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Numerical Simulation of Crevice Corrosion of Stainless Steel–Titanium in NaCl Solution

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Abstract: A multiphysics model based on the finite element method was adopted, emphasizing a deeper insight into the rarely studied crevice corrosion behavior of stainless steel and titanium overlapping. The model takes into account damage due to corrosion inside the crevice, different species transportation, local electrochemical reactions, homogeneous reactions in the electrolyte, and formation of a corrosion product and its influence on electrochemical reaction. The simulation results show that the location of the greatest attack for stainless steel is at the crevice opening; this finding is consistent with the IR drop theory. The potential increases gradually from the tip to the opening of the crevice, and the current changes smoothly following a sharp rise at the opening. The minimum and maximum values of pH and Cl⁻ concentration are both in the middle and opening of the crevice. The influence of the crevice size on corrosion is also discussed in detail.

Keywords: stainless steel; titanium; crevice corrosion; numerical simulation; multiphysics

1. Introduction

With the rapid development of the social economy, the requirements of industrial production on material performance are getting higher and higher, and the types of applied materials are becoming more and more extensive, especially under the condition of meeting performance, trying to reduce costs; thus, the joint use of various materials has become a new trend. For components used in combinations of multiple metals, crevices are easily formed between the metals. When the electrolyte solution enters the crevice, crevice corrosion will occur. For example, thermal spraying prepares a layer of titanium metal coating on the stainless-steel surface to improve the stainless-steel corrosion resistance in the marine environment, but the oxides in the coating will increase the brittleness of the coating. Therefore, once the titanium coating breaks, the coating forms a crevice with the stainless-steel substrate, and the stainless steel will be subjected to severe crevice corrosion, thus causing severe damage.

1.1. Crevice Corrosion Mechanism

Crevice corrosion can be regarded as a combination result of change in crevice solution composition and IR drop [1]. In the initial stage, the metal in contact with the electrolyte dissolves uniformly at the same rate both inside and outside the crevice, but as time goes on (also related to the size of the crevice itself), the oxygen inside the crevice will be gradually consumed, and the amount of dissolved metal ions gradually increases; thus, the pH inside



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the crevice gradually decreases, and the stability of the passivation film is destroyed. When the oxygen consumption rate is greater than the diffusion replenishment rate, the oxygen within the crevice will be exhausted, and the cathode reaction will be suppressed, but the cathode reaction on the external surface will maintain the anode dissolution reaction in the crevice to continue. At this time, the current flowing through the solution with a resistance value of *R* is *I*, and the resulting voltage drop is called the *IR* drop. A potential value, *E*(*y*), inside the crevice wall was produced at position *y*, and due to this, the *IR* drop is lower than the potential *E*(*s*), which is situated at the crevice opening (y = 0). The equation of IR drop can be written as follows [2]:

$$IR_l = E(s) - E(y)$$
$$\nabla \Phi^* = E(s) - E_{pass}$$

where $R_l = \sigma y / A$, σ is the conductivity in the solution, $\nabla \Phi^*$ is critical potential for crevice corrosion, E_{pass} is the transition electrode potential of the active/passive on the crevice wall, and Y_{pass} is the length from the outer surface to E_{pass} . For systems containing metal and electrolyte, when $IR > \nabla \Phi^*$, crevice corrosion occurs.

1.2. Research Progress of Crevice Corrosion Simulation

The detailed information on the reaction kinetics and water chemistry during the crevice corrosion process is extremely important for understanding mechanism and predicting occurrence of crevice corrosion. In this regard, in recent decades, researchers in many fields, including academia and industry, have conducted a large number of scientific experiments by different methods, such as in situ measurement of electrochemical and water chemistry parameters [3], frozen micro-zone solution [4], and acoustic emission technology [5]. However, due to the particularity of the geometry of the crevice, when studying the crevice corrosion through experimental methods, the external small interference signals may have a great influence on the measurement results of the precision test instruments used during the operation process. Therefore, characterizing the crevice corrosion process by experimental means alone cannot obtain very satisfactory information. The computational simulation method can simulate complex physical–chemical processes, visually analyze the results of specific physical or engineering problems, provide us with extremely rich information, and make up for the shortcomings of experiments, so it has attracted more and more attention from researchers [6,7].

For crevice corrosion simulation of stainless steel, Sharland [8] established a model of local corrosion of stainless steel, taking into account the mass transport and homogeneous reaction of ions in solution. The simulation found that the pH value in the crevice decreased as the anode dissolution current increased, and the pH value in the crevice declined as the Cr content rose in the metal. White et al. [9] established a model to study the chemical and electrochemical changes of the solution in the crevice during stainless-steel crevice corrosion. The model assumed that the stainless-steel crevice was in a passivated and activated state, respectively, and compared the simulation results with the experiment. It was found that, when the crevice was in the activated state, the results were consistent with the experimental results. This indicated that, in solutions that are nearly neutral, the typical passivation current density of stainless steel was too low to induce local chemical or potential changes in the crevice. Stroe et al. [10] established a crevice corrosion model of stainless steel in chloride media to investigate the effects of parameters such as pH, Clconcentration in bulk solutions, and crevice size on crevice corrosion. The results showed that the pH and crevice size would have a great impact on stainless-steel crevice corrosion, but the Cl^- concentration in the bulk solution had little effect on corrosion. Sun et al. [11] simulated the crevice corrosion of 304 stainless steel. The model assumed that the crevice of 304 stainless steel was activated and considered the effect of precipitation on the corrosion. The simulation results obtained the distribution of the pH value inside the crevice and the

effect of the diverse reaction constant of the corrosion product deposition and different current density on the crevice corrosion.

For a crevice corrosion simulation of titanium, Heppner et al. studied the crevice corrosion behavior of titanium immersed in NaCl solution. The model assumed that the crevice was in a passive state, and the fraction of the cathode current provided by the hydrogen ion reduction reaction changed from 0 to 0.8 in increments of 0.2. The pH distribution, conductivity, and IR drop distribution curve in the crevice were obtained [12]. Subsequently, Heppner et al. predicted the effect of the crevice opening size on the IR drop and solution in the titanium crevice. The results showed that reducing the size of the crevice opening would increase the potential inside the crevice, increase the conductivity of the solution, and increase the concentration of the solution metal composite [13].

The crevice corrosion simulations of single stainless steel and single titanium have been performed by many researchers; however, to the best of our knowledge, there has not yet been any report on the crevice corrosion simulation between the dissimilar metals of stainless steel and titanium. The main aim of this research was to study the crevice corrosion growth kinetics and solution water chemistry of 304 stainless steel and titanium overlapping based on a multiphysics model, thereby providing a lot of useful information that is difficult to obtain experimentally, then further supplementing the study of crevice corrosion mechanism, and making corresponding preventive and control measures to reduce crevice corrosion.

2. Crevice Model

2.1. Description of the Problem and Assumption

Assuming that the longitudinal section of the crevice formed by stainless steel and titanium is rectangular, whose opening size (w) is 90 μ m, and the height (r) is 8 cm. The schematic diagram of the crevice geometry can be found in Reference [14]. The metal in left side is 304 stainless steel, the right is Ti, and the solution is 0.6 mol/L NaCl with pH = 7.

The present model has the following main assumptions:

- (1) For 304 stainless steel, the simulation proceeds directly from the activated state because of the low pH value inside the crevice [15].
- (2) For titanium, the model assumes that Ti is always in the passivated state during the simulation. It is reported that, even under acidic conditions, when the potential value is above -0.4 V, titanium can be in the passivated state [16].
- (3) It is supposed that no oxygen reduction reaction occurs inside the crevice, and it only takes place on the external surface of crevice because the stainless steel is in an activated state, which can quickly deplete the oxygen within the crevice [17].
- (4) Because of the large aspect ratio of the crevice, convection is neglected in this model.

In the model, we considered electrochemical reactions, the chemical species transmission, the deformation of metal corrosion, and the precipitation that occurs during the corrosion process. All the equations needed were solved numerically by COMSOL software.

2.2. Transport Equations

Nernst–Planck equations, which include diffusion and electromigration, are the governing equations for different species in the solution [18]. The mass conservation and the concentration change formula containing Nernst–Planck equations for each species, *i*, in the solution can be depicted as follows:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i - \frac{z_i D_i F c_i \nabla \varphi_l}{RT} \right) = R_{i,tot}$$
(1)

where c_i is the concentration of species $i \pmod{m^3}$, t is time (s), D_i is the diffusion coefficient (m²/s), z is the number of charges, F is the Faraday constant (C/mol), φ_l is the electrolyte potential (V), R is the gas constant (J/(mol·K)), T is the temperature (K), and $R_{i,tot}$ is the source (mol/(m³·s)). The conservation equation of mass gives the expression of the

concentration of each substance, but there is another unknown quantity, the electrolyte potential, φ_l ; thus, it is necessary to solve the unknown quantity in conjunction with the electrical neutral equation:

$$\sum z_i c_i = 0 \tag{2}$$

The electronic conduction in the metal and the directional migration of ions in the solution form a complete current circuit, where electrolyte current density in the solution involved the Faraday constant, and the charge number can be described as follows:

$$i_l = -F \sum D_i z_i \nabla c_i - \frac{F^2}{RT} \nabla \varphi_l \sum z_i^2 D_i c_i$$
(3)

2.3. Electrical and Chemical Reactions

The electrochemical reactions contained in the model include the following:

$$Fe \rightleftharpoons Fe^{2+} + 2e \tag{4}$$

$$Cr \rightleftharpoons Cr^{3+} + 3e$$
 (5)

$$\mathrm{Ni} \rightleftharpoons \mathrm{Ni}^{2+} + 2\mathrm{e} \tag{6}$$

$$\Gamma i \rightleftharpoons T i^{4+} + 4e \tag{7}$$

Because stainless steel is composed of three different metal elements, the molar mass M_j (kg/mol) and number of charges transferred, z_j , of different metals are diverse; thus, when electrochemical reactions occur, it is necessary to normalize the metal composition, and determine the contribution of the composition coefficient to anodic current. Therefore, f_i is introduced [19]:

$$f_i = \frac{z_i M_i}{\sum_j z_j M_j} \tag{8}$$

Thus, the total flux of metal anodic dissolution can be expressed by following equation:

$$N_i = \sum_m f_i \cdot \frac{v_{i,\ m} i_m}{n_m F} \tag{9}$$

where *m* is the electrode reactions, n_m represents the electrons transferred number, $v_{i,m}$ is reaction coefficient, and i_m represents the localized current density of the electrochemical reaction.

The electrochemical parameters, including the equilibrium potential; exchange current density; and Tafel slope of Fe, Cr, Ni, and O₂ redox reactions used in the simulation can be found in Reference [20]. The homogeneous reactions with equilibrium constants, including Fe ion and Fe oxide, Cr ion and Cr oxide, Ni ion and Ni oxide, and Ti ion and Ti oxide, can be obtained in References [18,21].

2.4. Moving Mesh Method

The moving mesh technology refers to the finite element method in which the divided mesh moves according to the result of the previous calculation or an artificially specified speed during the calculation. The moving mesh method can adjust the density and shape of the mesh according to the change of the solution of the physical field. This method can not only accurately distinguish the material interface but also maintain the geometric characteristics of the mesh, so it has significant advantages in solving the deformation problem of the mesh [22]. The stainless-steel geometry changes when it is actively dissolved, and this change is simulated and solved by the moving mesh technology. The mesh displacement is described by the formula below:

$$\frac{\partial^2}{\partial X^2}\frac{\partial x}{\partial t} + \frac{\partial^2}{\partial Y^2}\frac{\partial y}{\partial t} = 0$$
(10)

$$\frac{\partial^2}{\partial X^2}\frac{\partial y}{\partial t} + \frac{\partial^2}{\partial Y^2}\frac{\partial x}{\partial t} = 0$$
(11)

where *X*, *Y*, *x*, and *y* are the coordinates in material framework and space framework, respectively. Assuming that the metal is dissolved in the normal direction of the metal crevice wall, the normal movement speed of the crevice wall can be expressed as follows:

$$\frac{\partial x}{\partial t} \cdot n = v_{tot}$$
 (12)

where v_{tot} represents the total movement rate, and it can be written as the sum of the anodic reactions rates of all metals according to Equation (12):

$$\nu_{tot} = \sum_{i} \frac{M_i}{\rho_i} \sum_{m} f_i \cdot \frac{\nu_{i,m} i_{loc,m}}{n_m F}$$
(13)

where ρ represents the metals' density (kg/m³).

2.5. Level Set Method

The level set method is a method that is suitable for dealing with the discontinuous changes in the physical and chemical properties between the new and original phases when new phases are generated. In the process of stainless-steel crevice corrosion, due to the small crevice size and the high concentration of substances inside the crevice, it is easy to produce precipitation. The resulting precipitate will affect the electrode dynamics during crevice corrosion, and the diffusion of ions in the solution and the precipitate will also change discontinuously. Therefore, the effect of simulated precipitation on crevice corrosion is realized by the level set method. The level set equation can be written as follows:

$$\frac{\partial \varphi}{\partial t} + u \cdot \nabla \varphi = \gamma \nabla \cdot \left(\varepsilon \nabla \varphi - \varphi (1 - \varphi) \frac{\nabla \varphi}{|\nabla \varphi|} \right)$$
(14)

The terms on the left-hand side give the correct motion of the interface, while those on the right-hand side are necessary for numerical stability. Where the interface moves with the velocity u (m/s), φ stands for the different phases in the system, the parameter γ (m/s) represents the amount of reinitialization or stabilization of the level set function, and ε (m) is the thickness of the transition zone. Because there are no reports on the precipitation kinetic parameters of stainless steel in the literature during corrosion in experiment, we assume the influence of the formation of precipitation as shown below:

$$\frac{1}{\varepsilon_d} \times \frac{\partial \varepsilon_d}{\partial t} = -c_{Fe^{2+}} \cdot c_{Cl^-} \cdot c_{O_2} \cdot k \tag{15}$$

where parameter ε_d represents precipitation porosity and is assumed to be 1, which indicates that no precipitation occurs; and $k = 10^{-11} \text{ m}^{-2}$.

Due to the production of precipitation, it will also affect the mass flux [23]; the influence can be expressed by the following equation:

$$n \cdot (N_{total} - N_{eff})_i = n \cdot N_{i,red} = \left(D_i - D_{eff}\right) \left(-\nabla c_i - \frac{z_i F}{RT} c_i \nabla \varphi_l\right)$$
(16)

where N_{total} is the flux without precipitation, N_{eff} describes the effective flux, $N_{i,red}$ represents the reduced flux, and D_{eff} is the effective diffusion coefficient after precipitation emerging.

3. Results and Discussion

3.1. Analysis of Crevice Corrosion Kinetics

Figure 1 exhibits the potential and current distributions predicted vs. distance from the crevice tip inside the crevice in this model at t = 90 h. The crevice potential gradually

becomes more negative from -0.21 V in the opening toward the direction of the crevice tip, -0.34 V, for the reason that the oxygen concentration decreases from the crevice mouth into the crevice. In DeForce's experiment, the researchers investigated crevice corrosion of stainless steel in a NaCl solution; they found potential distribution along the crevice within -0.34 to -0.15 V, though their crevice length was 1.2 cm, with opening size of 125 μ m, and the experiment time was 1 h [2]. A similar potential range of -0.4 to -0.2 V was given by Onishi's stainless-steel model, with a length of 2 cm and opening size of 25 μ m [24]. According to the simulation results of the 304–304 stainless-steel model, compared with Alavi's experiment [15] in the early stage, under acidic conditions, when the stainless-steel potential is above -0.35 V, the stainless steel is already in an activated state. This potential value is consistent with this model, so it can be considered that the stainless steel is in an activated state. Because stainless steel is in direct contact with Ti, the potential distribution on the Ti surface is the same as that of stainless steel, with a minimum potential of -0.34 V, which is above -0.4 V during the simulation, so Ti can remain in a passivated state, which is consistent with the assumption. It is worth noting that, for all spontaneously passive or active metals in which crevice corrosion does not occur immediately, the commencement of crevice corrosion through the IR mechanism can only emerge after an induction period, in which enough corrosion environment is formed inside the crevice to gradually destroy the stability of the passivation film, and the active peak in polarization curve will gradually form. As the active peak increases to a critical size at the end of the induction period, due to the solution continuing to acidify inside the crevice, the IR drop will exceed the critical potential, $\nabla \Phi^*$; thus, crevice corrosion starts [25].



Figure 1. Predicted (**a**) potential and (**b**) current distributions vs. distance from crevice tip for 304 stainless steel at t = 90 h.

The current inside the crevice changes smoothly, but it increases rapidly at the crevice opening, and the maximum value is 13 A/m^2 . The distribution and magnitude for current are consistent with the results of Wang's simulation [20]. Under the activation condition, the current density inside the crevice is affected by both the potential and the precipitation porosity. Figure 2 exhibits the precipitation porosity distribution vs. distance from crevice tip at t = 90 h. A porosity value of 1 indicates that the precipitate is loose and porous and will not affect the corrosion process. A porosity value of 0 indicates that there is no pore in the precipitate, and this will hinder the corrosion process. As shown in Figure 2, from the crevice tip to the crevice opening, the precipitation porosity first decreases and then increases, and there is an inflection point near the crevice opening with the minimum value 0.44. This change in porosity is related to the type of precipitated crystals that contain low-porosity crystalline precipitates that are easy to form when the precipitation growth rate is higher, and high-porosity amorphous precipitates emerge when the precipitation formation rate is higher [26]. The ions concentration near the crevice opening is high, and the precipitation formation rate is quick, leading to the formation of amorphous precipitates with high porosity near the crevice opening; thus, the porosity increases correspondingly. Only at the crevice opening do the potential and porosity values increase at the same time, so the current at the opening rises rapidly.



Figure 2. Predicted precipitation porosity distribution vs. distance from crevice tip at t = 90 h.

Figure 3 shows the propagation of crevice wall with time traced by moving mesh at t = 0 and t = 90 h. The legend on the right in the figure is the situation of mesh deformation. Green means less deformation, and red represents more deformation. It can be observed that 304 stainless steel undergoes activated dissolution to cause corrosion deformation. The corrosion depth inside the crevice increases with time, and the corrosion depth at the crevice mouth is the largest; the closer to the tip of the crevice, the lower the depth of corrosion is. This change in corrosion morphology corresponds to the current distribution in Figure 1. Titanium is always in a passive state, so that no corrosion deformation occurs. The crevice corrosion morphology in experiments has been reported in many works in the literature. Al-Khamis et al. [1] studied the crevice corrosion of stainless steel in an acidic Cl⁻ containing environment and found that the corrosion morphology is similar to the shape of the polarization curve with passivation–activation transition. The area near the crevice opening is the most severely corroded, and the closer to the crevice tip, the less severe the corrosion is. In addition, for passivable metals such as nickel, similar morphologies are also found when measuring the crevice-corrosion dimension changes in the experiment [27]. This corrosion morphology is a typical crevice corrosion morphology for passivable metals. The corroded crevice shape and the peak position of the corrosion depth predicted by this model qualitatively agree with the published experimental studies mentioned above; meanwhile, this morphology is rarely seen in other crevice corrosion simulations.



Figure 3. Propagation of crevice wall with time traced by moving mesh at (**a**) t = 0 and (**b**) t = 90 h for 304 stainless steel–Ti. The left side is 304 stainless steel, and the right is Ti. The scale on the right is the state of mesh deformation.

3.2. Crevice Solution Chemistry Evaluation and Ions Release

Figure 4 is the curve of pH change, with time at different positions, together with the pH distribution within the crevice at t = 90 h. For the crevice opening, the pH descends rapidly during the initial 5 h and then slowly reduces to 2.3. For the crevice middle, the pH basically stabilizes to approximately 1.93 after the initial 7 h; nevertheless, it is smoothly reduced to 2.4 after 30 h at the crevice tip. The reasons for the change of pH distribution shape are that, on the one hand, H⁺ comes from the hydrolysis of Cr³⁺, Fe²⁺, and Ni²⁺ produced by the activation dissolution of 304 stainless steel; on the one hand, it comes from the hydrolysis of Ti⁴⁺ dissolved under the effect of a passivation current. However, because Ti is uniformly corroded, the pH distribution is mainly affected by the dissolution of stainless steel. For 304 stainless steel, it corrodes quickly at the crevice opening, leading to more H⁺ produced; at the same time, OH⁻ generated due to the oxygen reduction reaction will make the pH of the crevice opening increase. Ultimately, the joint action of the both makes the pH of the crevice opening higher than it is for other parts. Regardless, the amount of metal ions generated at the tip of crevice and the middle of crevice is approximately the same (it can be known from the fact that the current value is similar inside the crevice in Figure 1). However, the highest concentration of metal ions emerges in the middle of the crevice in the process of simulation, and a comparable situation was reported in Reference [28], which manifests that the metal ions produced at the crevice opening will spread into the crevice middle to decrease the pH as a result of the concentration gradients.



Figure 4. Predicted pH profile change with time at (**a**) opening, (**b**) middle, (**c**) tip of the crevice, and (**d**) pH distribution vs. distance from crevice tip at t = 90 h.

The Cl⁻ time-varying concentration and distribution within the crevice at t = 90 h are shown in Figure 5. As time goes on, the concentration of Cl⁻ first increases to 1.08 mol/L and then decreases to 0.82 mol/L at the opening of the crevice; at the middle of the crevice, Cl⁻ first descends, then changes smoothly, and finally reaches 0.13 mol/L; and at the crevice tip, Cl⁻ rises initially and reaches 0.8 mol/L at last. The distribution trend of Cl⁻ shows that it decreases from the tip to the middle of the crevice, and then it increases toward the crevice opening. Sharland simulated the change of Cl⁻ concentration in the

crevice with time of the stainless-steel crevice under the current density of 10 A/m^2 . The results showed that, when the time is t = 90 h, the Cl⁻ concentration in the crevice was about 1.3 mol/L [8]. The current density in the crevice opening is 13 A/m^2 , and the corresponding Cl⁻ concentration is 1.6 mol/L in our model; these results are very consistent with the experiment results. Moreover, the Cl⁻ concentration obtained in this model is similar with Zuo [29] and Heppner's [18] results in the range of 1.4–3 mol/L. The Cl⁻ ultimate concentration distribution is determined by the difference between the increasing concentration, due to maintaining the electrical neutrality inside the crevice, and the consumption, because of the precipitation formation. The crevice opening is close to the bulk solution, and the metal dissolution rate is the largest, so the Cl⁻ concentration at the opening is the highest. In the middle of the crevice, the concentration valley of Cl⁻ (the lowest concentration) appears. This phenomenon is related to the diffusion of metal ions at the opening into the crevice to form a precipitate, leading to heavy Cl⁻ consumption.



Figure 5. Predicted Cl⁻ concentration profile change with time at (**a**) opening, (**b**) middle, (**c**) tip of the crevice, and (**d**) Cl⁻ concentration distribution vs. distance from crevice tip at t = 90 h.

3.3. The Influence of Crevice Geometry

One of the crucial objectives in investigating the electrochemical status inside the crevice is to forecast the metal dissolution rate, which is importantly influenced by the crevice size. In order to investigate the effect of the crevice size on corrosion, parametric crevice geometry factor $\log_{10}(r^2/w)$ is introduced, where r represents the crevice depth, and w describes the crevice opening size. For a narrower crevice, the value of $\log_{10}(r^2/w)$ becomes large, while for a wider crevice, the $\log_{10}(r^2/w)$ becomes a small value. The results aforementioned match $\log_{10}(r^2/w) = 8$. We add $\log_{10}(r^2/w) = 5$, 6, 7 to compare simulation results mutually in this part. Figure 6 exhibits the potential and current distributions along the crevice with different $\log_{10}(r^2/w)$ values at t = 90 h. When the value of $\log_{10}(r^2/w)$ decreases from 8 to 5, the potential at the crevice tip rises from -0.34 to -0.26 V, and the potential at the opening is between -0.23 and -0.21 V; as the crevice geometry factor decreases, the potential distribution becomes gentler. However, for the current density, when the $\log_{10}(r^2/w)$ reduces from 8 to 5, the maximum current density decreases quickly

from 13 to 5.6 A/m² at the crevice opening. This change trend is due to the reduction of the $\log_{10}(r^2/w)$, making the diffusion process more and more dominant within the crevice, and diffusion can eliminate the unevenness of the material inside the crevice in time.



Figure 6. Predicted (**a**) potential and (**b**) current distributions vs. distance from crevice tip under different $\log_{10}(r^2/w)$ at t = 90 h.

Figure 7 exhibits the pH and Cl⁻ distributions vs. distance from crevice tip inside the crevice in this model with different $log_{10}(r^2/w)$ values at t = 90 h. As the $log_{10}(r^2/w)$ decreases, the pH value increases from 3.3 to 3.7 at the crevice opening. When the $log_{10}(r^2/w) = 8$ and 7, the minimum pH value appears near the crevice middle, 1.93 and 2.9, respectively. Moreover, when the $\log_{10}(r^2/w) = 6$ and 5, the pH minimum appears at the tip of the crevice, as 3.4 and 3.6. The pH becomes gentle as the geometry factor decreases. The pH rises as the $\log_{10}(r^2/w)$ increases, and this behavior is consistent with Stroe's simulation results [10]. The reason why the pH becomes flat is related to the enhanced diffusion caused by the expansion of the crevice size. Nevertheless, the Cl⁻ concentration distribution inside the crevice becomes convoluted as a result of the rivalry emerging between precipitation and diffusion for consumption and supplement. When the $\log_{10}(r^2/w)$ drops from 8 to 7, the current density at the crevice opening decreases, the metal dissolution rate declines, and the amount of metal ions generated is reduced. Therefore, metal ions diffused from the opening to the inside of the crevice consume Cl^{-} to form precipitation that drops off, so the Cl⁻ concentration rises for $\log_{10}(r^2/w) = 7$. Nonetheless, when the crevice size is further increased and the $\log_{10}(r^2/w)$ continues to decrease, the diffusion effect is further enhanced, and Cl⁻ is not easy to accumulate in the crevice, so the Cl⁻ concentration will become closer to the bulk solution; this is why the Cl⁻ concentration of $log_{10}(r^2/w) = 6$ is higher than $\log_{10}(r^2/w) = 5$.



Figure 7. Predicted (**a**) pH and (**b**) Cl⁻ concentration distributions vs. distance from crevice tip under different $\log_{10}(r^2/w)$ at t = 90 h.

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4. Conclusions

The present study was designed to determine the circumstances of crevice corrosion of dissimilar metal stainless steel-titanium overlapping. The model considers the effect of multi-field coupling: electric field, mass transfer, moving mesh simulating corrosion deformation, and level set for precipitation generation. From the predicted results, the following is concluded:

- (1) The results show that, for stainless steel in the process of crevice corrosion, it corrodes most severely at the opening of the crevice; the closer to the tip of the crevice, the less corrosion deformation. However, titanium did not corrode, because it is in a passive state.
- (2) The potential increases gradually from the tip to the opening of the crevice and distributes between -0.34 and -0.21 V. The current inside the crevice changes smoothly, but it rises rapidly to 13 A/m² at the crevice opening.
- (3) The pH value in the crevice decreases from 2.4 at the crevice tip, reaches a minimum value of 1.93 near the middle, and then rises to a maximum value of 3.3 at the crevice opening. The Cl⁻ concentration is 0.8 mol/L at the tip of the crevice and drops to a minimum value of 0.13 mol/L in the middle, reaching the maximum value of 1.6 mol/L at the crevice opening.
- (4) The effect of the crevice size on corrosion is as follows: when the value of $\log_{10}(r^2/w)$ is reduced from 8 to 5, the potential at the tip of the crevice rises from -0.34 to -0.26 V, and the potential at the crevice opening is in between -0.23 to -0.21 V. As the $\log_{10}(r^2/w)$ decreases, the pH value increases from 3.3 to 3.7 at the crevice opening. When the $\log_{10}(r^2/w) = 8$ and 7, the minimum pH value appears near the middle, which is 1.93 and 2.9, and when the $\log_{10}(r^2/w) = 6$ and 5, the pH minimum appears at the crevice tip, which is 3.4 and 3.6. As the $\log_{10}(r^2/w)$ decreases, the overall Cl⁻ concentration appears to increase first and then decrease.

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