

A Statistical Study on Metastable Pitting of 304 Stainless Steel in Chloride Contaminated Carbonated Concrete Pore Solution

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Statistical characteristics of metastable pits on 304 stainless steel in chloride contaminated carbonated pore solution was investigated via potentiodynamic and potentiostatic polarization. The peak current, pit radius and stability product of metastable pits increased; the growth rate and repassivation rate were enhanced; and the metastable pits were easier to transform to stable pits when the concentration of chloride increased in the pore solution. Additionally, extreme value statistics and cumulative probability distribution on the parameters of metastable pits follow a semi-logarithmic linear distribution, and the former present a better fitting result.

Keywords: Statistical study; pitting corrosion; stainless steel; concrete; potentiostatic polarization.

1. INTRODUCTION

Pitting is one of the main failure types of stainless steels rebar in concrete structures in aggressive environment [1]. Many studies have investigated the environment factors, like the aggressive ions Cl^- , which would affect the pitting corrosion behavior of stainless steel [2-9]. Pardo et al. [2] studied the effect of chloride concentration on pitting corrosion of two high-alloy stainless steels in acid solutions (pH 2~6.5), and noticed that the pitting potential (E_{pit}) slightly decreased with the concentration of chloride. Similarly, Fajardo et al. [3] found that the pitting potential of a low-nickel stainless steel in carbonated alkaline solution decreased with the chloride concentration. Moreover,

Fajardo's further investigation indicated that there is an approximate linear relationship between decreasing E_{pit} and increasing chloride concentration. Pistorius and Burstein [4] investigated the metastable pitting on 304 stainless steel in acid (pH 0.7) and neutral (pH 7) solutions with different electrolyte composition. The results indicated that less metastable pitting events occurred for the samples in solution with the lower concentration of chloride. Moreover, the geometry site of the metastable pits is the determining factor to its growth. Zuo et al. [5] studied the statistical characteristics of metastable pitting on 316L stainless steel in solution with different chloride concentration. Applying Gumbel extreme value distribution to study the average growth rate, peak current and lifetime of metastable pitting, the authors noticed that the aforementioned parameters increased with chloride concentration and follow log-normal distribution. Additionally, they also proposed that the tendency of pitting corrosion can be predicted by statistical study of metastable pitting. In general, the chloride ions in solution significantly affect the metastable pitting on stainless steel. However, its effect on metastable pitting on the stainless steel samples in alkaline concrete pore solution has rarely been studied.

Statistical approaches have been widely applied to study pitting corrosion on stainless steel. Gholami et al. [6] investigated the effect of annealing temperature on pitting of 2205 duplex stainless steel via statistical approaches. The authors found that both the nucleation frequency and stability product of metastable pits increased with the annealing temperature. After comparing the trend of peak current and pit radius, the authors concluded that the higher current peak was the main cause to the high pit stability product at 1250 °C. Naghizadeh et al. [7] studied the pitting corrosion of 316 stainless steel in the presence of dichromate ion via cumulative distribution. After investigating the breakdown potential, peak current, pit radius, pit stability product and survival probability of pitting corrosion, Naghizadeh et al. suggested that the dichromate ion significantly inhibited the pits on 316 stainless steel. Abbasi Aghuy et al. [8] also used statistical approaches to study the effect of grain size on pitting corrosion of 304 stainless steel. They investigated the pitting potential, metastable pit frequency, lifetime, peak current, pit radius and stability product of metastable pitting and revealed that the transformation probability from metastable to stable pitting increased when the size of grain reduced. In another study, Nakhaie [9] studied pitting corrosion behavior on the cold-rolled 17-4 PH stainless steel via statistical approaches. Basing on the statistical results of growth time, repassivation time, as well as the growth rate of metastable pits, the authors suggested that the transformation probability from metastable to stable pitting were significantly enhanced by the cold rolling process.

Generally, extreme value statistics[5, 10-12] and cumulative probability distribution [6-9] are the main functions to investigate the statistical characteristics of pitting corrosion. However, the applications of extreme value statistics are mainly focused on the maximum depth of metastable pits [10-12]. Extreme value statistics applying on other parameters of metastable pits has rarely been reported. In the present study, a statistical study about metastable pits on 304 stainless steel in the concrete pore solution with different concentration of chloride was investigated. The parameters of metastable pitting were studied by extreme value statistics and cumulative probability distribution, respectively. The results suggest that the former can better describe the statistical characteristics of metastable pitting on the 304 stainless steel in the pore solution.

2. MATERIALS AND EXPERIMENTS

2.1. Materials

AISI 304 austenitic stainless steel, which chemical composition is: 0.075% C, 0.32% Si, 0.13% Mn, 0.02% P, 0.0068% S, 0.181% Cr, 0.082% Ni, 0.16% Mo and Fe, was used in the present study. Samples were fabricated by cutting plain ground bars (Φ 10 mm) into a length of 10 mm. Prior to the electrochemical tests, the stainless steel samples were ground to No. 1000 by using emery paper. Copper wires were welded at one end of the bars after degreasing the surface with alcohol. Thereafter, the samples were degreased with absolute ethyl alcohol. Then, the samples were coated with silica gel and an area of 0.1 cm^2 in the middle were exposed for electrochemical tests.

Cement extract solution was prepared by adding the ordinary Portland cement (P.O 42.5) into distilled water at a mass ratio of 1:5, and then stirred for 30 min. After 4 hour, the mixing liquid was filtered and the solution with a pH of 12.5 was taken as the concrete pore solution [13, 14]. Dilute nitric acid solution was used to prepared the simulated carbonated concrete pore solution, the pH of the filtered liquid was adjusted to 8. The effects of chloride ions on metastable pitting of 304 stainless steels were studied by electrochemical tests in solution with 0.05 mol/L, 0.5 mol/L and 5.0 mol/L NaCl, respectively.

2.2. Experiments

Electrochemical tests including potentiodynamic polarization and potentiostatic polarization was used in the present study. A conventional three-electrode cell was applied: an Ag/AgCl electrode, a platinum plate and the 304 stainless steel samples were used as the reference, counter and working electrodes, respectively. All electrochemical tests were performed by using a CS350 workstation (Corrtest Instrument, China) at room temperature. The stainless steel samples were potentiostatically polarized at -1.0 V (vs. Ag/AgCl) for 5 min to remove the oxide film formed in atmospheric environment, prior to the experiments [15]. The potentiodynamic polarization test was conducted at a scan rate of 0.2 mV/s in the range from -0.3 to 1.5 V [16], relative to open circuit potential. If stable pitting occurred on the surface of samples before the potential reach to the designed value, the potentiodynamic polarization test was stopped in advance. Basing on the potentiodynamic polarization results, the current transients were recorded by potentiostatic polarization. The applied potential was 200 mV (vs. Ag/AgCl), and the data was recorded at a frequency of 5 Hz. The tests were stopped if the current continuously rose and no longer decayed to background current, which implies stable pitting formed on the stainless steel. Two statistical functions (cumulative distribution and extreme value distribution) were applied to investigate the metastable pitting on the stainless steel in potentiostatically polarized testing. Each electrochemical test was performed in triplicate, and a new sample was used for each round. The middle curve was taken as the results to represent the effect of chloride ion on the electrochemical behavior of 304 stainless steels.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization curves

Figure 1 shows the typical potentiodynamic polarization curves of 304 stainless steel in the carbonated pore solution (pH 8) with different concentration of chloride. Typical passivation behavior was observed for the stainless steel in the carbonated concrete pore solution. The corrosion potential (E_{corr}) decreased from -400 to -200 mV (vs. Ag/AgCl) when the concentration of chloride increased from 0.05 to 5.0 mol/L, which agreed with the result in previous study [17]. Moreover, as can be seen, many current fluctuations exist in the anodic region. According to Tang et al. [18], the fluctuation of current higher than $0.2 \mu\text{A}/\text{cm}^2$ is a sign of single metastable pitting. It is easy to notice that there are more significant current fluctuations for the one exposed to the solution with higher concentration of chloride, which indicated that the higher concentration of chloride in pore solution may cause more obviously metastable pitting on the surface of the stainless steel. Moreover, the pitting potential (E_{pit}) sharply decreased with the increasing concentration of chloride. According to Pardo et al. [2], this situation suggested that the stable pitting is more easier to occur on the stainless steel samples when the pore solution with higher concentration of chloride. As Figure 1 shows, the lowest E_{pit} , which one in the pore solution with 5.0 mol/L Cl^- , is about 250 mV (vs. Ag/AgCl). Therefore, a potential of 200 mV (vs. Ag/AgCl) was chosen as the applied potential in potentiostatic polarization tests [19, 20].

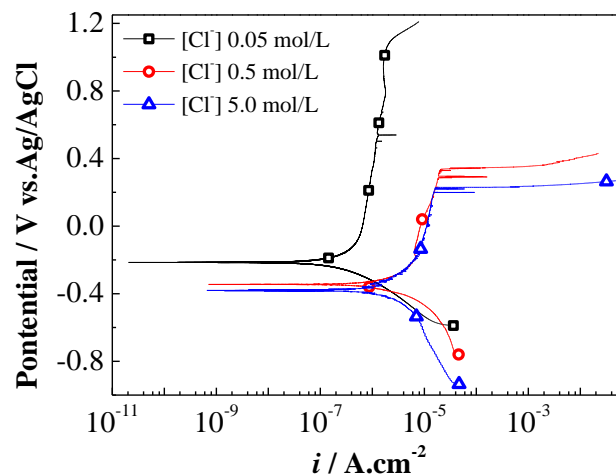


Figure 1. Potentiodynamic polarization curves of 304 stainless steel in pore solution contained various concentration of Cl^- , as measured at a scan rate of 0.2 mV/s.

3.2 Potentiostatic polarization

A typical current peak of metastable pitting on the sample in pore solution (pH 8) with 5.0 mol/L Cl^- is shown in Figure 2, and the parameters are defined as follow: i_{bg} is the background current, i_{peak} is the peak of current density, which is the gap between the maximum value of current density and i_{bg} . t_0 and t_2 are separately the time a metastable pit starts to grow and the time finishes repassivating, t_1 is the time corresponding to the peak of current density (i_{peak}). Therefore, $(t_1 - t_0)$, $(t_2 - t_1)$ and $(t_2 - t_0)$

represent the growth time (t_{grow}), repassivation time (t_{rep}) and life time of a metastable pit, respectively [21]. According to the aforementioned parameters, the growth rate (K_{grow}) and repassivation rate (K_{rep}) is given by [22-25]:

$$K_{\text{grow}} = i_{\text{peak}} / (t_1 - t_0) \quad (1)$$

$$K_{\text{rep}} = i_{\text{peak}} / (t_2 - t_1) \quad (2)$$

Figure 3 show the typical current transients of 304 stainless steel in the simulated pore solution (pH 8) with various concentration of chloride. As can be seen, for the ones in pore solution with low concentration of Cl^- , the i_{bg} obviously decreased with time, which suggested that stainless steel sample gradually passivated in solutions (Figure 3a, 3b). However, for the one immersed in high Cl^- pore solution (5 mol/L), the i_{bg} does not show significantly decreased in the experimental process (Figure 3c), which indicated that the stainless steel can't passivation in this situation. Additionally, more obvious current fluctuations can be observed in the curves of sample in high Cl^- pore solution, and the peak current of the single metastable pitting also significantly increased with the concentration of chloride, which is corresponding with the results of potentiodynamic polarization tests (Figure 1). Moreover, the incubation time, which is the time the current density sharply increased and does not turn back to i_{bg} , obviously decreased with the increasing concentration of chloride. These results directly suggested that the probability of metastable pitting transition to stable pitting increased with concentration of chloride in the carbonated pore solution [26].

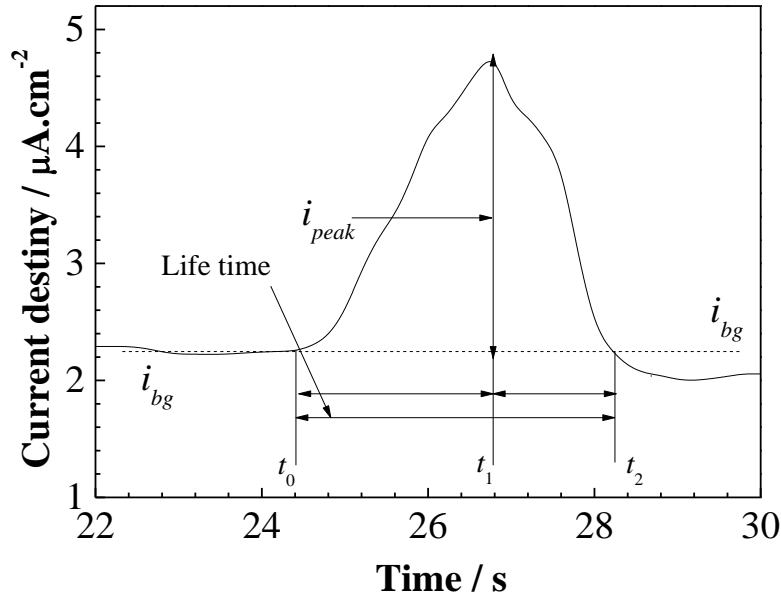


Figure 2. A typical current peak of sample in solution with 5.0 mol/L NaCl (pH 8), potentiostatic polarized at 200 mV (vs. Ag/AgCl).

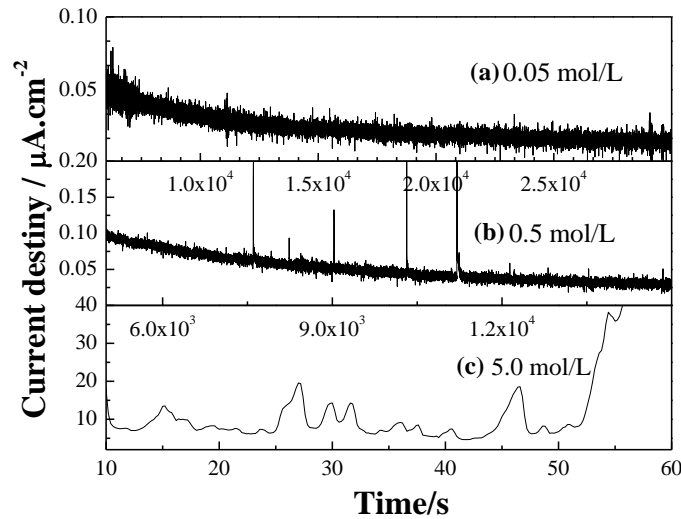


Figure 3. Typical current transient of 304 stainless steel in the carbonated concrete pore solution with different concentration of Cl^- , potentiostatic polarized at 200 mV (vs. Ag/AgCl), (a) 0.05 mol/L chloride, (b) 0.5 mol/L chloride, (c) 5.0 mol/L.

3.3 Statistical characteristics of metastable pitting

Previous studies [27-29] have reported that the probability distribution of the maximum depths of pits follows Gumbel extreme value distribution, as follow:

$$P(x \leq d_m) = \exp\{-\exp[-(d_m - x_m)/\bar{x}]\} \quad (3)$$

where x is the random variables of maximum depth of pits. x_m is the depth of pits with the highest probability density, and \bar{x} is the average depth of pits. Therefore, according to the distribution of pit depth in a small region and the analysis of Gumbel scatter diagram, the maximum pit depth of the entire material surface can be predicted.

3.3.1 Metastable pits peak current

The peak of current density is one of the most important parameters for studying the statistical characteristics of metastable pitting. In general, the higher peak of current means that the higher possibility for the metastable pits transforming to stable pits. According to Eq. (3), the extreme value distribution of the depths of pit was represented by the peak of current density (i_m), and then it is easy to conclude the equation as follow [5, 30]:

$$P(x \leq i_m) = \exp\{-\exp[-(i_m - x_m)/\alpha]\} \quad (4)$$

where x_m is the metastable peak with the highest probability current density, which indicated the value of current peak when $-\ln\ln(1/P)$ was equal to zero, α is the reciprocal slope of the probability lines and is called scale parameter. Previous study has reported that the interval of time does not show significant influence on the extreme value distribution of peak current [31]. Thus, in the present study, the current transient in the potentiostatic tests were equally divided into 9 segments. The maximum peak of current density in each segment was investigated, and then the max peaks were consecutively

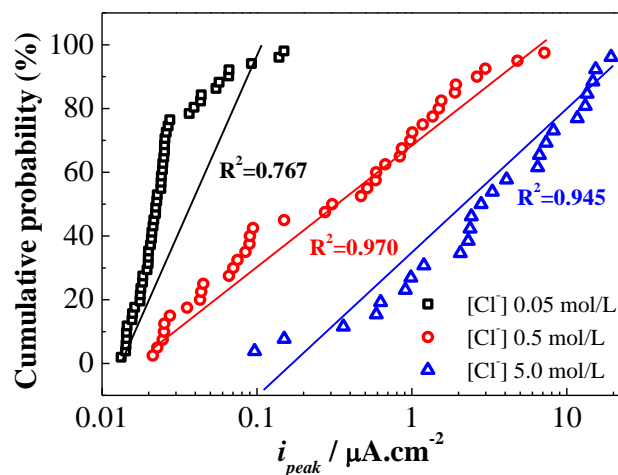
numbered from 1 to 9 according to its value. The statistical probability of maximum peak current P_j is calculated by Eq. (5):

$$P_j = \frac{j}{N+1} \quad (5)$$

where $N=9$, j is the serial number of the corresponding maximum peak of current density. The extreme value distribution diagram was plotted, and the results were presented in Figure 4b.

Figure 4a shows the cumulative distribution of peak current of metastable pits in the carbonated concrete pore solution (pH=8) with various concentration of Cl^- . For stainless steel samples in solution containing 0.05 mol/L, 0.5 mol/L and 5.0 mol/L chloride, the medium peak value of current density were $0.022 \mu\text{A}/\text{cm}^2$, $0.306 \mu\text{A}/\text{cm}^2$ and $2.80 \mu\text{A}/\text{cm}^2$, respectively. Simultaneously, the peak of current density increased with the concentration of Cl^- , indicating different growth kinetics of the metastable pits [23]. According to Heusler and Fischer [32], the adsorption of chloride would enhance the dissolution of oxide, which may thin the passive film until the film crack. Then, the chloride further accelerates the dissolution of alloy. Thus, as the results shown in Figure 4, the peak of current density for metastable pits increased with the concentration of chloride.

A semi-logarithmic linear distribution of current peak was observed for the ones immersed in the pore solution with higher concentration of Cl^- (0.5 mol/L and 5.0 mol/L). However, for the one in the solution with low concentration of Cl^- (0.05 mol/L), the goodness of linear fit (R^2) is only 0.767, which is much lower than that of the other fitting lines. In contrast, the extreme value distribution of peak of current, as shown in Figure 4b, presents a better semi-logarithmic linear distribution. The goodness of the fitting results (R^2) all exceeded 0.93 for samples in the pore solutions. The trend of the currents peak of metastable pits changed along with the concentration of Cl^- was similar to that of the cumulative distribution. Meanwhile, it is easy to observe that the value of α increase with the concentration of Cl^- , which suggests that the average peak current increased and the possibility of the peak current exceeding a certain value is larger. Consequently, as the results show, compared with the cumulative distribution, the extreme value distribution is the better function to investigate the statistical characteristics of metastable pitting.



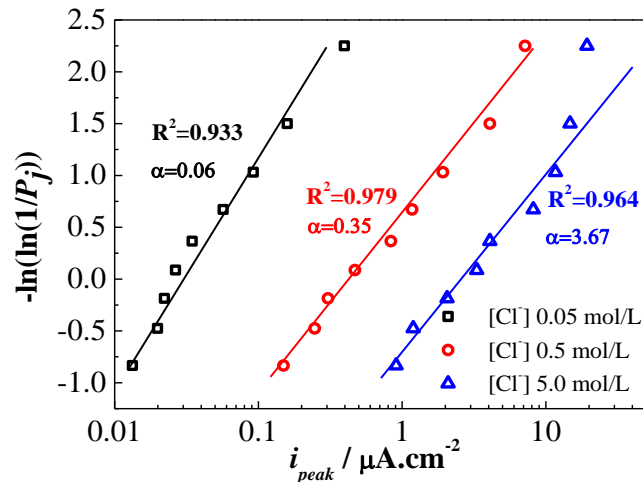


Figure 4. (a) Cumulative distribution and (b) extreme value distribution of i_{peak} for 304 stainless steel in the carbonated concrete pore solution with various concentration of Cl^- , potentiostatic polarized at 200 mV (vs. Ag/AgCl).

3.3.2 Metastable pit radius

In an earlier study [33], the metastable pits were assumed as hemispherical. Then, the radii of metastable pits can be calculated from the total electric charge according to the Faraday Equation, as follow [34]:

$$r_{pit} = \left[\left(\frac{3Z}{2\pi n F \rho} \right) \int_{t_0}^{t_1} (I_{peak} - I_{bg}) dt \right]^{\frac{1}{3}} \quad (6)$$

where Z is the molar mass of the material, n is the mean oxidation state of the cations, F is the Faraday constant and ρ (g/m^3) is the mean density of the material. t_0 and t_1 are the start time and end time of the increase in the current peak of metastable pits, respectively. The molar mass of AISI 304 stainless steel is 55.2 g/mol, the mean oxidation state of cations and mean density separately is 2.19 and 7.8 g/cm^3 [8].

The cumulative distribution and the extreme value distribution of metastable pit radius (r_{pit}) are shown in Figure 5. The medium values of r_{pit} were 0.75 μm , 1.8 μm and 3.8 μm for samples in pore solution with 0.05 mol/L, 0.5 mol/L and 5.0 mol/L Cl^- , respectively. The magnitude of r_{pit} (0.3–20 μm) is similar to the result in a previous study [7]. Clearly, comparing the r_{pit} of samples in pore solution with different concentration of Cl^- , it is easy to notice that the size of metastable pits significantly increased with the concentration of Cl^- . This situation can be explained by the enlargement of anodic charge caused by the increase of metastable pit current peak [8], as shown in Figure 3. According to Pistorius and Burstein [33], the radius of metastable pits must exceed a critical value, then the metastable pits could further growth. As figure 5 shows, the r_{pit} of metastable increased with the concentration of Cl^- , which indicates that the transformation possibility from metastable pits to stable pits also increased with the increasing chloride concentration.

On the other hand, in pore solution with 0.05 mol/L Cl^- , R^2 of the fitting line for the r_{pit} is about 0.895, which is similar to the situation of metastable peak current (figure 4). The results of extreme value distribution describing metastable pits radius are shown in figure 5b. The α in figure 5b

represents the average radius of metastable pits of samples. As can be seen, the value of α increased with the concentration of Cl^- . The values of R^2 in extreme value distribution were closer to 1, and much higher than those in the cumulative distribution. Especially, the value of R^2 in the extreme value distribution for samples in pore solution with 0.05 mol/L Cl^- improved the most significant, and this situation also corresponding to that of metastable peak current (figure 4). Consequently, the results in figure 5 further demonstrate that the Gumbel extreme value distribution better follows semi-logarithmic linear relationship than the cumulative probability function, especially for the stainless steel sample in low concentration Cl^- pore solution.

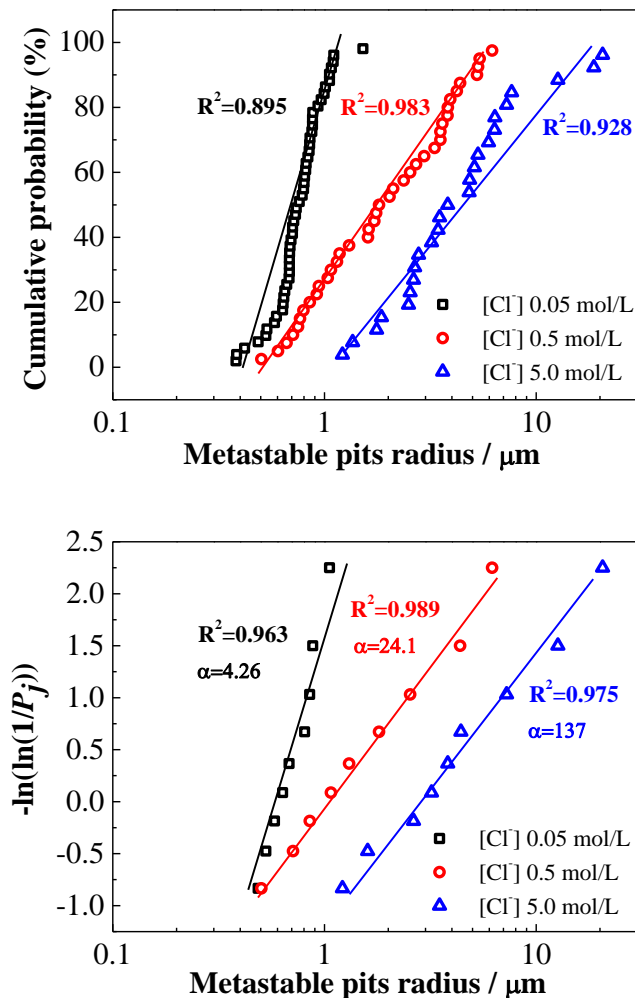


Figure 5. (a) Cumulative distribution and (b) extreme value distribution of r_{pit} for 304 stainless steel in the carbonated concrete pore solution with various concentration of Cl^- , potentiostatic polarized at 200 mV (vs. Ag/AgCl).

3.3.3 Evaluation of pit stability product

Previous studies [33, 35] have reported that the value of pit depths (a) multiply by current density (i) (stability product) can be used to estimate the probability of the transition from metastable pit to stable pit. The threshold value was suggested at a value of $3 \text{ mA}\cdot\text{cm}^{-1}$. When the multiply value

exceed the threshold values, the metastable pits could transform to stable pits. During the metastable pitting growth, the anode dissolution may be intensified when the the cover layer over the pit mouth ruptured, and the multiply value of pit depths (a) and current density (i) could exceed the threshold value ($3 \text{ mA}\cdot\text{cm}^{-1}$), then the metastable pits transform to stable pits on the stainless steel surface. Otherwise, the metastable pits would repassive and the growth of pits would stop. As the pits were assumed hemispherical, the values of pit depth equal to that of pit radius. Therefore, the stability product of each individual pits was calculated by metastable pit radius and peak current density, which were expressed as $i_{\text{peak}}\cdot r_{\text{pit}}$.

Figure 6 represents the cumulative distribution and extreme value distribution of stability product ($i_{\text{peak}}\cdot r_{\text{pit}}$) of metastable pits on the stainless samples in pore solution. As can be seen, the values of $i_{\text{peak}}\cdot r_{\text{pit}}$ are far below the critical value ($3 \text{ mA}\cdot\text{cm}^{-1}$), which indicated that the metastable pits could be repassivated in the present study. On the other hand, as the content of Cl^- in pore solution increased, the median value of pit stability product increased from $0.015\times 10^{-2} \mu\text{A}/\text{m}$ to $8.3\times 10^{-2} \mu\text{A}/\text{m}$. In the high Cl^- content (5.0 mol/L) pore solution, the pit stability product is closely to the critical value which proposed by Pistorius and Burstein [33]. The situation further confirmed that in solution with high concentration of Cl^- , the metastable pits are easier to transform to stable pits.

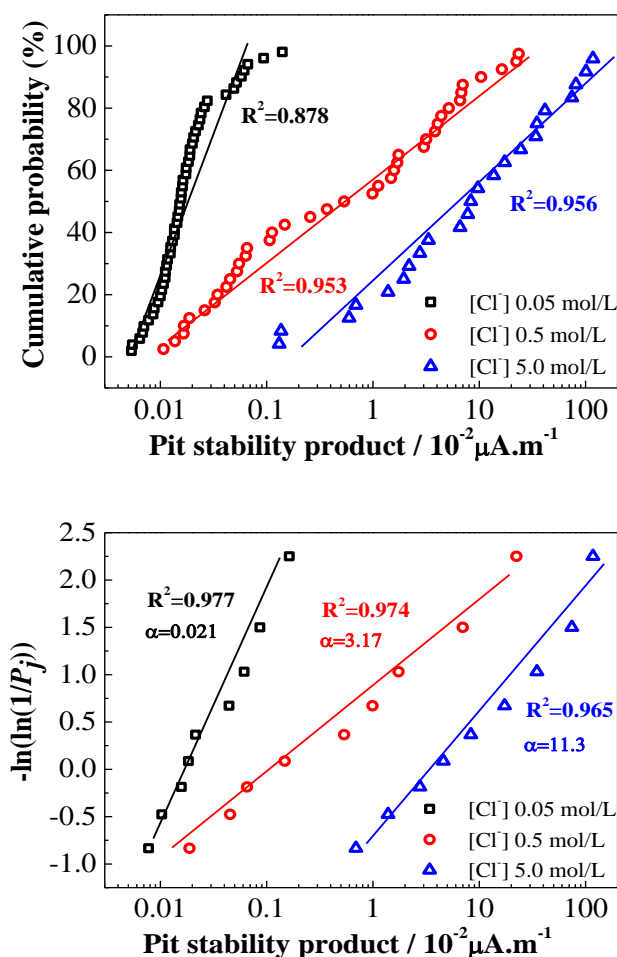


Figure 6. (a) Cumulative distribution and (b) extreme value distribution of stability product of metastable pits on 304 stainless steel in the carbonated concrete pore solution, potentiostatic polarized at 200 mV (vs. Ag/AgCl).

On the other hand, compared with the R^2 of Gumbel extreme value distribution, that value in the cumulative distribution is much lower. Especially for the one in pore solution with low content of Cl^- (0.05 mol/L), the goodness of the linear fitting of cumulative contribution is 10.1% lower than that of extreme value distribution. The value of α calculated from the slopes of fitting lines directly show the enhancement of the average pit stability (from $0.021 \times 10^{-2} \mu\text{A/m}$ to $11.3 \times 10^{-2} \mu\text{A/m}$) product with the increasing chloride concentration. The stability product ($i_{\text{peak}} \cdot r_{\text{pit}}$) results (figure 6), together with the current peak (figure 4) and pit depths (figure 5) results, confirmed that the extreme value distribution can better describe the distribution of metastable pitting than the cumulative distribution.

3.3.4 Metastable pits growth and repassivation

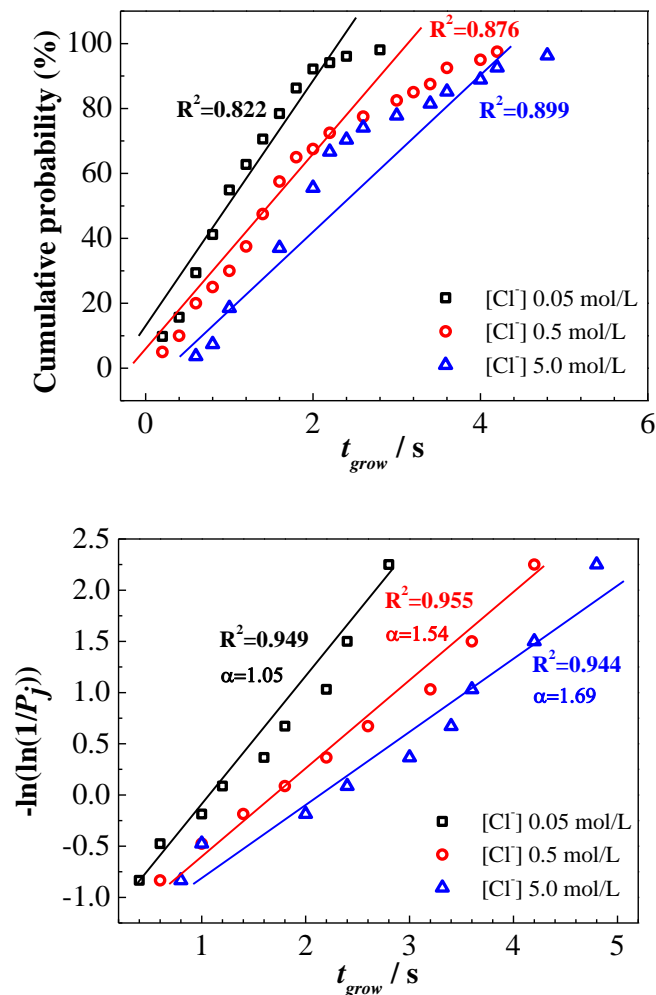


Figure 7. (a) Cumulative distribution and (b) extreme value distribution of metastable growth time (t_{grow}) for 304 stainless steel in the carbonated concrete pore solution, potentiostatic polarized at 200 mV (vs. Ag/AgCl).

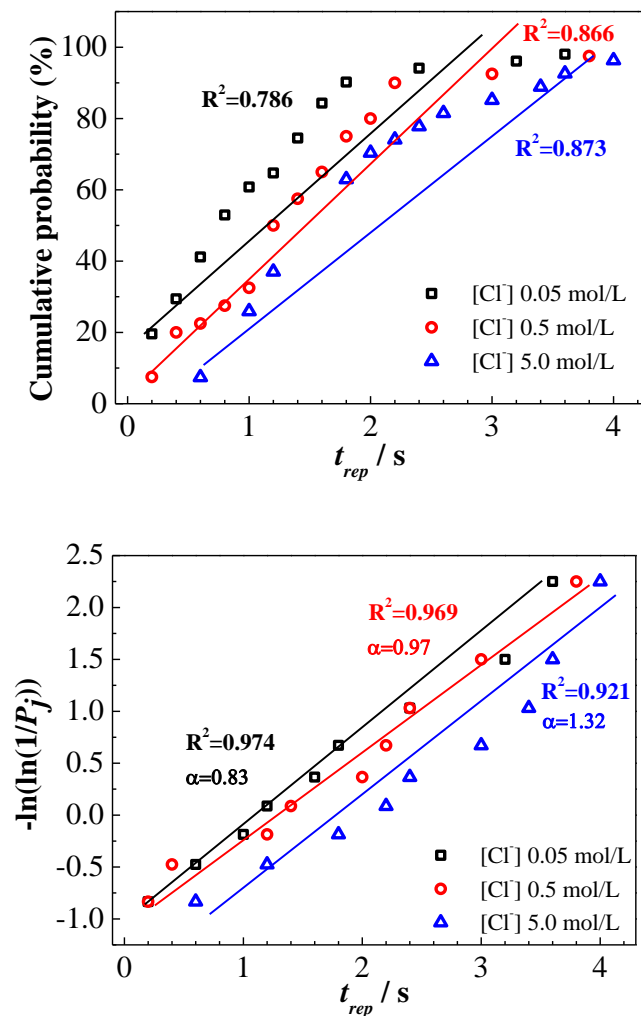


Figure 8. (a) Cumulative distribution and (b) extreme value distribution of metastable repassivation time (t_{rep}) for 304 stainless steel in the carbonated concrete pore solution, potentiostatic polarized at 200 mV (vs. Ag/AgCl).

The cumulative distribution and extreme value distribution in growth and repassivation time (t_{grow} and t_{rep}) of metastable pitting are shown in figures 7 and figure 8, respectively. As the results in figure 7 and figure 8 show, the median values of t_{grow} and t_{rep} increased with the concentration of chloride. For the stainless steel samples in the pore solution with 0.05 mol/L, 0.5 mol/L and 5.0 mol/L Cl^- , the median values of t_{grow} are separately 0.93 s, 1.45 s and 1.88 s, while the median values of t_{rep} are 0.75 s, 1.2 s, and 1.5 s, respectively. Clearly, the growth time t_{grow} of metastable pitting on 304 stainless steel in the pore solution is longer than its repassivation time t_{rep} . High concentration of chloride would promote the dissolution of inclusions and passive film, prolong the growth time, and degraded the repassivation ability, then the t_{grow} and t_{rep} significantly increased with the concentration of chloride [36]. As a result, the prolonged lifetime of metastable pitting indicated more substrate were reacted, which is conducive to the metastable pits transformation to stable pits [37].

The semi-logarithmic linear fitting in cumulative distribution and extreme value distribution of t_{grow} and t_{rep} are presented in figure 7 and figure 8, respectively. It is easy to notice that the goodness of

linear fit (R^2) of the former is much lower than that of the latter. The goodness of linear fit (R^2) of the former is lower than 0.9, while that of the latter is higher than 0.92. In particular, compared with the value of R^2 in cumulative distribution, the R^2 in the extreme value distribution were improved by 15.5% and 24.0% for t_{grow} and t_{rep} in pore solution with 0.05 mol/L Cl^- . Consequently, the extreme value distribution can better describe the statistical characteristics of growth time and repassivation time of metastable pitting on stainless steel in the concrete pore solution, and this situation is consistent with the aforementioned current peak (i_{peak}), pit radius (r_{pit}) and pit stability product ($i_{\text{peak}} \cdot r_{\text{pit}}$) results.

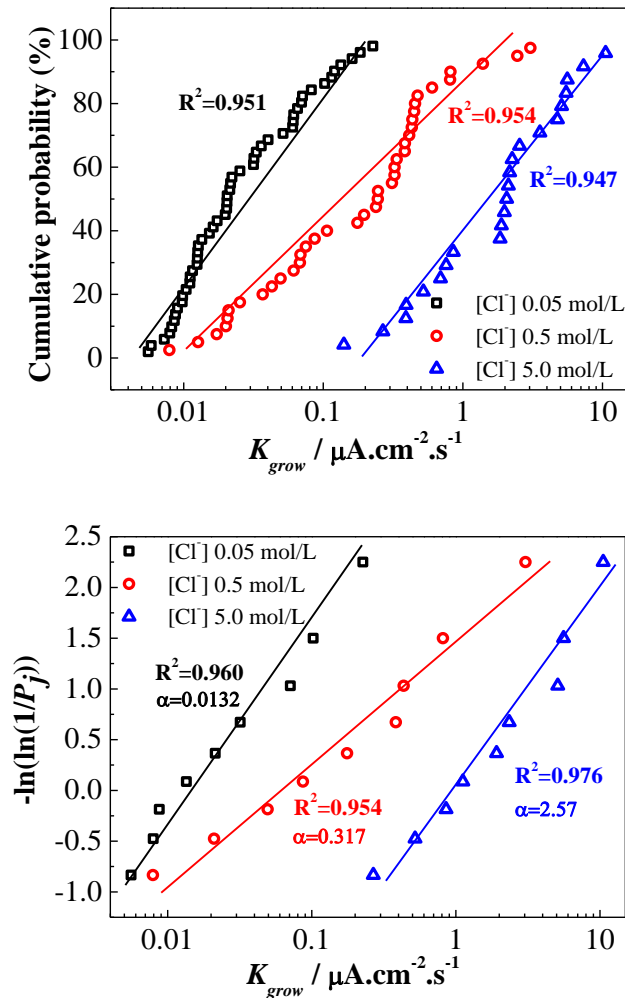


Figure 9. (a) Cumulative distribution and (b) extreme value distribution of growth rate for 304 stainless steel in carbonated concrete pore solution, potentiostatic polarized at 200 mV (vs. Ag/AgCl).

. The cumulative distribution and extreme value distribution in growth rate (K_{grow}) and repassivation rate (K_{rep}) of metastable pits on 304 stainless steel in concrete pore solution with different concentration of chloride are shown in Figure 9 and 10. The results show that the median values of K_{grow} and K_{rep} obviously increased with the concentration of chloride. Similarly, Zuo et al. [5] and Blanc et al. [38] have reported that the growth rate of metastable pitting on 316L stainless steel and aluminium alloy also increased with the content of chloride in solution. Anions and metal cations in

the pits always keep dynamic balance, and the diffusion of iron ions would be accelerated by the high concentration of Cl^- . As widely accepted that the diffusion of metal cations is the main controlling factor of the growth of metastable pitting [21, 33].

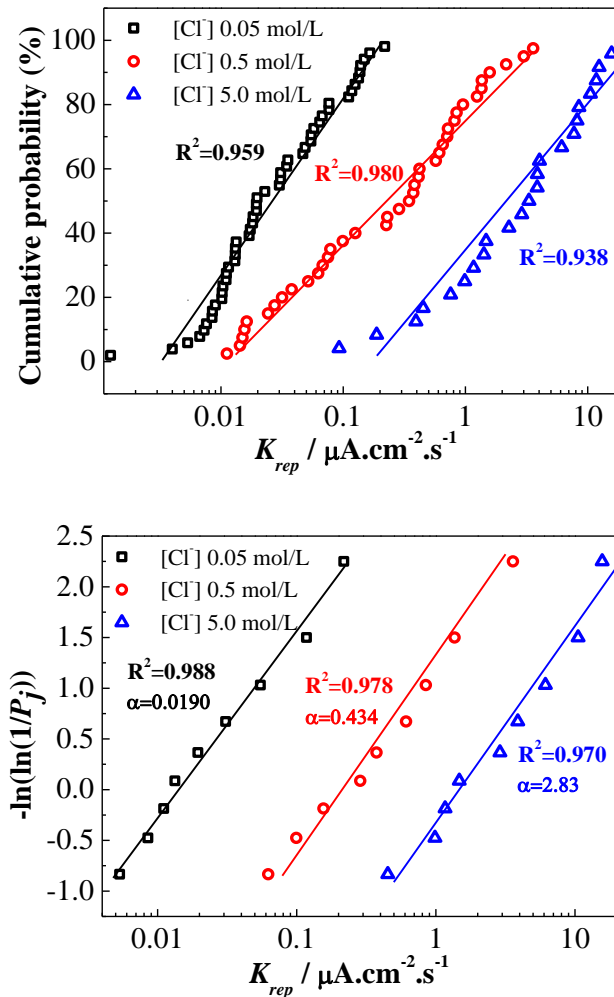


Figure 10. (a) Cumulative distribution and (b) extreme value distribution of repassivation rate for 304 stainless steel in carbonated concrete pore solution, potentiostatic polarized at 200 mV (vs. Ag/AgCl).

Thus, the growth rates of metastable pitting increased with the concentration of chloride in the pore solution. Simultaneously, the rupture of the flawed cover layer over the pit mouth [39, 40], which is suggested as the essential condition for the repassivation of metastable pitting, would be accelerated by the high concentration of chloride in the pits. Moreover, according to the PDM (point defect model) [41, 42], the oxygen vacancy in passive film usually increased with the concentration of Cl^- in solution, and the high concentration of oxygen vacancy could enhance the passivation rate of steel in the subsequent. Therefore, the repassivation rates of metastable pitting also increased with the content of chloride in pore solution.

In the pore solution with 0.05 mol/L, 0.5 mol/L and 5.0 mol/L Cl^- , the R^2 of liner fit for K_{grow} and K_{rep} of metastable pitting in cumulative distribution and extreme value distribution do not show significant difference. As shown in figure 9 and figure 10, the mean values of K_{grow} and K_{rep} increased with the concentration of chloride in pore solution. Although the extreme value distribution does not show obvious advantage in the semi-logarithmic linear fitting on the K_{grow} and K_{rep} , it still presents a slightly higher R^2 value during describe the statistical characteristics of metastable pitting.

4. CONCLUSION

Statistical characteristics of metastable pitting on AISI 304 stainless steel in a simulated carbonated concrete pore solution (pH 8) were investigated. The following conclusions can be drawn from the present study:

(1) The corrosion potential (E_{corr}) and pitting potential (E_{pit}) of the stainless steel decreased when the concentration of chloride increased. The peak of current density (i_{peak}), pit radius (r_{pit}), pit stability product ($i_{\text{peak}} \cdot r_{\text{pit}}$), and lifetime of metastable pitting also increased with the content of chloride concentration in pore solution, which suggested that the transformation probability from metastable pitting to stable pitting would increase with increasing concentration of chloride.

(2) The growth rate (K_{grow}) and repassivation rate (K_{rep}) of individual metastable pits increased with the chloride concentration in pore solution, and this situation indicated that growth and repassivation of metastable pitting would be accelerated by the concentration of chloride in the bulk solution.

(3) After comparing the semi-logarithmic linear fitting results of current peak, pit radius, pit stability product, and lifetime of metastable pitting in cumulative distribution and extreme value distribution, it is easy to found that the goodness of linear fit (R^2) of the extreme value distribution is much higher than the former, which suggested that the extreme value distribution function is more suitable for describing the statistical characteristics of metastable pitting.

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