Analytic studies of marine atmospheric corrosion based on multiphysics simulation

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Abstract. Because the environment at sea is more severe than inland, the corrosion of hull and ship equipment is extremely serious. It can be said that corrosion is one of the biggest factors affecting the life of ships. The cost of anti-corrosion for ships every year is one third or more of the total maintenance cost. The Marine atmosphere corrosion simulation of Q235 carbon steel is realized by Multiphysics simulation software. Due to the high probability and hazard of electrochemical corrosion in oceanic and atmospheric environment, this paper mainly analyzes electrochemical corrosion behavior and its influencing factors, providing a theoretical basis for monitoring and reducing corrosion hazards. The results show that the corrosion rate of Q235 steel in the oceanic atmosphere is 400 to 600 μm/a, and the corrosion rate is affected by temperature, humidity, limiting current density and other factors.

1. Introduction
Corrosion damage is one of the main failure forms of ship structures. Statistics show that about 90% of ship failures are caused by corrosion, including corrosion fatigue[1]. Oceanic atmospheric corrosion is mainly affected by temperature, relative humidity, sunshine, rainfall, PH and salt concentration in the air. The research on the mechanism of oceanic and atmospheric corrosion of structural materials is conducive to the development of more advanced ship corrosion protection technology. A large number of scholars have conducted extensive research on the mechanism of atmospheric corrosion and obtained excellent results, including the enhancement of corrosion behavior of alloy elements, acceleration of corrosive pollutants[2], influence of environmental parameters[3], and protection mechanism of corrosion products[4]. In this paper, the electrochemical corrosion of Q235 carbon steel in ocean atmosphere was simulated by multiphysics simulation software. The distribution of electrolyte potential and electrolyte current density was obtained by simulation under different environmental parameters. The simulation results are compared and analyzed to explore the law and influencing factors of oceanic and atmospheric corrosion.

2. Basic mechanism of atmospheric corrosion of carbon steel
Atmospheric corrosion of a metal is an electrochemical process, which is the sum of several reaction processes that occur when an electrolyte layer is formed on the metal surface. The electrolyte can be thin layers of water or hundreds of micrometers thick. Moisture (such as dew) caused by precipitation of rain, fog and other liquid phase and temperature change is the main factor leading to corrosion of metal atmosphere. The severity of corrosion basically depends on how long the metal has been wet, which is actually a function of a number of factors, such as rainfall, temperature, relative humidity, exposure conditions, atmospheric pollution, metal composition, corrosion products, etc. Atmospheric
corrosion includes simultaneous oxidation and reduction reactions, as well as other chemical reactions, in which some corrosion products participate. The anodic reaction consisting of metal oxidation can be expressed as:

\[
Fe \rightarrow Fe^{2+} + 2e^{-}
\]  

(1)

Oxygen, which is highly soluble in the water layer, may act as an electron acceptor. The reduction reaction of oxygen in neutral or alkaline medium is carried out according to the following reactions:

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^-
\]

(2)

When the content of acidic pollutants in the atmosphere is high, the cathode reaction of hydrogen ion discharge will become the main reduction reaction:

\[
2H^+ + 2e^- \rightarrow H_2
\]

(3)

The salinity of the atmosphere in coastal areas leads to a significant increase in atmospheric corrosion rates compared to the clean atmosphere inland[5]. The atmospheric corrosion products of iron and its alloys, that is, rust, include various oxides, water and oxides, hydroxides, and various crystalline and amorphous substances. These materials may come from the substrate itself (endogenous products) or from the atmosphere (exogenous products). Common corrosion products formed on the surface of carbon steel exposed to the atmosphere are \( \alpha \)-Fe\(_2\)O\(_3\), \( \gamma \)-Fe\(_3\)O\(_4\), Fe\(_5\)HO\(_6\)\( \cdot \)4H\(_2\)O, \( \alpha \)-FeOOH, \( \beta \)-FeOOH, \( \gamma \)-FeOOH, \( \delta \)-FeOOH. The rust layer usually has considerable pores and fractures, ruptures and unprotected oxide layers that allow the corrosive material to easily access the metal matrix, which is typical in highly corrosive environments. In contrast, a tight oxide layer helps to slow corrosion and protect the metal.

3. Simulation analysis of oceanic and atmospheric corrosion of carbon steel

3.1. The establishment of simulation model

The simulation process of oceanic atmospheric corrosion of Q235 carbon steel using multiphysics simulation software (such as COMSOL Multiphysics) is shown in figure 1. In this paper, the "corrosion, secondary current" interface in the electrochemical module of multiphysics simulation software is selected as the simulation physical field. This interface can be used to describe the current distribution, potential distribution, and geometric changes in the corroded battery. The interface also combines "secondary current" interface and "deformation geometry" interface to describe the change of geometric physical shape during the corrosion process. In addition, a "chemical transfer" interface is added to describe the concentration-dependent current distribution.

Parameter definition involves the calculation of the following steps and will affect the accuracy of simulation. The parameter variables involved in the paper are shown in table 1.
Table 1. Main parameter definition.

| Parameter | Value | Description |
|-----------|-------|-------------|
| LD        | 0.009375 kg/m² | Salt load density |
| RH        | 0.97 | Relative humidity |
| sigma     | 11.51 S/m | Electrolyte conductivity |
| d_film    | 1.159E-3 m | Electrolyte film thickness |
| m_salt    | 0.826 mol/kg | Concentration of salt in solution |
| p_sol     | 1035 kg/m³ | Density of salt solution |
| cNaCl     | 854.91 mol/m³ | NaCl concentration |
| d_O2      | 1.9259E-9 m²/s | Diffusion coefficient of O₂ |
| s_O2      | 0.157 mol/m³ | Solubility of oxygen |
| ilim      | 0.101 A/m² | Limiting current density for O₂ |
| Eeq_Fe    | -0.617 V | Equilibrium potential, Fe surface |
| i0_Fe     | 0.056 A/m² | Exchange current density |
| k_Q235    | 8.41 × 106 S/m | Conductivity of Q235 steel |

When electrochemical corrosion of Q235 steel occurs in the ocean atmosphere, iron is oxidized. Since the superpotential is greater than (120/2) mV, the kinetics of electrode reaction is described by the Tafel equation. Equation (4) is the cathode Tafel equation. Equation (5) is the anode Tafel equation.

\[
\log(I_a) = \log(I_0) + \frac{\beta nF}{2.3RT} \eta
\]  
\[
\log(I_c) = \log(I_0) - \frac{\alpha nF}{2.3RT} \eta
\]

Where, \(I_a\) and \(I_c\) are anode and cathode current density respectively; \(I_0\) is the exchange current density; \(\alpha\) and \(\beta\) are charge transfer coefficients, \(\alpha + \beta = 1\); \(n\) is charge; \(F\) is Faraday constant; \(\eta\) for overvoltage; \(R\) is the ideal gas constant; \(T\) is the absolute temperature of the reaction.

On the surface of the metal electrode, oxygen undergo a reduction reaction, and the oxygen transport in the film should be limited. The ultimate current density, \(I_{lim}\) (international unit A/m²), depends on the thickness of the electrolyte film, the solubility of oxygen, and the diffusion rate of oxygen. The correlation expression is:

\[
I_{lim} = \frac{4F \times D_{O2} \times S_{O2}}{d_{film}}
\]

Where, \(F\) is Faraday constant (96485C/mol), \(D_{O2}\) is the diffusion rate of oxygen in the film (m²/s). \(S_{O2}\) is the solubility of oxygen (mol/m³). \(d_{film}\) is the thickness of electrolyte film (m). The oxygen diffusion coefficient is related to the concentration of sodium chloride in electrolyte solution and the oxygen solubility and the thickness of electrolyte film are related to the relative humidity of atmosphere.

When studying the corrosion process through the kinetics equation of electrode process in simulation software, in addition to setting the exchange current density and the limit current density, it is also necessary to calculate the anode and cathode tafel slopes. The calculated formulas of anode tafel slope \(b_a\) and cathode tafel slope \(b_c\) are shown in equations (7) and (8).

\[
b_a = \frac{2.3RT}{βF}
\]  
\[
b_c = -\frac{2.3RT}{αF}
\]

When creating the geometric model, some secondary factors can be ignored and simplified reasonably, so as to reduce the difficulty of mesh generation and solution process. The two-dimensional
model established in this paper is shown in figure 2. In the atmospheric environment, the thickness of electrolyte film is generally 1μm~1mm[6]. Since the atmospheric relative humidity set in this paper is large (≥95%), the thickness of electrolyte film is set to 1mm, and the width of metal surface is set to 15mm.

![Figure 2. Build a two-dimensional model.]

The application of different mesh density in different regions can improve the calculation accuracy while reducing the calculation amount. Due to the small size of the model established in this paper, the cell size is ultra-refined.

3.2. Simulation results and analysis

In the two-dimensional model in this paper, the corrosion process is mainly reflected by such parameters as electrolyte potential, electrolyte current density and changes in electrode thickness, and the corrosion rate can be reflected by changes in the position of the right interface of electrolyte (solution/metal junction). When corrosion begins, the distribution of electrolyte potential is shown in figure 3. The distribution of electrolyte potential after one year of corrosion is shown in figure 4.

By comparing figure 3 and figure 4, it can be seen that the position of the interface on the right side of the electrolyte has changed, gradually moving to the right, indicating that the metal is gradually corroded. Electrochemical corrosion occurs, in figure 3 solution/metal on the right side of the border, metal oxidation reaction happened, losing electrons, the electrons could participate in the cathodic reduction reaction, thus electronic began to gather, the potential rise here, and on the left side of the solution do not react with the atmosphere border, so the potential is zero, and potential from right to left to decline. After a year the junction becomes more positive, indicating that the negative charge is accumulating and the reaction rate is increasing.

![Figure 3. Electrolyte potential distribution at the beginning of corrosion.](image1)

![Figure 4. Electrolyte potential distribution after one year corrosion.](image2)

Figure 5 shows the changes in electrode thickness at different locations one year later. It can be seen from the figure that, when the temperature is 25℃, relative humidity is 95% and sodium chloride concentration is 3.5%, the simulated average corrosion rate of Q235 steel is about 287.1 μm/a. In the figure, it can also be found that the Q235 steel electrode with a length of 15mm is mainly subject to uniform corrosion. The corrosion degree at both ends is slightly more severe than that at the middle part, and the corrosion degree in most areas is consistent.
Figure 5. Change of electrode thickness after corrosion for one year.

Figure 6 shows the changing trend of electrode corrosion thickness over time. It can be seen from the figure that when the multiphysics simulation software conducted atmospheric corrosion simulation, the corrosion thickness was linearly related to time, indicating that the influence of corrosion products and environmental changes was ignored in the simulation process, which would also affect the accuracy of simulation results.

Figure 6. Electrode corrosion thickness varies with time.

An important factor affecting the corrosion process is the limiting current density, which reflects the degree to which the electrode reaction is controlled by the diffusion step. The higher the value, the more reductants are diffused to the double layer for the reaction, and the better the electrochemical reaction can be satisfied. The relationship between the limiting current density and the corrosion rate is shown in figure 7. It can be seen from figure 7 that with the increase of the ultimate current density, the electrochemical reaction rate increases and the corrosion rate of the metal increases.

Figure 7. The relationship between limit current density and corrosion rate.

4. Conclusion
By simulating the oceanic and atmospheric corrosion of Q235 steel in multiphysics simulation software, the distribution of electrolyte potential and current density in the corrosion process can be intuitively
understood, and it is found that there is a small electric current inside the electrolyte film, which is formed by the movement of ions inside the film. It is also found that the corrosion rate decreases with the increase of exchange current density in a certain condition.

The simulated corrosion rate (200~400 m/a) is consistent with the results of the actual exposure test[7], which has certain reference significance. The simulation study of metal materials can provide theoretical basis for the application of Q235 steel on ships and Marine structures and the study of corrosion protection.

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