Numerical Simulation Based on a ZrO₂-Coated Stainless-Steel Corrosion Experiment

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ABSTRACT: In this work, ZrO₂-coated on the surface of 304 stainless steel was prepared by a sol–gel method to study the corrosion resistance. Based on the experimental results, an effective numerical model was established using a finite element method to simulate the electrochemical corrosion of ZrO₂-coated stainless steel in a 5% NaCl solution. This model simulates the changes in electrode/electrolyte potential, ion concentration, and oxygen concentration during the polarization process and provides a relatively reasonable explanation for the influence of the density of ZrO₂ on the corrosion resistance of stainless steel.

1. INTRODUCTION

Stainless steel has good corrosion resistance and is widely used in industrial areas. Nonetheless, in industrial production, stainless steel is normally accompanied by extremely rough environments (such as high temperature, high humidity, and halide ion environment) and causes its severe local corrosion phenomenon, which brings down the structural attributes of stainless steel. For such problems, a series of coating materials that improve the surface properties of stainless steel have emerged.

Ceramic material is one of the most important materials developed in recent years. Ceramic has the advantages of high temperature resistance, corrosion resistance, wear resistance, and so on. ZrO₂ ceramic material has good mechanical properties, chemical stability, and insulation, especially corrosion resistance, which has attracted widespread attention. In recent years, researchers have extensively studied ZrO₂ ceramics in the form of preparation coatings to study their ability to protect a matrix under high temperature and wear conditions. In terms of corrosion, Gao et al. found that the corrosion resistance of magnesia alloys was greatly improved by coating the surface of AZ31B magnesium alloy with a ZrO₂ film. In biomedicine, zirconia films deposited onto stainless steel can improve the performance of implanted materials, which not only reduces the formation of biofilms but also effectively improves the corrosion ability of plasma toward stainless steel. Yu et al. prepared ZrO₂ thin films on a stainless-steel surface by a sol–gel method. It was found that ZrO₂ thin films effectively prevented the penetration of hydrogen sulfide and other gases into a stainless-steel surface at high temperatures of 600 and 700 °C, which hindered corrosion.

At present, many experimental studies on the corrosion resistance of ZrO₂ thin films have been carried out, but few studies have been carried out from the point of view of numerical theory. In recent years, great progress has been made in finite element computer simulation of electrochemical corrosion. For example, in galvanic corrosion, Deshpande et al. established a galvanic corrosion model of magnesium alloy and low carbon steel, simulated an immersion experiment in a NaCl solution, and simulated the deformation of anodic corrosion using a moving grid technique based on an arbitrary Lagrangian–Euler (ALE) method. The predicted corrosion rate of the model was in good agreement with the experimental results. Sun et al. also established a similar galvanic corrosion model and simulated the variation of corrosion products with corrosion time on the electrode surface. According to the prediction of this model, it was found that the porosity of the corrosion products had a great influence on the corrosion morphology and depth of the anode area. The numerical model of the microgalvanic corrosion of aluminum alloy established by Wang et al. also reached similar conclusions. In terms of local corrosion, Fu et al. proposed a new

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experimental method based on using an applied current method to induce nonuniform corrosion of steel in mortar, established the normal distribution model for a rust layer in a steel bar, and predicted the corrosion behavior by simulating the change in the corrosion current. Cao et al.\(^{20}\) established a numerical model of the micro- and macrocorrosion of steel bars in chloride ion-corroded concrete. It was found that the macrocorrosion rate significantly decreased with time, but the microcorrosion rate changed slightly, and the corrosion changed from local corrosion to uniform corrosion. Wang et al.\(^{20}\) established a crevice corrosion model for 304 stainless steel. The model not only considered the anodic reaction of Fe, Cr, and Ni in 304 stainless steel but also considered the cathodic reaction of oxygen reduction, hydrogen evolution, and water reduction. Other numerical simulations have also taken into account the homogeneous reaction of ions in an electrolyte solution\(^{16,21,22}\) and have simulated the changes in pH and ion concentration inside and outside the corrosion pit or the crevice. In terms of coating protection, Cross et al.\(^{23}\) used a transient finite element simulation model to simulate galvanic corrosion of carbon steel/zinc and carbon steel/ aluminum coatings with a H\(_2\)SO\(_4\) electrolyte, and the geometric changes of the coating were tested using a surface profiler. According to the test and simulation results, it was shown that the electrode morphology changes had good consistency within the first 40 min of corrosion. Cross et al.\(^{24}\) also established an effective local model of one-dimensional continuously variable porosity adjustable electrolytes. By changing the porosity of the porous coatings, the diffusion coefficient of ions into the matrix through the coatings was controlled, reflecting the corrosion of different coatings with time.

This report proposes a new model based on experimental results to research the corrosion resistance of ZrO\(_2\)-coated stainless steel under dynamic potential polarization in a sodium chloride solution. In this work, we not only considered the kinetics in the electrochemical process but also considered the distribution of the pH and ion concentration inside and outside the corrosion pit caused by the homogeneous reaction of ions under a concentration gradient. The purpose of establishing the model in this paper is to simulate the phenomenon of electrode potential, substance transfer, and pH change during the electrochemical polarization process of the entire corrosion system. These phenomena can explain the reason why a ZrO\(_2\) film improves the corrosion resistance of a stainless-steel surface. Meanwhile, the porosity parameter is used to describe the compactness of the ZrO\(_2\) film, which is used to evaluate the effect of the film density on corrosion.

2. MODEL

2.1. Model System. Figure 1 shows a two-dimensional geometric model of localized corrosion in a 5% NaCl solution (pH = 7). This model assumes that the ion diffusion layer width in the NaCl solution is 3 \(\mu\)m. According to previous studies,\(^{25-27}\) the thickness of a ZrO\(_2\) film is assumed to be 150 nm. Figure 5 shows the corrosion morphology of the stainless steel under dynamic potential polarization test. It can be found that local corrosion occurred in all the three samples, although the stainless steel sintered at 600 °C had some uniform corrosion. The organization of local corrosion is because certain areas of the metal surface are more alive than others. There are many causes for this phenomenon, such as physical defects on the metal surfaces and metal inclusions.

When the phase changes on the surface, austenite and other social organizations are generated, which has internal stress and fractures along the stainless-steel surface. The structure of the local corrosion model is separated into two regions: the anode region and the cathode area. The response in the anode area is the dissolution reaction of the metal element and the reduction reaction of the oxygen occurs in the cathode area. The system considers the electrochemical reaction on the electrode surface, the dispersal and migration of ions in the electrolyte, and the homogeneous reaction with metal ions in the electrolyte.

The present model system has the following hypotheses:\(^{20}\)

1. The obstruction of corrosion products for ion transfer in the electrolyte solution is ignored.
2. The electrolyte solution is static and is not affected by the fluid flow.
3. The chemical reaction in the electrolyte is in equilibrium.

2.2. Governing Equations. From the point of mass transfer, the diffusion and electromigration of the ion concentration are considered and the convection term in the solution is neglected. According to the Nernst–Planck equation

\[
\frac{\partial \bar{c}_i}{\partial t} + \nabla J_i = 0
\]

\[
J_i = -D_i \nabla \bar{c}_i - z_i F \frac{D_i}{RT} \bar{c}_i \nabla \varphi_i
\]

where, \(D_i\) is the diffusion coefficient of ions, \(\bar{c}_i\) is the ion concentration (Tables 1 and 2),\(^{21,22,24,28}\) \(z_i\) is the valence state of the ions participating in the reaction, \(F\) is the Faraday constant (C/mol), \(R\) is the general gas constant (J/(K·mol)), \(T\) is the temperature (25 °C), and \(\varphi_i\) is the electrolyte potential. The electrical neutral conditions are also considered as

\[
\sum_i D_i \bar{c}_i = 0
\]

The material conservation equation is controlled by the electrolyte current density and the electromigration portion follows Ohm’s law. It is known from eqs 4 and 5 that

\[
i_t = F \sum_i z_i \left( -D_i \nabla \bar{c}_i - \frac{D_i}{RT} \bar{c}_i \nabla \varphi_i \right)
\]

\[
i_t = i_e + i_c
\]
Table 1. Transport Properties of Ions in an Electrolyte Solution at 25 °C

| parameter | diffusion coefficient (m²/s) |
|-----------|-----------------------------|
| DCI⁻       | 2.023 × 10⁻⁶                |
| DN⁺        | 1.334 × 10⁻⁹                |
| DH⁺        | 9.31 × 10⁻⁹                 |
| DOH⁻       | 5.273 × 10⁻⁹                |
| DFe²⁺      | 0.71 × 10⁻⁹                 |
| DFeOH⁺     | 0.75 × 10⁻⁹                 |
| DFe(OH)₂⁺₂⁻| 2.78 × 10⁻⁹                 |
| DFeCl⁺      | 0.75 × 10⁻⁹                 |
| DFeCl₂⁻     | 0.78 × 10⁻⁹                 |
| DFeCl₂⁻⁻    | 1.1 × 10⁻⁹                 |
| DCr²⁺       | 0.59 × 10⁻⁹                 |
| DCrOOH⁺     | 0.73 × 10⁻⁹                 |
| DCr(OH)₂⁺⁻ | 0.77 × 10⁻⁹                 |
| DCr(OH)₂⁺₂⁻| 0.82 × 10⁻⁹                 |
| DCrCl⁺       | 0.73 × 10⁻⁹                 |
| DCrCl₂⁺     | 0.77 × 10⁻⁹                 |
| DNiCl⁺       | 0.72 × 10⁻⁹                 |
| DNi(OH)⁺     | 0.73 × 10⁻⁹                 |
| DNiCl₂⁻     | 0.73 × 10⁻⁹                 |
| DO₂         | 1.4 × 10⁻⁸                  |

Table 2. Constant Table Used in an Electrolyte Solution

| parameter | description | value            |
|-----------|-------------|------------------|
| cCl⁻      | bulk chloride ion concentration | 1031 mol/m³ |
| cOH⁻      | bulk hydroxide ion concentration | 10⁻⁷ mol/m³ |
| ρFe       | density of iron | 7.8 g/cm³ |
| ρCr       | density of chromium | 7.19 g/cm³ |
| ρNi       | density of nickel | 58.69 g/mol |
| ρO₂       | bulk oxygen concentration | 0.25 mol/m³ |
| ρM       | density of metal | 10⁻¹⁴ |
| Keq       | molar mass of iron | 56 g/mol |
| Meq       | molar mass of nickel | 6.2 g/mol |
| Mcr       | molar mass of chromium | 9.5 g/mol |
| Ms        | density of nickel | 0.996 |

where, \( i_i \) is the electrolyte current density, \( i_c \) is the reduced cathode reaction current density of oxygen, and \( i_o \) is the oxidation reaction of the stainless-steel metal dissolution.

2.3. Boundary Conditions. As shown in Figure 1, the ionic concentration of the diffusion layer is set to the bulk concentration (shown in Table 2). The initial potential of the electrolyte is set to 0 (vs SCE)

\[ E_i^0 = 0 \]

(7)

The electrode surface follows the principle of electrode reaction kinetics. The kinetic expressions of the anodic and cathodic reactions are as follows

\[ i_a = i_{0,a} \exp \left( \frac{2.303 \nabla \phi}{\beta_a^i} \right) \]

(8)

\[ i_c = i_{0,c} \exp \left( \frac{2.303 \nabla \phi}{\beta_c^i} \right) \]

(9)

where \( \nabla \phi \) is the overpotential and \( E_{eq} \) is the equilibrium potential of the anode or cathode, respectively.

The ion flux variation produced by the anodic reaction and the cathodic reaction can be further determined by the current density formula for the reaction between the anode and the cathode

\[ -J_n = \frac{v_i}{n_i F} \]

(11)

where \( v_i \) is the stoichiometric coefficient, \( n_i \) is the number of ions participating in the reaction, and \( F \) is the unit normal vector. Assuming that the metal element in 304 stainless steel is proportional to its mole fraction, 304 stainless steel is mainly composed of 71% iron, 19% chromium, and 10% nickel. Therefore, the ion flux for the anode can be expressed as

\[ -J_n = 0.71 \frac{v_{Fe} a}{n_i F} + 0.19 \frac{v_{Cr} a}{n_i F} + 0.1 \frac{v_{Ni} a}{n_i F} \]

(12)

The homogeneous reaction of metal ions in the electrolyte is introduced. Since the hydrolysis reaction in the corrosion process is very complicated, only 14 equilibrium reactions are considered (Table 3). The reaction rate of related substances can be expressed by related hydrolysis kinetic constants

\[ K_{eq} = \frac{k_f}{k_r} \]

(13)

where \( k_f \) and \( k_r \) are the forward and reverse kinetic constants, respectively, and \( K_{eq} \) is the equilibrium constant. It is assumed that the chemical reaction on the electrode surface is in an equilibrium state during the polarization process according to the formula

\[ -J_n = v_i J_{eq} \]

(14)

\[ J_{eq} = -K_{eq} \prod_{i \in \text{reactions}} (c_i)^{-n_i} + \prod_{i \in \text{products}} (c_i)^{n_i} \]

(15)
where \( f_i \) is the flux generated by the equilibrium reaction ions (mol/(m²·s)) and \( c_i \) is the concentration, with the other boundaries set to no flux

\[
-J^t_n = 0
\]  

(16)

Based on the coupled electrode dynamics and mass transfer, the corrosion deformation of the anode region exposed to the NaCl electrolyte solution is further simulated, and the variation in the grid with time is simulated by the ALE method mobile grid technology. According to the Laplace equation

\[
\frac{\partial^2}{\partial x^2} \frac{\partial x}{\partial t} + \frac{\partial^2}{\partial y^2} \frac{\partial x}{\partial t} = 0
\]

\[
\frac{\partial^2}{\partial x^2} \frac{\partial y}{\partial t} + \frac{\partial^2}{\partial y^2} \frac{\partial y}{\partial t} = 0
\]

(17)

\((x, y)\) and \((X, Y)\) represent the space coordinates and the reference frame coordinates, respectively, on the basis of which the dissolution rate of metal ions can be studied according to Faraday’s law

\[
-nv = 0.71i_f \frac{v_{Fe}M_{Fe}}{n_{Fe}F} + 0.19i_f \frac{v_{Cr}M_{Cr}}{n_{Cr}F} + 0.1i_f \frac{v_{Ni}M_{Ni}}{n_{Ni}F} \rho
\]

(18)

where \( M \) is the molar mass and \( \rho \) is the density. Inserting an external potential vs time-dependent linear function to simulate the polarization process of electrochemical potential-dynamic scanning

\[
\frac{\partial E}{\partial t} = E_0 + vt
\]

(19)

\( E_0 \) is the initial value of the potentiodynamic sweep and \( v \) is the experimental scan rate used, i.e., 0.5 mV/s.

### 2.4. Optimization of Kinetic Parameters

The simulation data were optimized using the Levenberg–Marquardt nonlinear least-squares method. The optimization result is shown in Figure 2. In the weak polarization region, the simulation results are in good agreement with the experimental data. When the potential moves in the strongly polarized region of the anode, the simulation results are different from the experimental results. It may be that activation polarization affects the change of the Tafel slope in an electrode reaction. To create the simulation results reasonable, experimental data in the strong polarization region of the anode are used. When the potential is scanned along the positive direction, the influence of the cathodic reaction on the corrosion system gradually decreases. Thus, it is assumed that the total current density in the strongly polarized region of the experimental portion is the anode current density, and the anode and cathode current densities are introduced into the local corrosion model as \( i_a \) and \( i_c \). Figure 3 shows the polarization curves obtained from the numerical model and the experiment. It can be seen that the two have a good consistency. The corresponding kinetic parameters are presented in Table 4. Since the equilibrium potential is linked up to the nature of the electrode and it is hard to test experimentally, the fitted parameters may not be consistent with the true value, but the fitting parameters can accurately report the true state of affairs of the polarization curve.

### 3. RESULTS AND DISCUSSION

#### 3.1. Corrosion Resistance of ZrO\(_2\)-Coated Stainless Steel

Figure 4 shows the surface shape of the experimental sample before corrosion was observed under a metallurgical microscope. It can be observed that the surface of unsintered 304 stainless steel at 600 °C is relatively smooth. However, the stainless-steel surface sintered at 600 °C has been completely carbonized. The surface of stainless steel covered with a ZrO\(_2\) film clearly show the austenite and pearlite produced after high-temperature treatment, and no carbonization occurs. The reason is that the ZrO\(_2\) film has the characteristics of chemical inactivity and a high melting point, thereby improving the heat insulation ability of the stainless-steel surface. The corrosion morphology of different experimental samples after polarization is shown in Figure 5. It can be seen that the corrosion of 304 stainless steel and ordinary 304 stainless steel sintered at 600 °C is the most serious, and some of the 304 stainless steel sintered at 600 °C has uniform corrosion. Compared with the two, the corrosion pit of the sintered stainless steel has a smaller diameter—depth ratio, which is extremely disadvantageous in industrial production. By comparison, it can be observed that ZrO\(_2\)-coated stainless steel has better corrosion resistance. Although there was more serious local corrosion on the surface of the stainless steel coated with ZrO\(_2\), no serious damage occurred in other areas. The polarization curve in Figure 3 shows that with the positive movement of the potential, the coated stainless steel has a lower current density than the uncoated stainless steel, although the unsintered stainless steel has a significant passivation zone during the anodic polarization stage. However, as the potential moves to the pitting potential, the passivation film is destroyed, and the sharp increase in current density promotes the occurrence of pitting corrosion. The worst cause of corrosion resistance of sintered stainless steel may be that the surface of the stainless steel is cracked due to phase change at high temperature or chromium carbide is produced due to the precipitation of chromium at high temperature.

Figures 6 and 7 show the simulated results based on experiments. When the dynamic potential \( E = 0.1 \) V, the potential is in the passivation region of 304 stainless steel and is close to the pitting potential of stainless steel. It can be seen that the anode area of the stainless steel sintered at 600 °C has the lowest electrode potential and shows a strong tendency to

![Figure 2. Polarization test curve of stainless steel covered with one layer of a ZrO\(_2\) film.](https://doi.org/10.1021/acsomega.1c01461)
Figure 3. (a) Experimental polarization curve in 5% NaCl. (b) Polarization curves in the experiment and the model.

| experimental sample          | parameter   | description                              | value                  |
|------------------------------|-------------|------------------------------------------|------------------------|
| 600 °C stainless steel       | $\beta_a$  | Tafel slope of the anodic reaction       | 0.155 V                |
|                              | $\beta_c$  | Tafel slope of the cathodic reaction     | −0.165 V               |
|                              | $i_{corr}$ | self-corrosion current density           | $1.175 \times 10^{-7}$ A/cm$^2$ |
|                              | $E_{eq,a}$ | equilibrium potential of the anodic reaction | −0.55 V                   |
|                              | $E_{eq,c}$ | equilibrium potential of the cathodic reaction | −0.073 V                   |
|                              | $i_{a,a}$  | exchange current density of the anodic reaction | $6.247 \times 10^{-9}$ A/cm$^2$ |
|                              | $i_{c,c}$  | exchange current density of the cathodic reaction | $1.164 \times 10^{-8}$ A/cm$^2$ |
|                              | $i_{o,a}$  | limiting current density for oxygen reduction | $1.51 \times 10^{-5}$ A/cm$^2$ |
| 304 stainless steel          | $\beta_a$  | Tafel slope of the anodic reaction       | 0.712 V                |
|                              | $\beta_c$  | Tafel slope of the cathodic reaction     | −0.149 V               |
|                              | $i_{corr}$ | self-corrosion current density           | $1.077 \times 10^{-7}$ A/cm$^2$ |
|                              | $E_{eq,a}$ | equilibrium potential of the anodic reaction | −0.526 V                   |
|                              | $E_{eq,c}$ | equilibrium potential of the cathodic reaction | −0.05 V                   |
|                              | $i_{a,a}$  | exchange current density of the anodic reaction | $1.007 \times 10^{-7}$ A/cm$^2$ |
|                              | $i_{c,c}$  | exchange current density of the cathodic reaction | $1.855 \times 10^{-8}$ A/cm$^2$ |
|                              | $i_{o,a}$  | limiting current density for oxygen reduction | $5.958 \times 10^{-5}$ A/cm$^2$ |
| one layer of ZrO$_2$-coated  | $\beta_a$  | Tafel slope of the anodic reaction       | 0.243 V                |
|                              | $\beta_c$  | Tafel slope of the cathodic reaction     | −0.181 V               |
|                              | $i_{corr}$ | self-corrosion current density           | $7.083 \times 10^{-8}$ A/cm$^2$ |
|                              | $E_{eq,a}$ | equilibrium potential of the anodic reaction | −0.58 V                   |
|                              | $E_{eq,c}$ | equilibrium potential of the cathodic reaction | −0.07 V                   |
|                              | $i_{a,a}$  | exchange current density of the anodic reaction | $1.637 \times 10^{-8}$ A/cm$^2$ |
|                              | $i_{c,c}$  | exchange current density of the cathodic reaction | $1.61 \times 10^{-8}$ A/cm$^2$ |
|                              | $i_{o,a}$  | limiting current density for oxygen reduction | $2.8 \times 10^{-8}$ A/cm$^2$ |
| two layers of ZrO$_2$-coated | $\beta_a$  | Tafel slope of the anodic reaction       | 0.194 V                |
|                              | $\beta_c$  | Tafel slope of the cathodic reaction     | −0.177 V               |
|                              | $i_{corr}$ | self-corrosion current density           | $4.1 \times 10^{-8}$ A/cm$^2$ |
|                              | $E_{eq,a}$ | equilibrium potential of the anodic reaction | −0.63 V                   |
|                              | $E_{eq,c}$ | equilibrium potential of the cathodic reaction | −0.1 V                   |
|                              | $i_{a,a}$  | exchange current density of the anodic reaction | $3.524 \times 10^{-9}$ A/cm$^2$ |
|                              | $i_{c,c}$  | exchange current density of the cathodic reaction | $6.05 \times 10^{-8}$ A/cm$^2$ |
|                              | $i_{o,a}$  | limiting current density for oxygen reduction | $1.3 \times 10^{-6}$ A/cm$^2$ |
| three layers of ZrO$_2$-coated | $\beta_a$  | Tafel slope of the anodic reaction       | 0.158 V                |
|                              | $\beta_c$  | Tafel slope of the cathodic reaction     | −0.036 V               |
|                              | $i_{corr}$ | self-corrosion current density           | $3.54 \times 10^{-8}$ A/cm$^2$ |
|                              | $E_{eq,a}$ | equilibrium potential of the anodic reaction | −0.6 V                   |
|                              | $E_{eq,c}$ | equilibrium potential of the cathodic reaction | −0.15 V                   |
|                              | $i_{a,a}$  | exchange current density of the anodic reaction | $2.19 \times 10^{-9}$ A/cm$^2$ |
|                              | $i_{c,c}$  | exchange current density of the cathodic reaction | $1.46 \times 10^{-8}$ A/cm$^2$ |
|                              | $i_{o,a}$  | limiting current density for oxygen reduction | $8.8 \times 10^{-8}$ A/cm$^2$ |
corrode. At this stage, although the Cl\(^-\) concentration distribution of the three samples did not vary significantly, it can be found out in the figure that Cl\(^-\) compiled in the anodized area. When \(E = 0.3\) V, the polarization potential is a lot larger than the pitting potential of stainless steel, and the anode region of stainless steel has obvious deformation. Meanwhile, ZrO\(_2\)-coated stainless steel has a higher electrode potential. As the potential moves in the positive direction, corrosion deformation occurs on the electrode surface, and a large amount of Cl\(^-\) begins to accumulate in the corroded area. As can be seen from Figure 7, the Cl\(^-\) concentration in the corrosion pits of stainless steel sintered at 600 °C is the highest, and the corrosion deformation of the anode region is the largest, followed by the unsintered stainless steel. Compared with the other two experimental samples, ZrO\(_2\)-coated stainless steel has the best corrosion resistance. As shown in Figure 8, the pH value of the ZrO\(_2\)-coated stainless steel activation zone slowly decreases during the.
corrosion process, which indicates that the ZrO$_2$ film can reduce the formation of H$^+$ in the anode zone and inhibit the corrosion of stainless steel. Combined with the change of the Cl$^-$ concentration in Figure 9, it can be determined that during the corrosion process, the corrosion ability of Cl$^-$ on the electrode surface is positively correlated with the H$^+$ accumulation ability.

3.2. Effect of ZrO$_2$ Compactness on Corrosion. A ZrO$_2$ ceramic film is a kind of amphoteric oxide with strong chemical stability and good insulation. It is difficult for the film to react chemically and electrochemically at normal temperature. According to previous reports, the reason for the corrosion of the ZrO$_2$ and other ceramic coatings is that micropores and cracks are formed on the film surface due to the compactness of the surface or the preparation process. For the above-mentioned reasons, halide ions such as Cl$^-$ in the electrolyte solution invade the coating and contact the stainless-steel substrate, leading to corrosion of the stainless steel. Since the mechanism for the destruction of the coating during the corrosion process is complicated and the model only considers the electrode dynamics problem, the phase field of the ZrO$_2$ film is simulated from a kinetic point of view. According to the following formula

$$\frac{\partial \varnothing_{ZrO_2}}{\partial t} + n \nabla \varnothing_{ZrO_2} = \gamma \nabla \left( \frac{\varepsilon \varnothing_{ZrO_2} - \varnothing_{ZrO_2}(1 - \varnothing_{ZrO_2})}{\varnothing_{ZrO_2}} \nabla \varnothing_{ZrO_2} \right)$$

where $\varnothing_{ZrO_2}$ is the film phase field-level set variable, which lies in the range of $0 < \varnothing_{ZrO_2} < 1$; when $\varnothing_{ZrO_2} = 0$, it is expressed as the electrolyte solution area and $\varnothing_{ZrO_2} = 1$ is expressed as the
Where $u$ is the phase transition velocity, $\gamma$ is the maximum phase transition velocity, and $\varepsilon$ is the interface thickness, which is defined as $h_{\text{max}}$, where $h_{\text{max}}$ is the size of the largest mesh in the phase domain. The active and cathode regions of the ZrO$_2$ film area can be described as: active ($x$, $y$) and 1-active ($x$, $y$). Since the electrode reaction occurs inside the ZrO$_2$ film, assuming that the film destruction rate is related to the dissolution of the metal, the phase transition process of the film during the polarization process can be based on the following formulas:

$$R = -Jn$$

$$V = R \sum_i M_i \frac{\rho_i}{\rho_{\text{active}}}$$

$$u_x = Vn_x$$

$$u_y = Vn_y$$

where $R$ is the electric flux during the phase change of the ZrO$_2$ film (mol/(m$^2$·s)), $V$ is the phase transition rate, and $n_x$ and $n_y$ are the interface unit normal components. The corrosion changes during the polarization of ZrO$_2$-coated stainless steel are described in Figure 10. It can be observed that during the cathode depolarization process of the potential, the electrode surface and the ZrO$_2$ film are not damaged, and the reduction reaction of cathode oxygen is dominant. When the applied potential moves in the positive direction, the anode reaction rate of the anodic reaction is much faster than the cathode reaction rate, the electrode surface begins to dissolve, and the coating is destroyed.

The previous section describes the ZrO$_2$ film to significantly improve the corrosion resistance of stainless-steel surfaces. The main reason is that the ZrO$_2$ film improves the resistance of the stainless steel. Since the ZrO$_2$ film has a porous structure that hinders the diffusion of oxygen, this section discusses the effect of film pores on corrosion. Assuming that the diffusion coefficient is linear with porosity, a simple numerical relationship has been demonstrated in other corrosion models.$^{17}$ The effective diffusion coefficient of the corrosion system is

$$D_{\text{eff}} = \varepsilon_{\text{po}} D^0 \varphi_{\text{ZrO}_2} + D^1 (1 - \varphi_{\text{ZrO}_2})$$

where $\varepsilon_{\text{po}}$ is the porosity of the ZrO$_2$ film. Assuming that the porosity of the film is 5%, the simulation results are compared with the model without considering the influence of the pores, and the simulation results are shown in Figure 11a. When the potential is in the depolarization phase of the cathode during...
the initial period, the oxygen concentration in the cathode region with a porosity of 5% is lower because the lower porosity affects the diffusion of oxygen into the stainless steel. As time passes, the applied potential moves in the positive direction, the reduction reaction of oxygen becomes weaker, and the oxygen concentration on the surface of the electrode gradually increases. Figure 11b shows the change in the pH on the surface of the electrode during the polarization process. It can be seen from the figure that the 5% porosity model has a lower pH, which is because the ZrO$_2$ film inhibits the reduction reaction of oxygen. In fact, the ability of oxygen to diffuse to the electrode surface during the entire electrochemical polarization process directly affects the depolarization of the cathode. Since this simulation only changes the diffusion capacity of the film to the transfer material, it is not clear that the diffusion ability of the oxygen in the film can promote corrosion, which will be further explained in the next section.

### 3.3. Effect of the ZrO$_2$ Layer Number on Corrosion

The effect of different layers on the surface of the sol coated onto the stainless-steel surface under the same conditions was investigated. According to previous studies, the ZrO$_2$ film density is improved as the number of layers increases,$^26$ and the compactness of the ZrO$_2$ film has an effect on the ability of the electrolyte to diffuse to the surface of the stainless-steel-substrate. Figure 12 shows EIS test results for one, two, and three layers of ZrO$_2$ films coated onto stainless steel. The electrochemical impedance increases with increasing ZrO$_2$ film layers. The Bode diagram in Figure 13 describes the relationship between impedance and frequency. The impedance of the high-frequency part is embodied by the ZrO$_2$ film micropore resistance and capacitance. The low-frequency part reflects the information of the interface between the inner dense layer and the solution, which is derived from the charge-transfer resistance and electric double-layer capacitance of stainless steel.$^{31,32}$ It can be seen that the impedance of the low-frequency and high-frequency parts increases with increasing number of film layers, which indicates that it is more difficult for the electrolyte to penetrate into the surface of the stainless-steel matrix from the multilayer ZrO$_2$ film.

In order to better understand the experimentally obtained EIS data, an equivalent circuit was established (shown in Figure 14), where $R_s$ is the impedance of the electrolyte, $R_{ct}$ is the resistance of the micropores on the surface of the ZrO$_2$ film, and $CPE_{c}$ and $CPE_{dl}$ are the electric double-layer capacitances of the ZrO$_2$ film and the stainless-steel surface, respectively. Since the parameters fitted by the equivalent circuit are consistent with the results obtained by the impedance spectrum (shown in Table 5), it can be explained that as the thickness of the ZrO$_2$ film increases, the permeability of substances in the solution decreases, thereby reducing the chance of oxygen-consuming corrosion.

Figure 11a shows the concentration of oxygen on the surface of the cathode electrode during the polarization process. It can be seen that with the increase of the polarization time, the electrode reaction is gradually dominated by the anode oxidation reaction, and the cathode oxygen reduction reaction gradually weakens. When the number of ZrO$_2$ film layers increases, the consumption of oxygen concentration decreases, indicating that the density of the ZrO$_2$ film affects the progress of the oxygen reduction reaction. Table 6 shows the concentration of metal ions at the bottom of the corrosion pit. Among them, the concentration of stainless steel coated with three layers of the ZrO$_2$ film is relatively small, while the concentration of stainless steel coated with one layer of a ZrO$_2$ film is relatively large. The reason is that the anode oxidation reaction makes the surface of the stainless steel lose electrons and frees metal ions in the corrosion pit.

![Figure 11](https://example.com/fig11.png)

**Figure 11.** (a) Oxygen concentration change on the electrode surface and (b) pH change on the electrode surface.

![Figure 12](https://example.com/fig12.png)

**Figure 12.** Nyquist plots of EIS data for different layers of the ZrO$_2$ film.

$R_s$ is the surface charge-transfer resistance of the stainless steel, and $CPE_c$ and $CPE_{dl}$ are the electric double-layer capacitances of the ZrO$_2$ film and the stainless-steel surface, respectively.
Therefore, the stronger the anode reaction ability, the more metal ions accumulate in the corrosion pit, the more severe the corrosion occurs. Figure 15b shows the changes of the pH of the bottom of the corrosion pit after corrosion of the ZrO2-coated stainless steel. According to the simulation results, the reduction reaction of one layer of a ZrO2-coated stainless-steel cathode can generate more OH\(^-\) ions and transfer to the anode area to reduce the acidity in the corrosion pit. However, with the positive potential moving forward, a large amount of H\(^+\) produced by the homogeneous reaction makes the effect of the reduction reaction of the corrosion system negligible. Meanwhile, as the compactness of the ZrO2 film increases, the resistance of the stainless steel is enhanced, which effectively suppresses the corrosion of the stainless-steel substrate by Cl\(^-\) ions and the metal corrosion caused by the anodizing reaction. It also reduces the possibility of hydrolysis and local acidification of metal ions.

The polarization curves of ZrO2-coated stainless steel with different layers are shown in Figure 16. It can be seen in the figure that the self-corrosion current density decreases with the increase of the number of thin-film layers (Table 4). The increase in film density decreases the absolute value of the current density. According to the current–potential characteristic equation

\[
I = nFk_0\exp\left(\frac{anF}{RT}(E - E^\circ)\right) - C_0\exp\left(-\frac{(1 - \alpha)nF}{RT}(E - E^\circ)\right)
\]

(26)

Among them, \(A\) is the contact area of the electrode–electrolyte heterogeneous reaction, \(k_0\) is the standard rate constant, \(\alpha\) is the transfer coefficient, and \(E^\circ\) is the formal potential of the electrode. According to eq 26, it can be known that the polarization current is affected by the contact area \(A\) of the electrolyte solution and the electrode surface. The ZrO2 film has insulation and porosity, and the electrode reaction equation is established to further verify the influence of film compactness on corrosion

\[
i_\alpha = \epsilon_{po,a}\exp\left(2.303\frac{V}{\beta_a}\right)
\]

(27)

\[
i_\beta = -\epsilon_{po,c}\exp\left(2.303\frac{V}{\beta_c}\right)
\]

(28)

The abovementioned electrode reaction equation describes a simple relationship between the electrode reaction rate and the porosity. This relationship is consistent with the relationship between the electrode reaction current and the contact area in eq 26. Although this method is rough in processing the microstructure of the film, it can deal with complex mechanisms and provide relatively reasonable results. The simulation of the polarization curve is described in Figure 17, and the porosity parameters are set to 1, 0.1, and 0.01. It can be seen that the corrosion current density decreases with the decrease of the porosity, and the result is similar to that in Figure 16. The change in the corrosion depth of the anode region during the

| sample  | \(R_s\) (\(\Omega\cdot\text{cm}^2\)) | \(R_{po}\) (\(\Omega\cdot\text{cm}^2\)) | CPE\(_{\alpha}\) (F\(\cdot\text{cm}^{-2}\)) | \(n_1\) | \(R_{\alpha}\) (\(\Omega\cdot\text{cm}^2\)) | CPE\(_{\beta}\) (F\(\cdot\text{cm}^{-2}\)) | \(n_2\) |
|--------|----------------|----------------|----------------|------|----------------|----------------|------|
| three-layer | 7.35 | 16 853 | 2.16 \times 10^{-7} | 0.93 | 448 560 | 1.47 \times 10^{-6} | 0.66 |
| two-layer | 6.53 | 7093 | 2.38 \times 10^{-7} | 0.96 | 360 320 | 1.12 \times 10^{-6} | 0.68 |
| one-layer | 8.38 | 5622 | 4.40 \times 10^{-7} | 0.95 | 251 820 | 4.27 \times 10^{-6} | 0.67 |
The polarization process is shown in Figure 18a. As the film porosity decreases, the impedance of ZrO$_2$-coated stainless steel also increases and the amount of corrosion depth decreases. The changes in the oxygen consumption and pH in the corrosion pits in Figure 18b,c are the same as the development trends of stainless steel with different ZrO$_2$ film layers, shown in Figure 16, during the polarization process.

### 4. CONCLUSIONS

In this work, a ZrO$_2$ film was prepared on the surface of 304 stainless steel by a sol–gel method to modify the surface of stainless steel. The influence of the ZrO$_2$ film on the corrosion resistance of stainless steel is discussed. Based on the experimental results, a finite element mathematical model was established. Taking into account the growth of corrosion pits, the chemical equilibrium reaction of each ion in the electrolyte, and the compactness of the ZrO$_2$ film, this model simulates the corrosion process of the experimental sample in a 5% NaCl solution. Based on experiments and simulations, the following conclusions can be drawn:

1. According to the electrochemical polarization test results of 304 stainless steel, sintered stainless steel at 600 °C, and ZrO$_2$-coated stainless steel and the surface morphology after corrosion, it is proved that the ZrO$_2$ film can improve the corrosion resistance of stainless steel. By simulating the corrosion changes of the experimental samples during the polarization process, it is found that the ZrO$_2$-coated stainless steel has the smallest corrosion deformation during the entire polarization process. During the entire corrosion process, the anodic reaction of the ZrO$_2$-coated stainless steel anode area has a higher electrode potential, which reduces the corrosion ability of Cl$^-$ and the ability of H$^+$ accumulation in the corrosion pit.
The test method using potentiodynamic polarization and EIS proves that the improvement of the ZrO2 film’s compactness helps to improve the corrosion resistance of stainless steel. By controlling the porosity of the model to adjust the density of the coating, it is found that enhancing the density of the ZrO2 film can prevent oxygen from contacting the electrode surface and inhibit the progress of the cathode reduction reaction and the formation of OH\(^-\). Simulating the corrosion of different layers of ZrO\(_2\)-coated stainless steel shows that the density of the film increases, which reduces the oxygen required for the cathode reaction. This means that increasing the density of the film can effectively inhibit the reduction reaction and reduce the contact ability between the electrolyte and the stainless steel substrate, which inhibits the aggregation of Cl\(^-\) and the generation of H\(^+\).

5. EXPERIMENTAL SECTION

5.1. Preparation of ZrO\(_2\) Coating. The ZrO\(_2\) film was prepared by a sol–gel method. Zirconium butoxide (Macklin, Shanghai), ethyl alcohol absolute (Fengchuan, Tianjin), and acetic acid (Fuyu, Tianjin) were added to a beaker in a certain proportion, and then a magnetic stirrer was used to fully stir at 25 °C for 4 h. The prepared sol was deposited by spin-coating using a spin coater. In particular, the sol was sprayed onto the mirror surface of a 304 stainless steel sample with dimensions of 2 cm × 1 cm × 0.1 cm and spin-coated at a speed of 3000 rad/min; before spin-coating, the stainless steel was ultrasonically washed with ethanol and distilled water. The sol-coated sample was then placed in a drying oven at a temperature of 100 °C for 20 min, followed by sintering at 600 °C. After sintering, a ZrO\(_2\) film-coated stainless steel sample was obtained after natural cooling.
The precursor sol for preparing a ZrO₂ film was dried and heat-treated at 600 °C to obtain xerogel powder. It can be viewed from the XRD pattern (Figure 19) that after heat treatment at 600 °C, the xerogel powder mainly has a tetragonal phase structure, and a certain amount of monoclinic phase exists.

Figure 19. XRD pattern of the ZrO₂ xerogel sintered at 600 °C.

5.2. Potentiodynamic Polarization Test. The electrochemical test was carried out on the experimental samples in a 5% NaCl electrolyte solution using a CS350H electrochemical workstation manufactured by Wuhan Corrtest Instrument Co., Ltd. The battery system had a three-electrode configuration; the auxiliary electrode was a platinum electrode and the reference electrode was a calomel electrode (SCE). The specimens were submerged for 60 min to establish a stable open-circuit potential (OCP). EIS measurement was performed under OCP. The frequency range was 100 kHz to 0.01 Hz, and a voltage disturbance amplitude of 10 mV was used. The potential scanning of the potentiodynamic polarization test was −0.3 to 1 V (relative to OCP), and the scanning rate was 0.5 mV/s.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Ma, Y. F.; Guo, Z. Z.; Wang, L.; Zhang, J. R. Probabilistic life prediction for reinforced concrete structures subjected to seasonal corrosion-fatigue damage. J. Struct. Eng. 2020, 146, No. 04020117.
(2) Guo, Z. Z.; Ma, Y. F.; Wang, L.; Zhang, J. R.; Harik, I. E. Corrosion fatigue crack propagation mechanism of high-strength steel bar in various environments. J. Mater. Civ. Eng. 2020, 32, No. 04020115.
(3) Karthik, A.; Arunmetha, S.; Srither, S. R.; Manivasakan, P.; Rajendran, V. High temperature corrosion resistance of silicate based nanostructured thermal barrier coatings using Al₂O₃ – (Y₂O₃) ZrO₂/SiO₂ nanocomposite. Surf. Coat. Technol. 2016, 292, 110–120.
(4) Ng, K. W.; Man, H. C.; Yue, T. M. Corrosion and wear properties of laser surface modified NiTi with Mo and ZrO₂. Appl. Surf. Sci. 2008, 254, 6725–6730.
(5) Obadele, B. A.; Lepule, M. I.; Andrews, A.; Olubami, P. A. Tribocorrosion characteristics of laser deposited Ti–Ni–ZrO₂ composite coatings on AISI 316 stainless steel. Tribol. Int. 2014, 78, 160–167.
(6) Gao, Y. E.; Zhao, L. F.; Yao, X. H.; Hang, R. Q.; Zhang, X. Y.; Tang, B. Corrosion behavior of porous ZrO₂ ceramic coating on AZ31B magnesium alloy. Surf. Coat. Technol. 2018, 349, 434–441.
(7) Kaliaraj, G. S.; Vishwakarma, V.; Alagarsamy, K.; Kirubaharan, A.M.K. Biological and corrosion behavior of m-ZrO₂ and t-ZrO₂ coated 316L SS for potential biomedical applications. Ceram. Int. 2018, 44, 14940–14946.
(8) Yu, J.; Ji, G. J.; Liu, Q. S.; Zhang, J. B.; Shi, Z. M. Effect of solution ZrO₂ films on corrosion behavior of the 304 stainless steel in coal-gases environment at high temperature. Surf. Coat. Technol. 2017, 331, 21–26.
(9) Cross, S. R.; Woollam, R.; Shademan, S.; Schuh, C. A. Computational design and optimization of multi-layered and functionally graded corrosion coatings. Corros. Sci. 2013, 77, 297–307.
(10) Mai, W.; Soghrati, S. New phase field model for simulating galvanic and pitting corrosion processes. Electrochim. Acta 2018, 260, 290–304.
(11) Kennell, G. F.; Evitts, R. W.; Heppner, K. L. A critical crevice solution and IR drop crevice corrosion model. Corros. Sci. 2008, 50, 1716–1725.
(12) Cao, C.; Cheung, M.M.S.; Chan, B.Y.B. Modelling of interaction between corrosion-induced concrete cover crack and steel corrosion rate. Corros. Sci. 2013, 69, 97–109.
(13) Amri, J.; Gulbransen, E.; Nogueira, R. P. Numerical simulation of a single corrosion pit in CO₂ and acetic acid environments. Corros. Sci. 2010, 52, 1728–1737.
(14) Xu, L. Y.; Cheng, Y. F. Development of a finite element model for simulation and prediction of mechatro-electrochemical effect of pipeline corrosion. Corros. Sci. 2013, 73, 150–160.
(15) Deshpande, K. B. Validated numerical modelling of galvanic corrosion for couples: Magnesium alloy (AE44)–mild steel and AE44–aluminium alloy (AA6063) in brine solution. Corros. Sci. 2010, 52, 3514–3522.
(16) Sun, W.; Wang, L. D.; Wu, T. T.; Liu, G. C. An arbitrary Lagrangian–Eulerian model for modelling the time-dependent evolution of crevice corrosion. Corros. Sci. 2014, 78, 233–243.
(17) Wang, Y. C.; Yin, L. Y.; Jin, Y.; Pan, J. S.; Leygraf, C. Numerical Simulation of Micro-Galvanic Corrosion in Al Alloys: Steric Hindrance Effect of Corrosion Product. J. Electrochem. Soc. 2017, 164, C1035–C1043.
(18) Fu, C. Q.; Jin, N. G.; Ye, H. L.; Liu, J. M.; Jin, X. Y. Non-uniform corrosion of steel in mortar induced by impressed current.
method: An experimental and numerical investigation. Constr. Build. Mater. 2018, 183, 429−438.

(19) Cao, C.; Cheung, M.M.S. Non-uniform rust expansion for chloride-induced pitting corrosion in RC structures. Constr. Build. Mater. 2014, 81, 75−81.

(20) Wang, W.; Sun, H. Y.; Sun, L.; Song, Z. W.; Zang, B. N. Numerical Simulation for Crevice Corrosion of 304 Stainless Steel in Sodium Chloride Solution. Chem. Res. Chin. Univ. 2010, 26, 822−828.

(21) Heppner, K. L.; Evitts, R. W.; Postlighthwaite, J. Prediction of the Crevice Corrosion Incubation Period of Passive Metals at Elevated Temperatures: Part II – Model Verification and Simulation. Can. J. Chem. Eng. 2002, 80, 857−864.

(22) Yaya, K.; Khelfaoui, Y.; Malki, B.; Kerkar, M. Numerical simulations study of the localized corrosion resistance of AISI 316L stainless steel and pure titanium in a simulated body fluid environment. Corros. Sci. 2011, 53, 3309−3314.

(23) Cross, S. R.; Gollapudi, S.; Schuh, C. A. Validated numerical modeling of galvanic corrosion of zinc and aluminum coatings. Corros. Sci. 2014, 88, 226−233.

(24) Cross, S. R.; Schuh, C. A. Modeling localized corrosion with an effective medium Approximation. Corros. Sci. 2017, 116, 53−65.

(25) Ji, G. J.; Li, M.; Zhang, Z. H. Effect of Sintering Temperature on the Surface Morphology and Mechanical Properties of ZrO2 Films. Bull. Chin. Ceram. Soc. 2015, 34, 185−187.

(26) Bu, A. M.; Ji, G. J.; Zhang, W. Corrosion Behavior of Zirconia Thin Films on 304 Stainless Steel. J. Synth. Cryst. 2015, 44, 3652−3654.

(27) Yu, J.; Ji, G. J.; Shi, Z. M.; Wang, X. H. Corrosion resistance of ZrO2 films under different humidity coal gas conditions at high temperature. J. Alloys Compd. 2019, 783, 371−378.

(28) Walton, J. C.; Cragnolino, G.; Kalandros, S. K. A numerical model of crevice corrosion for passive and active metals. Corros. Sci. 1996, 38, 1−18.

(29) Wang, D.; Bierwage, G. P. Sol Gel Coatings on Metals for Corrosion Protection. Prog. Org. Coat. 2009, 64, 327−338.

(30) Nouri, E.; Shanhmiri, M.; Rezaie, H. R.; Talaylan, F. Investigation of Structural Evolution and Electrochemical Behaviour of Zirconia Thin Films on the 316L Stainless Steel Substrate Formed via Sol-Gel Process. Surf. Coat. Technol. 2011, 205, 5109−5115.

(31) Liu, F.; Yu, J.; Shan, D. Y.; Han, N. H.; Ke, W. Corrosion Process of a Zirconium Oxides Plasma Electrolytic Oxidation (PEO) Coating on AM30 Alloy. Aerosp. Mater. Technol. 2014, 44, 37−41.

(32) Zhang, J. Q. Electrochemical Measurement Technology; Chemical Industry Press: Beijing, 2010; p 260.