The study on the corrosion resistance of hot-dip galvanized aluminum coating in simulating the urban utility tunnel environment

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Abstract: The urban utility tunnel is an important infrastructure to ensure the operation of the city. Because the environment in which the urban utility tunnel is located is relatively humid, the steel in this environment is susceptible to electrochemical corrosion. In this paper, the corrosion resistance of weathering steel with hot-dip galvanized aluminum coating in simulating the urban utility tunnel environment is studied. The corrosion resistance of Q345 steel, weathering steel and hot-dip galvanized aluminum coating in the initial immersion of 3.5 wt.% NaCl solution was compared by means of the electrochemical test (polarization test and electrochemical impedance spectroscopy (EIS)). The results show that the hot-dip galvanized aluminum coating can greatly improve the corrosion resistance of the substrate, and this coating can be applied to the urban utility tunnel.

1. Introduction
With the rapid development of urban construction in recent years, the problems of unclear urban underground pipeline construction and low management level have become increasingly prominent. Since municipal pipelines are laid out in the shallow space of the road without planning, in the expansion, reconstruction, and maintenance, the road surface or green space is often destroyed, resulting in frequent "pull link" phenomenon. This not only causes a great economic waste but also leads to the frequent occurrence of pipeline accidents, which greatly affects the safe operation of the city.

Urban utility tunnel refers to the urban underground tunnel space containing two or more pipes, which integrates various engineering pipelines such as electricity, communication, gas, heat supply, water supply, and drainage. It has a special inspection port, hoisting port and monitoring system, and implements unified planning, unified design, unified construction, and management. In the design of the urban utility tunnel, 50 to 100 years of development and expansion space can be reserved according to the urban development plan, to avoid repeated excavation of the road surface [1].

To meet the development planning requirements of the urban utility tunnel for 50 to 100 years, it is necessary to consider the corrosion resistance of the steel for the pipe bracket and ensure the service life of the pipe bracket. Considering the matrix of steel, weathering steel performance is superior to ordinary carbon steel in the utility tunnel, and the cost of use in thousands of kilometers of utility tunnel is acceptable. Considering surface treatment, hot dip galvanizing has been widely used in various industries, and the cost is low, which is beneficial to a large number of applications. The new
multi-purpose hot dip galvanizing alloy has become the main research direction [2~4]. To study the corrosion resistance of weathering steel with hot-dip galvanized aluminum coating in simulating the urban utility tunnel environment, the electrochemical behavior of Q345 steel, weathering steel and hot dip galvanized aluminum coating in the 3.5 wt.% NaCl solution was tested.

2. Experimental materials and methods
Wires were soldered to the back of all electrochemical samples. The samples only left a working area of 1cm×1cm, and the rest part was encapsulated by epoxy resin. The coated sample needs to be cleaned with deionized water, then degreased with alcohol and blown dry with a blower before testing. The uncoated samples were polished with sandpaper before each test. A three-electrode system was selected, the sample was used as a working electrode, the auxiliary electrode was a platinum electrode, and the reference electrode was a saturated calomel electrode (SCE). The polarization curve was tested at a scan rate of 1 mV/s, and the electrolyte was a 3.5 wt.% NaCl solution. The electrochemical impedance spectroscopy (EIS) was performed at a self-corrosion potential with a scanning frequency range of 10 mHz to 100 kHz.

3. Results and analysis
3.1 Polarization curve
Figure 1 and Figure 2 show the polarization curves of hot dip coating, Q345 steel and weathering steel after immersion for different time. Figure 3 shows the results of corrosion potential and corrosion current density obtained by fitting. Comparing the corrosion current density of the three samples after the same immersion time, it can be seen that the corrosion rate of the hot dip coating is the smallest and the corrosion rate of Q345 steel is the largest. All three samples experienced the process of reaching the maximum corrosion current after 48h immersion and then decreasing. This indicates that the initial film and corrosion products formed on the surface of the material protect the material.

![Polarization curve of the hot-dip galvanized aluminum coating in 3.5 wt.% NaCl solutions](image)

Fig.1 Polarization curves of the hot-dip galvanized aluminum coating in 3.5 wt.% NaCl solutions

Among the three samples, the corrosion current density of Q345 steel changed the most, and the corrosion current density decreased at 24h, but then continued to rise after 48h. It shows that the corrosion products formed by Q345 steel play a certain protective role. After 48h, the corrosion products increase, but the subsequent corrosion current continues to increase, indicating that the corrosion products produce later cannot reduce the corrosion rate. Comparing the corrosion current density and potential of weathering steel and hot dip galvanized aluminum coating, the variation trend of the two samples is similar, while the corrosion current density and corrosion potential of hot dip Zn-aluminum coating are less than that of weathering steel. It is proved that the coating does protect the substrate.
3.2 Electrochemical Impedance Spectroscopy (EIS)

Figure 4-6 shows the EIS results of Q345 steel, weathering steel and hot dip galvanized aluminum coating after different immersion time in 3.5 wt.% NaCl solution. At the initial stage of immersion, the surface of the sample is exposed to the bare state. The main corrosion process is anodic dissolution. The Nyquist diagram of Q345 steel and weathering steel is expressed as single-capacity arc resistance, which can be fitted by the equivalent circuit diagram of Figure 7(a). The equivalent circuit consists of the following three components: $R_{ct}$ represents the charge-transfer resistance, and Phase angle element CPE2 represents the capacitance generated by the electric double layer. $R_s$ is the solution resistance. As the immersion time is prolonged, the rust layer begins to appear on the surface of the sample. It can be seen that the arc of the high frequency region of the Nyquist diagram of Q345 steel is not obvious, and the arc is elongated and deformed. The low-frequency zone of the weathering steel impedance spectrum exhibits a distinct 45° line and has begun to superimpose the Warburg impedance. This indicates that the reaction rate is now controlled by the diffusion rate, and the greater the Warburg impedance, indicating that the diffusion has a stronger inhibitory effect on the reaction. The equivalent circuit diagram in Figure 7(b) should be used for fitting, where $Z_W$ is the Warburg impedance.

![Nyquist plot and Bode plot of the Q345 steel in 3.5wt.%NaCl solutions](image-url)
After soaking for 24h, the coverage area of corrosion products gradually expanded as the immersion time prolonged, and the linear slope of the low frequency zone of Q345 steel gradually increased, indicating that the impedance value decreased, and the oxygen diffusion rate was increased. The slope of the low frequency zone of weathering steel decreases first and then increases, which may be related to the accumulation and shedding of corrosion products. After 72h, the $R_{ct}$ and Warburg impedance values of Q345 steel decreased to the minimum value since immersion, which indicates that the corrosion product of Q345 steel does not slow down the corrosion rate and this result is consistent with the polarization curve. While the resistance values of $R_{ct}$ and Warburg impedance of weathering steel reached the maximum value since immersion, indicating that the corrosion rate slowed down by the corrosion products of weathering steel, which is also consistent with the variation of polarization curve.

![Fig.5 Nyquist plot and Bode plot of the weathering steel in 3.5wt. % NaCl solutions](image)

It shows that there are two obvious time constants in the Bode diagram of the hot dip galvanized aluminum coating soaked for 1h. The high-frequency partial capacitive arc corresponds to the surface of the Zn-Al alloy oxide film, and the low-frequency capacitive arc can reflect the properties of the coating. This can be fitted by the equivalent circuit diagram in Figure 7(c). The equivalent circuit consists of the following components: $R_r$ is oxide film resistance or corrosion product film resistance $CPE_1$ is the capacitance of the oxide film or corrosion product film, $R_{ct}$ is the coating charge transfer resistance, $CPE_2$ is the capacitance of the electric double layer. After soaking for 24 hours, since the peak is hardly seen at high frequencies in the Bode diagram, Fig. 7(d) is used for fitting. The fitted $R_r$ value and the Warburg impedance value are both small, indicating that the surface of the Zn-Al alloy oxide film is almost completely corroded. After 48h, there is an inconspicuous high-frequency peak in the Bode diagram. Corresponding to the corrosion product film of the coating, it needs to be fitted with the Figure 7(c). The $R_r$ value after 48h is higher than the $R_r$ value at 1h. It shows that the corrosion product film of the coating has better protection ability. After immersion for 48h, the $R_{ct}$ is greatly reduced compared with the initial immersion, indicating that the first 48h of immersion is the fastest stage of corrosion rate. The macroscopic phenomenon at this stage is that the rust layer begins to appear at the sample and the area of the rust layer gradually increases. The $R_r$ and $R_{ct}$ values after immersion for 72h-120h continued to decrease, but the rate slowed down, which indicates that the coating had entered a stable stage.
Fig. 6 Nyquist plot and Bode plot of the hot-dip Zn-Al coating in 3.5wt. % NaCl solutions

Fig. 7 Electrical equivalent circuit models after different soaking times: (a) Q345 steel (0.5-1h), weathering steel (0.5h); (b) Q345 steel (24-72h), weathering steel (1-72h); (c) hot-dip galvanized aluminum coating (1h, 48-120h) and (d) hot-dip galvanized aluminum coating (24h)

Table 1 EIS fitting results of the three specimens in 3.5wt.% NaCl solutions.

| Sample                   | t/h | \( R_\text{ct} (\Omega \cdot \text{cm}^2) \) | \( \text{Y}_0 (S \cdot \text{sec}^{-0.5} \cdot \text{cm}^{-2}) \) |
|--------------------------|-----|---------------------------------|---------------------------------|
| Q345 steel               | 0.5 | -                              | 479                             |
|                          | 1   | -                              | 699                             |
|                          | 24  | -                              | 522                             |
|                          | 48  | -                              | 574                             |
|                          | 72  | -                              | 489                             |
| weathering steel         | 0.5 | -                              | 581                             |
|                          | 1   | -                              | 354                             |
|                          | 24  | -                              | 259                             |
|                          | 48  | -                              | 295                             |
|                          | 72  | -                              | 424                             |
| hot-dip galvanized       | 1   | 62                             | 8825                            |
| aluminum coating         | 24  | 25                             | 6392                            |
|                          | 48  | 457                            | 4461                            |
|                          | 72  | 347                            | 4026                            |
|                          | 120 | 270                            | 3676                            |

4. Conclusion
In this study, the corrosion resistance of hot dip galvanized aluminum coating + weathering steel was analyzed by means of electrochemical test. Based on the above results, it can be concluded: Q345 steel corrosion product has little protection to the substrate after immersion for 72 hours, while the corrosion products of the weathering steel slow down the corrosion. The impedance modulus of the weathering steel in the Bode diagram is higher than those of Q345 steel, which means that the corrosion resistance of the weathering steel is better than that of Q345 steel. The corrosion current...
density of hot dip galvanized aluminum coating is lower than weathering steel, and the impedance modulus of hot dip galvanized aluminum coating is higher. It shows that the hot dip galvanized aluminum coating can greatly improve the corrosion resistance of the substrate. This method of hot dip galvanizing aluminum coating on weathering steel can be applied to the selection of urban utility tunnel.

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