG_A^0 are the change in standard Gibbs energy for the Schottky-pair reaction and for the absorption of chloride anions into oxygen vacancies at the film/solution interface, respectively [41,42].

Figure 7 shows the relationship between chloride ions activity and breakdown potential in SPS1. It can be found that as the chloride ions activity increases, the breakdown potential decreases. The relationship is consistent with Eq.(4), in which the molar activity coefficient (γ_{\pm}) for different NaCl concentrations is taken from the Ref. [40]. Therefore, the polarizability α (barrier layer and solution interface) can be calculated as 0.147 from Eq.(4). This value agrees well with the research of Sharifi et al. [26] (α =0.15, pH=12.45, t=25°C) and Tan et al. [43] (α =0.16, pH=12.5, t=23°C). In fact, the polarizability α in this paper is obtained at pH of 13.5. Tan et al. furtherly propose that with the increase of pH value, the polarizability α usually decreases [43]. But α is also related to NaHCO₃ in solution. There is a positive correlation between polarizability α and HCO₃⁻⁷/CO₃²⁻ [43]. The pH of the solution in this study is 13.5, but it contained a small amount of HCO₃⁻. Therefore, the polarizability is smaller than the proposed given by Tan et al. [43]. On one hand, it is because the pH is greater. On the other hand, the amount of HCO₃⁻ is small, which is not enough to offset the change caused by pH. The effects of pH and HCO₃⁻ on polarizability need a further investigation.



Figure 7. Relationship between mean breakdown potential and chloride ion activity in SPS1 (pH=13.5)



Figure 8. Breakdown potential of carbon steel in SPS1 (pH=13.5) measured under different scanning rates (0.1667 mV/s, 1.667 mV/s, 6.667 mV/s and 10 mV/s)

The measuring result of the pitting potential is not only related to the ions in the solution, but also to the scan rate during the measurement. Figure 8 shows the relationship between the breakdown potential and scan rate. It can be seen from Figure 8 that the square root of the scan rate ($v^{1/2}$) is proportional to the pitting potential. The point defect model also proposes the relationship between breakdown potential and scan rate as follows [26,27,42,44]:

$$E_{\rm b}(v) = \left(\frac{2\xi RT}{J_{\rm m}\chi\alpha F}\right)^{1/2} v^{1/2} + E_c(v=0)$$
(8)

Where ξ is the critical cation vacancy areal concentration to evaluate whether the passive film

(barrier layer) and the metal base are separated, which mainly depends on the crystal structure of the metal and the passive film; J_m represents the annihilation rate of cation vacancies between the metal base and the barrier layer. In Figure 10, the fitted slope of the straight line is 1.66 (Vs)^{1/2}. Yield the parameter into Eq.(8), ξ/J_m can be calculated as 15.77s.



(a) Dynamic forming process of passive film on surface of Fe described by point defect model



(b) Breakdown process of passive film on surface of Fe described by point defect model.

Figure 9. Forming and breakdown process described by point defect model

The PDM has a good quantitative and qualitative explanation for the formation and annihilation of metal passive films, as shown in

Figure 9.

Figure 9(a) shows the forming process of the passive film. The PDM assumes that there are three types of point defects moving in the passive film: cation vacancies $(V_{Fe}^{2^+})$, cation interstitial $(Fe_i^{2^+})$, and oxygen vacancies (V_o^{**}) . These three types of point defects generate and annihilate at the metal/barrier layer (m/bl) interface and barrier layer/solution (bl/s) interface. As shown in Figure 11, reaction (1), (2), (4), (5) and (6) are lattice conservation reactions. The growth of the barrier layer is mainly controlled by generation reaction (3) and annihilation reaction (7).

Figure 9(b) shows the damage of the passive film when there are aggressive ions such as chloride ions. Reaction (4) occurs at the bl/s interface, and the generated cation vacancies (V_{Fe}^2) move to the m/bl interface due to the action of the electric field. Then the cation vacancies are consumed by combination with metal following reaction (1). Similarly, oxygen vacancies (V_0^{**}) generate at the m/bl interface following reaction (3), and move to the bl/s interface to be consumed according to reaction (6). When

aggressive ions such as chloride ions are introduced into the solution, the chloride ions will bind to the oxygen vacancies (V_0^{**} + Cl^{*} © Cl^{*}₀). Because of the presence of the Schottky-Pair Reaction (Null « $V_{Fe}^{2}+V_0^{**}$), the generation of cation vacancies is promoted, which causes a large number of cation vacancies to move from the bl/s interface to the m/bl interface. As a result, the flux J_{ca} is enhanced. Based on reaction (1), the annihilation rate of cation vacancies is expressed by J_m . So, the cation vacancies will accumulate at the m/bl interface when $J_{ca}>J_m$. But once the concentration of aggressive ions reaches the critical concentration ξ , the passive film will rupture [25,41,44].

According to the M-S analysis, the semiconductor structure of the passive film on the surface of carbon steel is n-type. The main point defect in the passive film is cation interstitial or oxygen vacancies. Therefore, the current density generated by the cation vacancies will be less than the measured passive current density. The J_{ca} at a certain critical time will be equal to J_m , then the relationship between them and the passive current density is as follow:

$$J_{\rm m} = J_{\rm ca} < \frac{I_{\rm ss}^{\rm bd} N_{\rm v}}{\chi \rm F}$$
⁽⁹⁾

Where I_{ss}^{bd} is passive current density (v=0.1667mV/s, 2.546µA/cm²); N_v (6.023×10²³) is Avogadro's number.

However, the actual breakdown current density will be greater than the current density measured by the external circuit. In addition, the rupture of the passive film may also be caused by metal vacancies generated by reaction (2) instead of cation vacancies. This can be explained by the catalytic reaction of chloride ions at the bl/s interface and metal interstitials. The reaction formula is $Cl_0^*Fe_i^{2+} \otimes Fe_i^{2+} + V_0^{*+} + Cl^*$. Therefore Eq.(9) can also be written as [28,42]:

$$J_{\rm m} = J_{\rm ca} \pounds \frac{I_{\rm ss}^{\rm bd} N_{\rm v}}{\chi \rm F}$$
(10)

Based on Eq.(10), it can be calculated that $J_m \leq 7.95 \times 10^{12}$ No./cm², the critical cation vacancy areal concentration $\zeta \leq 1.25 \times 10^{14}$ No. The unit cell for the barrier layer (FeO) is a cube with the lattice parameter of 4.33Å whereas Fe is body centered cubic (BCC) with a = 2.86Å or face centered cubic (FCC) with a = 3.59Å [45–47]. The density of Fe atoms per unit area in a monolayer of the unit cell on the barrier layer and the base metal can be calculated as ~10¹⁴ and ~10¹⁵. This value is like that calculated from the relationship between the breakdown potential and the scan rate. Comparing the results obtained by the two methods, it can be concluded that the point defect model is effective for characterizing the cracking of the carbon steel passive film. However, due to the limitations of the material itself and the external environment, it cannot be accurately determined whether the vacancies are on the crystal lattice of the barrier layer or the base metal.

As mentioned earlier, PDM supposes that the barrier layer contains point defects and the transmission of these defects in the barrier layer has a certain distribution law. Therefore, PDM assumes that the diffusion coefficient of metal cation vacancies has a normal distribution. At this time, the breakdown potential is also normally distributed accordingly, which can be seen in Figure 5. The point defect model also gives the expression of the specific distribution law of the breakdown potential as:

$$\frac{\mathrm{d}N}{\mathrm{d}E_{\mathrm{b}}} = \frac{-b\gamma'}{\sqrt{2\pi}\sigma_{D}a_{\mathrm{CT}}^{\chi/2}} \exp\left[\frac{-\left(e^{-\gamma' E_{\mathrm{b}}} - e^{-\gamma' \overline{E}_{\mathrm{b}}}\right)^{2}b^{2}}{2\sigma_{D}^{2}a_{\mathrm{CT}}^{\chi}}\right] \exp\left(-\gamma' E_{\mathrm{b}}\right)$$
(11)

$$P(V_c) = 100 \Box \frac{\int_{E_b}^{-\infty} \left(\frac{dN}{dE_{bc}}\right) dE_b}{\int_{-\infty}^{+\infty} \left(\frac{dN}{dE_b}\right) dE_b}$$
(12)

Where $\gamma' = \frac{\chi \alpha F}{2RT}$ and $\overline{E}_{b} = \frac{1}{\gamma'} \ln\left(\frac{b}{\overline{D}} \Box a_{CT}^{-\chi/2}\right)$, \overline{E}_{b} is the mean critical breakdown potential.

The calculation results are listed in Table 4 through Eqs.(4)~ (8), and the cumulative probability about the breakdown potential can be obtained according to Eqs. (12). The theoretically calculated and experimentally measured cumulative probability are shown in Figure 10. In order to obtain a better fitting effect, the standard deviation of the distribution is optimized to be 0.25 \overline{D} . From the comparison between the experimental results and the calculation results based on the point defect model, the point defect model can well describe the breakdown mechanism of the carbon steel passivation film.



Figure 10. Comparison of calculated and experimental results of cumulative distribution probability in breakdown potential for carbon steel with SPS1 (pH=13.5) containing 0.5mol/L NaCl

Table 4. Parameter	values used in	calculating	cumulative	probabilities	in the	breakdown	potential	for
carbon steel								

Parameters	Values	Units	Sources
E Faraday's constant	06487	C/mol	Fundamental
r, raiaday s constant	90407	C/III0I	constant
P the gas constant	8 3144	I/(mol K)	Fundamental
R, the gas constant	0.5144	\mathbf{J} (IIIOI K)	constant
T, absolute temperature	298.15	Κ	Defined
M. Avogadro's number	6.023×10^{23}	No /mol	Fundamental
Ny, Avogadio's humber	0.023×10	110./11101	constant
χ (FeO), the oxide stoichiometry	2	-	Assumed
Ω , molar volume of FeO per cation	12.52	cm ³ /mol	From density

ε , the electric filed strength	3×10 ⁶	V/cm	Assumed
α , the dependence of $\phi_{\rm f/s}$ on the V	0.147	-	From Figure 7
β , the dependence of $\phi_{f/s}$ on the pH	-0.01	V	Assumed
<i>J</i> _m , the annihilation rate of cation vacancies at m/bl interface	7.95×10 ¹²	No./ (cm ² s)	From Figure 8
ξ , critical cation vacancy areal concentration	1.25×10^{14}	No./cm ²	From Figure 8
\overline{D} , the mean cation vacancy diffusion coefficient	5×10 ⁻²⁰	cm ² /s	Assumed [42,48]
$\sigma_{\rm D}$, the standard deviation for D	$0.25 \ \overline{D}$	cm ² /s	From Eq. 12
$\omega = \Delta G_s^0 + \frac{\chi}{2} \Delta G_A^0 - \frac{\chi}{2} F \phi_{f/s}^0$	-14102	J/mol	From Eqs.(4)(5)(6)(7)

3.4. DISCUSSION

3.4.1. Chloride threshold

The chloride thresholds of HPB335 carbon steel in several solutions are given in this research. It can be found that the chloride ion thresholds of carbon steel in SCPS and SPS1 are close to 2.8mol/L and 2.6mol/L, respectively. In SPS2, the chloride ion threshold of carbon steel is 0.6mol/L. It is clear that the pH value of the solution has a deep impact on the chloride threshold. This research indicates that the ionic species and pH of the solution have a great influence on the characteristics of the passive film of carbon steel, including donor density $(N_{D1}+N_{D2})$, thickness, and resistance. Table 5 shows the relationship between the chloride threshold and these characteristics. It can be revealed that the donor density and resistance decrease with the increase of chloride threshold, and the passive film thickness has a positive correlation with the chloride threshold. It is well known that the larger the thickness of the passive film, the stronger the corrosion resistance of carbon steel is. At the same time, a larger the donor density means more defects in the passive film, indicating the greater the possibility of pitting corrosion [14,36]. So that the passive film thickness is positively correlated with the chloride threshold and the donor density is negatively correlated. However, as for resistance, different scholars have different views. Ghods et al. [20] find that samples with higher resistance have lower chloride thresholds. Luo et al. [31] believe that a higher pH value indicates a higher polarization resistance, thus the higher chloride threshold. The difference between these scholars' study of resistance can be attributed to the experimental method. The samples in Ghods's research were measured without adding chloride ions, while chloride ions were added Luo's study. When chloride ions are mixed into the solution, the passive film will change accordingly, as well as the resistance [14]. Therefore, it is more meaningful to study the resistance of the passive film before depassivation, because the resistance of carbon steel to corrosion usually formed after the formation of the passive film. Table 5 shows that all three types of passive film characteristics can determine the chloride threshold. However, it can be seen from the table that the resistance is linearly related to the chloride ion threshold. The largest R² for resistance among the three totally proves the phenomenon. This may be because the M-S analysis is an ideal analysis established based on assuming that the passive film is a double-layer capacitor. But the resistance here is directly measured objectively and experimentally, including all resistance between the carbon steel and the solution interface. So, the correlation between chloride threshold and resistance is better.

	SPS2	SPS1	SCPS	\mathbb{R}^2	Linear correlation
Chloride threshold (mol/L)	0.6	2.6	2.8		
Donor density (10^{21}cm^3)	8.23	6.49	2.14	0.61	Negative correlated
Thickness (nm)	0.5	0.54	1.06	0.39	Positive correlated
Resistance (100k Ω ·cm ²)	7.09	2.86	2.79	0.98	Negative correlated

Table 5. The relationship between the chloride threshold and passive film characteristic

3.4.2. Probability

For carbon steel with the same surface treatment placed in the same solution, the chloride threshold will also be different. This article did not do a lot of experiments to explore the probability of the chloride threshold, but it can be inferred from the point defect model that the chloride threshold has a certain distribution law [25,44]. As can be inferred from Figure 5 and Figure 10, the breakdown potential distribution of carbon steel is normal distribution. In addition, the point defect model assumes that the diffusion coefficient has a distribution law, so the combination of chloride ions and oxygen vacancies may also have a certain distribution law. Therefore, for certain external conditions, the chloride threshold of carbon steel also has a distribution law. As we all know, when the open circuit potential of a metal in a certain environment exceeds a critical potential, the metal will corrode [8,17,49]. In generally, we consider this critical potential as a repassivation potential. It can be concluded from the point defect model that the breakdown potential has a certain distribution law, and the breakdown potential is related to the chloride ion activity. In addition, the repassivation potential is also related to chloride ion activity [8,38]. Therefore, the relationship between the repassivation potential and the chloride ion activity can be sought, and the distribution rule of the repassivation potential can be derived. Then for carbon steel in a certain situation, as long as we know its open circuit potential, we can get the chloride ion threshold distribution law of carbon steel in this case. Of course, this is only an inspiration from the point defect model, and a lot of experimental work is needed to complete it in the future.

4. CONCLUSIONS

In this research, the passive characteristics and critical chloride threshold of carbon steel in different solutions were discussed. Then the point defect model was used to explain the breakdown mechanism of carbon steel due to chloride ions. The following conclusions can be drawn from this research:

(1). The passive film of carbon steel in highly alkaline solution is a double-layer, and pH has a great influence on the quality of the passive film. The characteristics of passive film and pH both have a relationship with chloride threshold, the correlation between pH and resistance is close to the chloride threshold.

(2). The critical cation vacancy areal concentration ξ (1.25×10¹⁴ No.) calculated from the scan rates and breakdown potentials is similar to the result (~10¹⁴ or ~10¹⁵) estimated by the barrier layer and the base metal.

(3). The statistical analysis on the experimental breakdown potential and the results calculated by PDM both follow normal distribution. This phenomenon illustrates the effectiveness of PDM. In addition, a calculation method about the threshold probability of chloride ion was proposed, which was inspired from the point defect model.

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