Crack Corrosion Simulation of H62 Copper Alloy Coating Under Damage Condition

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ABSTRACT: Objective To study the crevice corrosion under the condition of damaged coating. Methods The simulation was carried out by using COMSOL software. The influence of the distance between the damage zone (W) and the gap width (H) of the damage zone was discussed. As a result, the corrosion enters the stable corrosion stage after a very short initial stage, and the current is much longer than the stable stage in the initial stage. The electrolyte potential and the electrode potential are completely different in the initial and stable stages; the anode reaction occurs uniformly in the damaged area, and the cathode reaction focuses on the crack mouth in the stable stage; the increase of W and H is aggravated by corrosion, but when W is greater than 0.7mm, the effect is very weak and can be considered to be stable. Conclusion The crevice corrosion under the condition of coating damage is the corrosion controlled by the cathode oxygen reduction reaction. The oxygen is quickly consumed in the initial stage and cannot be replenished. The cathodic reaction is mainly concentrated in the crack mouth. The change of W at small time will affect the corrosion. The increase in H will exacerbate corrosion.

1. The introduction
The corrosion location is relatively concealed, and corrosion and corrosion products will reduce the structural strength and cause connection failure, which not only reduces the service life of structural parts, but also brings hidden safety risks[1-4]. Electric connector is a kind of form in pin jack contact electrical signal connection of electronic equipment, extensive use in all kinds of equipment, to strengthen the contact performance, often with basal materials coating structure, it in actual use, due to the external environment, such as vibration, temperature and humidity and man-made repeatedly plug, scratches, can lead to coating damage, no longer contact, at this time will occur in a suitable environment[5] crevice corrosion phenomena. Especially for the harsh environment of high temperature, high humidity and high salt fog on islands and reefs in the South China Sea, airborne electronic equipment is prone to corrosion, which has become one of the main weak links affecting the period of island stationing[8]. Therefore, the study of this kind of corrosion phenomenon is of great significance to the design and use of corrosion protection.

A great deal of research has been carried out on crevice corrosion. Rosenfeld[9] studied the effect of gap width and depth on the corrosion rate of 2Cr13 stainless steel in 0.5mol/L NaCl solution, and found that the corrosion was most sensitive when the gap width was 0.1 ~ 0.15. M.Abdulsalam[10] studied the influence of temperature change on crack corrosion. A. Conde[11] studied the crack corrosion rate of 304 stainless steel in different concentrations of NaCl solution. Hu Qian[12] studied the crack corrosion of Q235 carbon steel by using electrochemical noise and electrochemical impedance technology, and found...
that the external and internal surface areas of the cracks had an important influence on the breeding and development of the crack corrosion. Fan Yuguang\cite{13} used COMSOL software to simulate crack corrosion of 0Cr18Ni10Ti in 3.5%NaCl solution at 50°C, and the model results were consistent with the experimental values in the literature. Liu Quanbing\cite{14} studied the crack corrosion behavior of X70 pipeline steel in tropical oceanic and atmospheric environment, and the results showed that the closer to the coast, the higher the wind speed, and the higher the atmospheric Cl\textsuperscript{−} deposition rate, the more serious the crack corrosion was.

Most of the literature did not involve contact with the crevice corrosion under the coating damage, because this kind of gap size is small, the environment is relatively sensitive, actual measurement is difficult, but as a new means of numerical simulation, simulation of corrosion is increasingly attention in recent years, therefore the crevice corrosion by software simulation to actual test and research have certain guiding significance. Based on the COMSOL software simulation, this paper studied the crack corrosion behavior under the coating damage, studied the influence of the distance between the coating damage area and the gap and the gap width on the crack corrosion rate, and provided guidance for revealing such corrosion phenomenon.

2. Gap model under coating damage

Common H62 copper alloy is taken as the research object. To simplify the calculation, the model is set as a two-dimensional geometric model, as shown in Figure 1. \( L_1 \) is contact with the electrolyte of crack depth, the boundary of contact area, the upper boundary for the no flux boundary, \( L_2 \) is plating damaged area, to set it as \( a = 0.25 \) mm, \( b = 0.005 \) mm of elliptic damaged structure, \( W \) is the plating broken zone of crack mouth distance, \( H \) is the gap width, the left side to contact with the outside air gaps in the mouth, the right end to the bottom of the gap. The contact part is copper base gold-plated material, the damaged area of the coating is copper, the rest is gold. The free triangular mesh was used to refine the electrode reaction surface.

![FIG.1 Two-dimensional slit model](image)

Coating damage under the condition of corrosion, essence is the gap of galvanic corrosion, compared to a single material corrosion, the corrosion rate faster, faster consumption of oxygen in corrosion stability stage, so in this paper, we consider the early stage of oxygen concentration difference due to corrosion, select the secondary current distribution and loose material physical interface, two-way coupling calculation.

Crack corrosion is affected by a variety of factors, considering the impact of the width of the gap, the distance between the coating damage and the gap, the external electrode potential three factors on the corrosion, because the depth of the gap can be expressed by the coating damage position, so do not do too much consideration. The oxygen environment factor has a great influence on the crack corrosion, considering the actual use environment, given the boundary and the atmospheric oxygen environment fixed by the solution.

3. The boundary conditions

The electrolyte is NaCl solution with a mass fraction of 3.5%, and its conductivity is measured as 5.6 S/m. The gap is in contact with the atmospheric environment, and the oxygen concentration is set as 0.258mol/m\textsuperscript{3}. The oxygen diffusion coefficient in the solution is \( 1.98\times10^{-9}\text{m}^2/\text{s} \).

The electrode dynamics is expressed by Tafel equation.
\[ I_{\text{loc}} = i_0 \times 10^4 \eta \]  

(1)

Where \( I_{\text{loc}} \) is local current density; \( i_0 \) is the exchange current density; \( \eta \) is the amount of deviation of electrode potential; \( A \) is the electrode area. The other parameters are shown in Table 1.

| Materials | Parameter | \( E_{eq} \) (V) | \( i_0 \) (A/m\(^2\)) | \( A \) (mV) |
|-----------|-----------|-----------------|-----------------|---------|
| Cu        |           | 0               | 10\(^{-4}\)     | 100     |
| \( O_2 \) |           | 1               | 10\(^{-3}\)     | -100    |

The cathode reaction exchange current density is affected by oxygen concentration, which satisfies the following relation:

\[ I_{o_2} = c_{o_2} / c_{o_2,0} \times i_0 \times e^{nF/A_{o_2}} \]  

(2)

Where \( c_{o_2} \) and \( c_{o_2,0} \) are the oxygen concentration after the reaction and the initial oxygen concentration; \( A_{o_2} \) is the cathode Tafel slope and \( A_{o_2} = -118 \text{mV} \).

The cathode reaction results in oxygen consumption satisfying the following coupling relation:

\[ R_{o_2} = -i_{\text{loc}} / 4F \]  

(3)

Where \( R_{o_2} \) is the oxygen reaction source term in the electrolyte; \( F \) is Faraday constant and \( F = 96485 \text{C/mol} \). The remaining boundary of the gap conforms to the condition of insulation and no flux.

4. The simulation results

The three parameters of gap width, distance between the damaged area of the coating and the gap and the external electrode potential were scanned by transient study. The simulation results showed that the influence of the external electrode potential on the corrosion was very small, so the influence of the first two parameters on the gap corrosion rate was not analyzed. The distance \( W \) and width \( H \) between the damaged area and the gap are set as shown in the following Table2.

| \( W \) (mm) | 0.4 | 0.7 | 1.0 | 2.0 |
|-------------|-----|-----|-----|-----|
| \( H \) (mm) | 0.1 | 0.15| 0.2 |     |

FIG.2 shows the distribution of electrolyte potential, electrode potential and oxygen concentration in the gap, and the distribution under various geometric dimensions roughly accords with this law. It can be seen from figure 2 (a) and figure 2 (b) that electrolyte potential is completely different between \( t = 0 \) and \( t = 600 \text{s} \) due to the occurrence of corrosion. At the beginning of 0s, electrolyte potential in the damaged area of the coating is the largest and shows a decreasing trend towards both ends, while when the corrosion is stable, its potential distribution increases from the gap to the bottom of the gap. The electrode potential distribution at 2(c) and 2(d) shows that the electrode potential is the smallest in the damaged area of the coating. The electrode potential near the gap at 0s is obviously lower than that in the inside area of the gap. The two situations are completely opposite at 600s, indicating that the metal corrosion situation is different at 0s and 600s. The graph of 2(e) and 2(f) shows the oxygen concentration distribution diagram. It can be seen that the oxygen concentration at the gap decreases rapidly. Due to the occurrence of cathode reaction, the oxygen concentration at the top near the gap is higher than that at the bottom, and gradually decreases towards the bottom right corner. The larger the gap width and the smaller the distance between the damaged area and the gap, the more favorable the oxygen diffusion. In actual situation, due to the significant changes in \( H \) is less, and \( W \) can appear in any position, so \( W \) is more likely to affect the oxygen diffusion, \( W = 0.4 \text{mm} \) can influence on the oxygen concentration makes the crack near the mouth of oxygen concentration variation range is bigger, and \( W = 0.7 \) and above crack mouth internal cathodic reaction can quickly consume oxygen, thus influence on the oxygen concentration distribution hardly.
FIG. 2 Distribution of electrolyte potential, electrode potential and concentration

FIG. 3 shows the influence of the change of \( W \) on the corrosion rate under the condition of \( H=0.2 \text{mm} \). The figure of 3(a) and 3(b) shows the change of anode current density at the beginning and stability. It can be seen that the current density in the damaged area is approximately U-shaped distribution at the beginning, with the current value above 50A/m\(^2\). The minimum value appears at the left of the center first, and gradually approaches the center with the increase of \( W \), and then the current is distributed symmetrically. This is due to the asymmetry of electrode polarization caused by the geometry size, which leads to the asymmetry of current distribution on both sides. The current density at the stable state differs greatly from the initial value, only about 1.5A/m\(^2\). Although the current density increases with the increase of \( W \), when \( W \) is above 0.7mm, the current density does not increase significantly and is basically at a stable value. 3(c) The graph shows the change of current density per second in the initial stage. It can be seen that the current density can quickly reach the stable value within 20s, which indicates that the oxygen in the gap is rapidly consumed in the initial stage of the reaction. 3(d) and 3(e) are the changes of the cathode current density at the beginning and at the stability. At the initial reaction time, the cathode current density is in direct proportion to the size of the cathode area. At the stable reaction time, the cathode reaction is mainly concentrated in the gap, with the current density up to 20A/m\(^2\), which rapidly decreases to close to 0 along the gap. This indicates that a small amount of oxygen diffused into the crevice in the reaction stage is rapidly consumed, and the corrosion reaction is controlled by the concentration of cathode oxygen. Figure 3(f) shows the corrosion thickness under different \( W \). According to the change of anode current, the corrosion can be considered as uniform corrosion over time. Figure 3(g) shows the corrosion thickness after 3 days, with the maximum corrosion thickness up to 0.014mm.
FIG. 3 The effect of $W$ on the corrosion rate at $H = 0.2\text{mm}$

FIG. 4 shows the influence of the change of $H$ on the corrosion rate under the condition of $W=1\text{mm}$. The figure 4(a) and 4(c) shows that the change of $H$ at the initial stage has no influence on the trend of current density change, but with the increase of $H$, the current density also increases, and the trend of increase slows down. This is because the increase of $H$ will lead to a wider range of oxygen diffusion at the gap, but with the increase of $H$, its influence will become more and more slow. 4(b) and 4(d) show that the current density at the initial stage and at the stable stage also have a huge gap, but the influence of $H$ change on the corrosion rate at the stable stage is very small. 4(e) shows the influence of $H$ on the corrosion thickness. More uniform corrosion occurs in the damaged area of the coating and the corrosion thickness increases with the increase of $H$. 

(a) Initial effect of $W$ on anode current density

(b) Steady effect of $W$ on anode current density

(c) Anode current density at steady state

(d) Initial effect of $W$ on the current density of the cathode

(e) Steady effect of $W$ on the current density of the cathode

(g) Corrosion thickness changes after 3 days
5. Conclusion

(1) The corrosion reaction is controlled by the cathode reaction and reaches a stable state quickly. The initial reaction rate of corrosion was much higher than the stable reaction rate, and the oxygen concentration decreased rapidly, so that the cathode reaction under the stable state was mainly concentrated in the gap. The change of the cathode reaction also led to the completely different distribution of electrolyte and electrode potential at the initial and stable state.

(2) The crack corrosion under the coating damage is stable and uniform corrosion with time. The increase of W and H can aggravate the corrosion, but a W of more than 0.7mm will basically have no influence on the oxygen environment of the crevice, so the corrosion rate is in a stable state, while H can have a continuous influence on the corrosion within a certain range.

(3) According to the effect of W and H, the coating can be gradually thickened with the gap in the contact part design; in practice, large gaps should be avoided, such as reducing the number of unnecessary insertions and increasing fixed measures for vibration environment.

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