

STUDY ON ATMOSPHERIC CORROSION BEHAVIOUR AND MECHANISM OF Q235 STEEL AFTER PASSIVATION

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Q235 steel components have poor corrosion resistance and are susceptible to erosion by corrosive media, so they are generally passivated before being put into service. This paper investigates the corrosion behaviour and corrosion mechanism of passivated Q235 steel in atmospheric environments through macro and micro morphological characterisation and electrochemical simulation analysis.

Keywords: Q235 steel, atmospheric corrosion, surface, results

INTRODUCTION

Q235 steel is widely used in construction, metallurgy, machinery, petroleum and chemical industry due to its good plasticity and welding properties, low cost and good forming ability [1,2]. Compared to stainless steel and alloy steel, Q235 steel parts have poor corrosion resistance and are susceptible to corrosive media intrusion and corrosion damage effects exerted on their surfaces, seriously threatening the service life and material properties of Q235 steel [3-5]. Common types of corrosion include external corrosion represented by pitting and internal corrosion represented by corrosive gas intrusion [6]. Therefore, Q235 steel parts are generally treated against corrosion before they are put into use to produce a passivated film of no more than 10 μ m on the surface, which effectively protects the Q235 steel substrate. However, the passivation film will inevitably show some defects or weak spots due to the quality of the metal surface [7,8]. When Q235 steel materials are exposed to atmospheric conditions, both the passivation film and the weakness of the passivation film have an impact on corrosion behaviour and corrosion rates, and there are no studies on these issues [9,10]. Therefore, research into the corrosion behaviour and mechanism of passivated Q235 steel in typical atmospheric environments is of great significance in improving the life and reliability of Q235 steel materials, and also provides technical and theoretical support for the study of Q235 steel in other corrosive environments.

EXPERIMENTAL AND SIMULATION MODEL

Generally speaking, metal corrosion that occurs in the natural environment is mostly attributed to electro-

chemical corrosion. Among them, atmospheric corrosion can be understood as the contact between the metal material and its surrounding atmospheric environment. Under the action of the electrolyte, the non-uniform parts inside the metal material or between different metal materials form one after another tiny galvanic cells. Each galvanic cell is regarded as a short-circuit electrochemical system, the directional movement of metal ions M^{n+} in the electrolyte, and the flow of electrons lost by the anode between the cathode region and the anode region inside the metal conductor form a closed loop, that is, self-corrosion closed system. Among them, the directional movement of metal ions M^{n+} in the electrolyte forms the so-called corrosion current. Due to the mutual conversion of electrical energy and chemical energy, it is bound to be accompanied by the loss of anode material. With the continuous progress of the reaction, the anode loss continues to intensify, and finally the macroscopic electrochemical corrosion phenomenon occurs.

Q235 steel is generally treated against corrosion before it is put into service, but the corrosion resistant

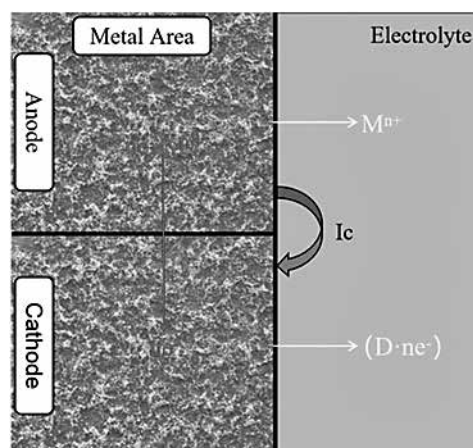


Figure 1 Basic principles of electrochemical corrosion of metals

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layer is highly susceptible to minor defects due to the development of process levels, complex and variable service environments and unexpected factors such as knocks and bumps during use. However, the atmospheric environment contains many corrosive ions. Here the ions are highly adsorptive and destructive and continue to exert a corrosive and destructive effect on the carbon steel passivation film through the thin liquid film, resulting in a localised rupture of the passivation film, with electrolyte penetrating from the defect and coming into contact with the Q235 steel substrate, resulting in electrochemical corrosion. As the corrosion reaction proceeds, the corrosion depth increases rapidly and the corrosion products continue to pile up, generating expansion forces and eventually leading to the corrosion resistant layer falling off, the metal pipe will no longer have the ability to resist corrosion. It is therefore presumed that corrosion of Q235 steel in atmospheric environments tends to start at the point of passivation film defect or weakness.

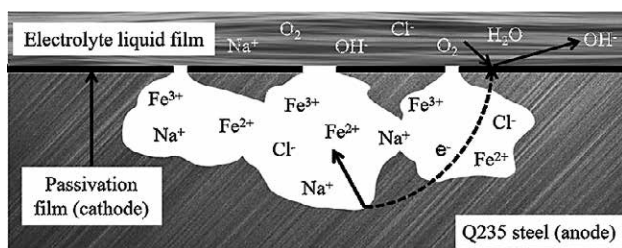


Figure 2 Principle of multiple pitting on metal surfaces

A 2D axisymmetric corrosion model was established in COMSOL Multiphysics software covering electrolyte film, initial corrosion pits and Q235 steel matrix, and was defined using the Tertiary Current Distribution interface and the Nernst-Planck equation. The fundamental mechanism of pit growth is investigated by simulating electrode kinetics, mass transfer and the resulting geometric deformation and dissolution deposition. It is assumed that the formation of corrosion products is irreversible as a homogeneous reaction, and the oxygen-iron mixed potential is constant, that is, not affected by the pitting process. We assume that the concentration of the thin liquid film is fixed under the constant replenishment of the marine atmosphere and that the electrolyte phase potential is set at the top horizontal electrolyte boundary facing the electrolyte body. The kinetics of iron dissolution at the electrode surface is based on the concentration-dependent Butler-Volmer equation, with the exchange current density set to be proportional to the H^+ ion concentration. Furthermore, the etch pit surface is assumed to be porous due to the production of iron hydroxide and other iron-oxygen compounds, and the transport properties of the electrolyte in the pit including ion diffusivity and mobility depend on the porosity of the Bruggeman relation, so that the effective diffusivity in the etch pit is approximately that of the electrolyte body. In addition, due to the high relative humidity of the set marine atmosphere ($\geq 95\%$), the

thickness of the electrolyte film was set to $1\mu\text{m}$ and the initial pit depth at the passivation film defect was set to $5\mu\text{m}$ to highlight the change in pit morphology during corrosion.

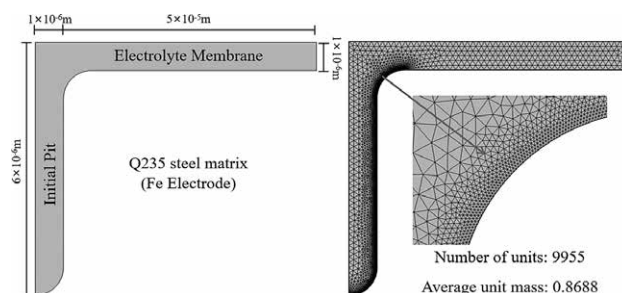


Figure 3 Pitting growth corrosion model and meshing

Considering that the smallest feature size in the model is $1\mu\text{m}$, a more refined free triangular mesh should generally be used when meshing the model for the micron level. Since the geometric model of the pitting crater at the defect changes with time, the surface mesh of the crater is partially refined and an auto-dissecting mesh is chosen, with a total number of 9,955 cells and an average mesh quality of 0,8688. This is shown in Figure 3. The transient solver was selected and the solution range was set from 0 to 20 days, with a solution step of 5 days.

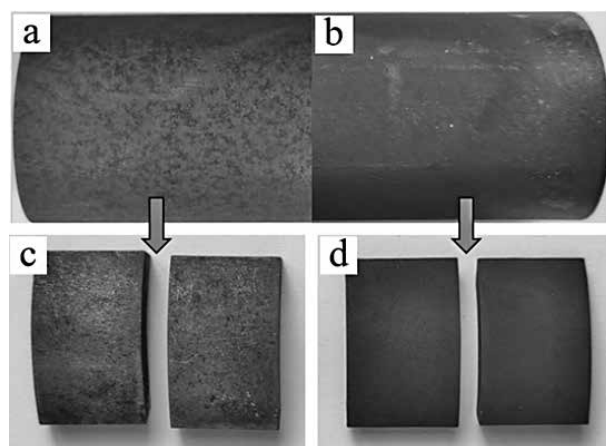


Figure 4 Before and after pickling passivation

In addition, to verify the simulation results, a natural environment exposure pitting test was designed. The specific experimental procedure was to passivate the Q235 steel parts using a special pickling passivation solution to produce a uniform and dense passivation film on its surface. A comparison of the results before and after acid washing is shown in Figure 4. The passivated Q235 steel samples were exposed to the natural environment and the environmental factors were strictly controlled so that no major changes occurred. The surface macro and micro morphology of the samples were observed and recorded every 3 days until multiple pitting occurred on the Q235 steel surface and the test was completed.

RESULTS AND DISCUSSION

Corrosion of the Q235 steel in atmospheric environments often starts with pitting at passivation film defects. In this corrosion model, the corrosion process is mainly reflected by changes in parameters such as electrolyte potential and electrolyte current density, and the corrosion rate can be reflected by changes in the shape of the initial etch pits. As time grows, the geometry of the initial pitting pits deforms as the Q235 steel base material dissolves, and the deformation results are shown in Figure 5. As the material is homogeneous by default, the growth of the crater is a uniform outward “fattening” process, with a distinct convex crater forming beneath the metal surface after 20 days. Where the boundary growth rate is proportional to the matrix dissolution current density, the corrosion rate in the pit increases with time, and in the process of pit growth, the normal phase direction of the current also dissipates outwards. With the gradual expansion of pitting, Q235 steel surface corrosion gradually developed from intergranular corrosion to full-scale corrosion, at the same time, the corrosion products generated by the dissolved Q235 steel matrix at the etch pits will accumulate at the junction of the electrolyte thin liquid film and the substrate, and with the growth of time continue to pile up and expand, until the connection formed a layer of flat corrosion products layer, due to the corrosion products layer dense degree is high, the electrolyte The corrosion product layer will slow down the corrosion process of Q235 steel as it is presumed to be a barrier to the penetration of the electrolyte.

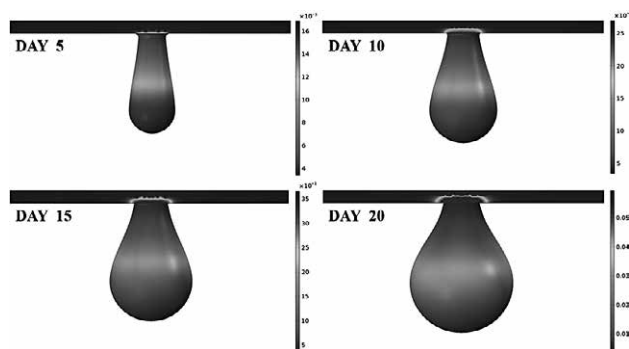


Figure 5 Pitting growth model simulation results

Due to the presence of α -FeOOH, γ -FeOOH and $\text{Fe}(\text{OH})_2$ in the corrosion products and the depletion of hydroxide ions at the bottom of the etch pits, the pH value will be lower near the electrode surface. When the iron oxidation reaction is catalyzed by H^+ ions, i.e. de-passivation, the lower pH value inside the etch pits will accelerate the dissolution of the Q235 steel substrate compared to the metal surface outside the etch pits. In addition, the limiting current density is an important factor affecting the dissolution rate of the electrode, which reflects the extent to which the electrode reaction is influenced by the diffusion of the electrolyte. A higher limiting current density means that more redox dif-

fuses to the electrode surface for the reaction, the stronger the electrochemical reaction and the higher the rate of metal corrosion. Time is also an important factor affecting the electrochemical corrosion rate, using COMSOL software to plot the electrode dissolution rate curve on the surface of the iron electrode at different times, the results are shown in Figure 6. It is not difficult to find that the dissolution rate of the electrode in the pit increases rapidly with time and reaches its maximum at 20 days, which also lays a theoretical foundation for the subsequent natural environment exposure pitting test.

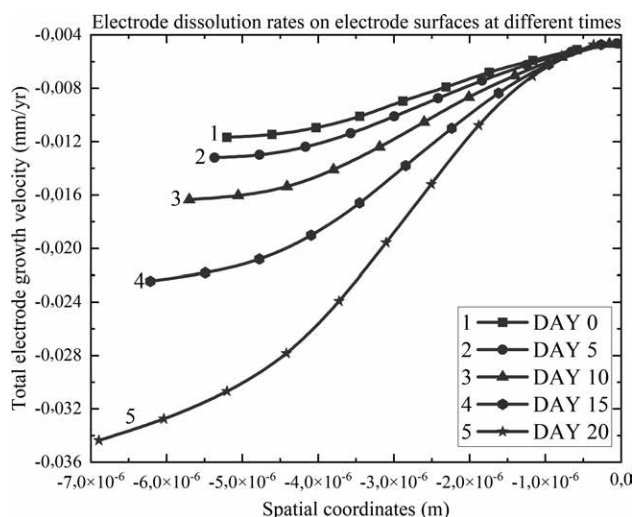


Figure 6 Change in electrode dissolution rate

Pitting is a corrosion area is very small but deep inside the metal corrosion form, its typical characteristics are small diameter and depth, its main forms include narrow body type, oval, wide shallow type, subcutaneous type, bottom cut type, horizontal type and vertical type and so on. In general, the dissolution rate within the pitting hole is quite large, the adhesion of corrosion products will usually cover the pitting crater so that it is not easy to be found, while the loss of metal quality after the occurrence of pitting is also very small, it is difficult to use the amount of wall thickness reduction as a criterion for the occurrence of pitting. Therefore, pitting is very dangerous, often suddenly leading to accidents, is one of the more destructive and hidden local corrosion patterns. The ratio between the maximum corrosion depth of pitting and the average corrosion depth of the metal surface is called the pitting coefficient, which is usually used to describe the metal pitting situation, the larger the pitting coefficient the more severe the pitting.

Figure 7 shows some of the results of the natural exposure pitting test, can be clearly found, Q235 steel surface morphology from the original flat and dense dark black passivation film gradually transformed into yellow-brown and pitting pits all over the form of metal rust layer, with the passage of time, pitting pits have gradually expanded the trend, part of the pits have been connected together. In addition, the corrosion products

within the pits gradually accumulate and rise, and the thickening rust layer exerts an expansion force on the passivation film, forcing the passivation film to fall off and full-scale corrosion occurs.

From the microscopic morphology, the Q235 steel surface shows a random distribution of the location of each corrosion pit, with varying depths of corrosion. This is due to the uncertainty of the location of defects or weaknesses in the surface of the passivation film generated when passivating Q235 steel. The degree of vulnerability also varies from point to point. In other words, at the beginning of corrosion, each pit is exposed to a different content of corrosive media and the initial corrosion rate is not the same, which is why there is a difference in the depth of pitting.

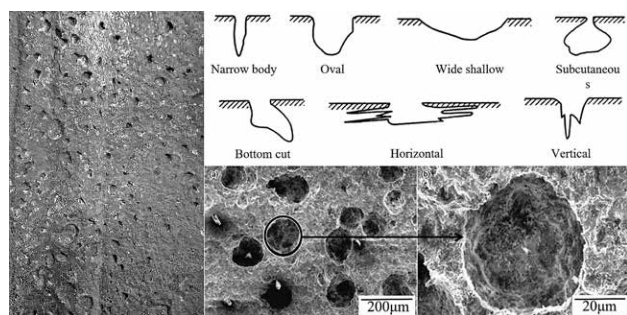


Figure 7 Natural environment exposure pitting test results

However, another phenomenon is very noteworthy, adjacent etch pits connected together, the bottom of the etch pits gradually tends to level off, the gap between the corrosion depth gradually reduced, corrosion tends to smooth. This is due to the rapid increase in the contact area between the metal substrate and the corrosive medium when etch pits are joined together on the metal surface and the effect of the corrosive medium content on the corrosion rate is reduced. Compared to the low concave area on the inner surface of the etch pits, the raised area is exposed to the corrosive medium earlier and the corrosion rate is higher. When the height of the inner surface of the etch pit is close, the corrosion rate tends to be equal. This is another way of verifying that corrosion of passivated Q235 steel in the atmospheric environment is a gradual progression from pitting to full-scale corrosion.

CONCLUSION

This paper investigates the corrosion behaviour and mechanism of Q235 steel in a typical atmospheric environment. Based on the electrochemical corrosion module in COMSOL Multiphysics, a pitting growth model was developed for Q235 steel at passivation film defects. The morphological changes of pitting on the surface of Q235 steel at different stages were investigated

and the results of the simulation were verified by designing a natural environment exposure pitting test to characterise the morphology of the exposed sample parts in detail. It was concluded that corrosion of Q235 steel in a typical atmospheric environment after passivation often starts at the passivation film defect, where pitting occurs under the action of corrosive media such as chloride ions, and gradually progresses from intergranular corrosion to full-scale corrosion over time.

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Note: The responsible translator for English language is Y. BIAN - Hebei Normal University, China