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Short Communication

Corrosion Behaviour of Hot-dip Galvanized Steel Treated by Electrolyte Containing Lanthanum-salts in Simulated Concrete Pore Solution

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The passivation treatment for bare hot-dip galvanized steel (HDGS) which is widely used as construction material was carried out by immersion in conventional lanthanum salt solution and improved lanthanum salt solution containing citric acid respectively. The corrosion behaviour of passivated HDGS in simulated concrete pore solution was studied. The results show that the passivation films prepared on the surface of HDGS from conventional lanthanum salt solution and improved lanthanum salt solution both present similar morphology and are mainly composed of Zn, La, C and O elements, which can hinder the corrosive medium contact with HDGS and effectively inhibit the electrochemical corrosion. The corrosion current density of passivation film prepared from the improved lanthanum salt remains at a low level and gradually tends to be constant with the extension of immersion time. Compared with the conventional lanthanum salt passivation film, the improved lanthanum salt passivation film has a more uniform surface, better corrosion resistance and ideal durability, which can protect HDGS well and improve its corrosion resistance in simulated concrete pore solution.

Keywords: Simulated concrete pore solution; Hot-dip galvanized steel; Lanthanum salt passivation; Corrosion behaviour

1. INTRODUCTION

Hot-dip galvanized steel (HDGS) is smooth with decent corrosion resistance, which is widely used as industrial building structures to form concrete structures and play a supporting role [1-4]. However, the HDGS is easy to rust in the alkaline environment of concrete for a long time due to the corrosion of various media such as chloride ion, sulfate and calcium hydroxide, which affects its service life. Many kinds of surface treatment can be used to improve the corrosion resistance of

HDGS, such as electrodeposition, passivation treatment and so on [5-9]. Meanwhile, passivation treatment of HDGS is a kind of simple and effective surface treatment approach [10-12].

For a long time, chromate solution is usually used for passivation treatment of HDGS. Although the effect is good, chromate solution is highly toxic and will cause serious harm, and will be gradually replaced by environmental protection passivating solution.

In recent years, some scholars have carried out some researches on the passivation treatment of HDGS from rare earth salts solution, such as cerium salt solution [13-14]. Lanthanum salt also belongs to the category of rare earth salts which are stable and cheap. It is significant to carry out research in this area, so as to further improve the corrosion resistance of HDGS in concrete environment. In this paper, the passivation treatment of HDGS commonly used as construction material was carried out by immersion in conventional lanthanum salt solution and improved lanthanum salt solution containing citric acid respectively, and corrosion behaviour of the passivated HDGS in simulated concrete pore solution was studied.

2. MATERIALS AND METHODS

2.1 Pre-treatment of HDGS

The HDGS selected in the experiment is a 20 μ m thick zinc layer on the surface of the Q235 steel substrate, which is cut into 50 mm × 24 mm samples. The pre-treatment process of the sample is as follows: (1) The substrate is immersed in a mixed solution of sodium hydroxide (45 g/L) and sodium carbonate (10 g/L) at 65 °C for 8 min to remove oil; (2) After cleaning, the substrate is immersed in hydrofluoric acid at room temperature (volume fraction 10%) for 1 min activation; (3) The substrate is repeatedly rinsed with deionized water; (4) Finally, the substrate is dried in a drying oven.

2.2. Passivation treatment of HDGS in lanthanum salt solution

Conventional lanthanum salt solution and improved lanthanum salt solution were prepared respectively. The main composition and operating conditions were shown in Table 1. Among them, the improved lanthanum salt solution is prepared by adding a proper amount of citric acid to the conventional lanthanum salt solution. The specific steps of lanthanum salt passivation treatment of HDGS were as follows:

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Chemical agent and conditions	conventional lanthanum salt	improved lanthanum salt
	solution	solution
lanthanum nitrate/	24	24
$(g \cdot L^{-1})$		

hydrogen peroxide/	9	9
$(mL \cdot L^{-1})$		
citric acid/ $(g \cdot L^{-1})$	—	12
temperature/ °C	74	74

First step: The pre-treated sample is suspended and immersed in conventional lanthanum salt solution and improved lanthanum salt solution respectively. Multiple reactions occur to form a layer of conventional lanthanum salt passivation film (CLSPF) and improved lanthanum salt passivation film (ILSPF) covered on the surface of HDGS.

Second step: Take out the sample after passivation for 10 min and clean it with deionization and then dry it in a constant temperature drying oven.

2.3. Preparation of simulated concrete pore solution

Saturated calcium hydroxide solution was selected, and an appropriate amount of sodium hydroxide was added to adjust the pH value to about 12.5. Then, 0.015 mol/L sodium chloride and 0.005 mol/L sodium silicate were added to prepare a simulated concrete pore solution. The mixture solution was evenly mixed and left to stand for 24 h.

2.4 Characterization and performance test of different passivation films

2.4.1 Surface morphology and composition characterization

The surface morphology of HDGS and different passivation films were characterized by scanning electron microscopy (SEM) with Quanta FEG450 equipped with X-MAX 80 energy spectrometer.

2.4.2 Corrosion testing

The passivated HDGS was processed into a sample with an exposed area of 1 cm^2 , and the wire was welded on the back to make a working electrode that met the requirements of electrochemical corrosion testing. The reference electrode was a saturated calomel electrode, and the auxiliary electrode was a platinum electrode. The reference 600 electrochemical workstation was used to test the polarization curves of passivated HDGS after immersion in simulated concrete pore solution at 25°C for different time (0~12 days), and the polarization curves of HDGS were also tested as comparison. The tests were carried out at open circuit potential, the scan rate of the polarization curve was 1 mV/s, and the scan potential range was -300 mV to +300 mV. The corrosion potential and corrosion current density were obtained by fitting the test data. According to the equation given in the reference [15], the protection efficiency of CLSPF and ILSPC on HDGS was calculated. Combined with the corrosion morphology, the corrosion behaviour of passivated HDGS in simulated concrete pore solution was evaluated.

$$\eta = \frac{J_{corr}^{HDGS} - J_{corr}^{Film}}{J_{corr}^{HDGS}} \times 100\%$$
(1)

Where, J_{corr}^{HDGS} represents the corrosion current density of HDGS, and J_{corr}^{Film} represents the corrosion current density of CLSPF or ILSPC, the unit is A/cm².

3. RESULTS AND DISCUSSION

3.1 Surface morphology and composition of different passivation films

Figure 1 shows the surface morphology of bare HDGS and different lanthanum salt passivation films. By comparing Figure 1(a), Figure 1(b) and Figure 1(c), it is found that different passivation films prepared on bare HDGS using conventional lanthanum salt solution and improved lanthanum salt solution both show similar morphology characteristics. Some cracks are formed on the surface. This similar morphology of passivation film has been reported in some literatures [16-18]. For example, Kong prepared a kind of lanthanum salt passivation film with crossed cracks morphology which is a little bit different from the passivation prepared in the paper due to different temperature and different concentration of citric acid [19].

Compared with CLSPC, the surface of ILSPC has finer gaps and better uniformity. This increases the resistance of the corrosive medium penetrating into the passivation film to contact with HDGS, which is beneficial to improve the corrosion resistance. The reason is that citric acid combines with lanthanum ions in the solution to form $La(H_2Cit)^{2+}$, which adsorbs on the surface of HDGS during the passivation reaction and plays a certain role in inhibiting corrosion, which weakens the dissolution process of passivation film, thereby forming a more uniform passivation film.



Figure 1. Surface morphology of bare HDGS and different lanthanum salt passivation films

EDS spectra and surface element distribution of different passivation films are shown in Figure 2. Combined with Figure 2(a) and Figure 2(b), it can be seen that the main composition of both CLSPC and ILSPC are Zn, La, C and O elements, and each element is evenly distributed without obvious aggregation phenomenon. Compared with CLSPC, the mass fraction of Zn element in ILSPC decreases while the mass fraction of La element increases. This is because the complex formed by the

interaction of citric acid and lanthanum ions is also involved in the passivation film formation process, which makes ILSPC more uniform and compact resulting in the increase of the mass fraction of La element.



(b) ILSPS

Figure 2. EDS spectrum and surface element distribution of different lanthanum salt passivation films

3.2 Corrosion behaviour

3.2.1 Polarization curves analysis

Figure 3 shows the polarization curves of bare HDGS and different lanthanum salt passivation films immersed in simulated concrete pore solution for different time. It can be seen from Figure 3 that, immediately after immersion, the polarization curves of CLSPS and ILSPS are lower right than that of HDGS, indicating more positive corrosion potential and smaller corrosion current than that of HDGS. After immersion in simulated concrete pore solution for 3 day, the polarization curves of HDGS, CLSPS and ILSPS all shift upward to the left, and the corrosion current density increases, indicating the decrease of corrosion resistance. With the extension of immersion time, although the polarization curves of HDGS, CLSPS and ILSPS and ILSPS continue to shift upward to the left, the corrosion current density of CLSPS and ILSPS are still lower than that of HDGS, and the corrosion current density of ILSPS is the lowest. The growth and corrosion behaviour of lanthanum salt passivation film is explained in detail in some papers [20-22].



Figure 3. Polarization curves of bare HDGS and different lanthanum salt passivation films immersed in simulated concrete pore solution for different time

Figure 4 shows the variation tendency of the corrosion potential of HDGS and different lanthanum salt passivation films, and Figure 5 shows the variation tendency of corrosion current density of HDGS and different lanthanum salt passivation films. As can be seen from Figure 4, with the extension of immersion time, the corrosion potential of HDGS and different lanthanum salt passivation films change less. As can be seen from Figure 5, immediately after immersion, the corrosion current densities of HDGS, CLSPS and ILSPS are 2.23×10^{-6} A/cm², 6.38×10^{-7} A/cm² and 3.68×10^{-7} A/cm², respectively. However, the corrosion current density of HDGS and different lanthanum salt passivation films show significantly different trends with the extension of immersion time. Among them, the corrosion current density of HDGS shows a significant increase trend. The corrosion current density of CLSPS increases slightly, while the corrosion current density of ILSPS tends to be constant gradually.



Figure 4. Variation tendency of the corrosion potential of bare HDGS and different lanthanum salt passivation films



Figure 5. Variation tendency of the corrosion current density of bare HDGS and different lanthanum salt passivation films

The reason is that at the initial stage of immersion in simulated concrete pore solution, both CLSPS and ILSPS remain intact, thus preventing the contact between corrosive medium and HDGS which can effectively inhibit electrochemical corrosion. Their corrosion current density is lower than that of HDGS. With the extension of immersion time, the integrity of CLSPS is damaged to a large extent, which make the corrosion medium easy to contact HDGS for electrochemical reaction, thus showing the increase of corrosion current density. However, the integrity of ILSPS is lightly damaged, and it can still effectively prevent the corrosive medium from contacting HDGS and inhibit electrochemical corrosion current density.

Figure 6 shows the variation tendency of the protection efficiency of different lanthanum salt passivation films on bare HDGS after immersion in simulated concrete pore solution for different times. According to the protection efficiency, the protection effect of the passivation film on HDGS can be judged. In general, the higher the protection efficiency, the better the passivation film can protect the substrate [23-25]. The protection efficiency is often used to evaluate the corrosion resistance of materials reported in some literatures [26-28]. It can be seen from Figure 6 that, immediately after immersion, the protection efficiency of CLSPS and ILSPS on HDGS is 71.4% and 83.5%, respectively. With the extension of immersion time, the protection efficiency of ILSPS shows a slight upward trend. In the initial stage of immersion in simulated concrete pore solution, both CLSPS and ILSPS remain intact, which can effectively hinder the corrosive medium and inhibit electrochemical corrosion, so their protection efficiency for HDGS is higher. With the extension of immersion time, the integrity of CLSPS is largely destroyed, while ILSPS can still effectively prevent the corrosive medium from contacting HDGS and inhibit electrochemical corrosion.



Figure 6. Variation tendency of protection efficiency of different lanthanum salt passivation films on bare HDGS after immersion in simulated concrete pore solution for different time

However, when immersed in simulated concrete pore solution for the same time, the corrosion current density of ILSPS is significantly lower than that of CLSPS, and the protection efficiency for HDGS is higher, reflecting that ILSPS has good corrosion resistance and ideal durability. Due to the

better surface uniformity, ILSPS can effectively hinder the corrosive medium to inhibit electrochemical corrosion, play a good role in protecting HDGS and improve the corrosion resistance in simulated concrete pore solution.

3.2.2 Corrosion morphology analysis

Figure 7 shows the corrosion morphology of bare HDGS and different lanthanum salt passivation films after immersion in simulated concrete pore solution for different time. After immersion in simulated concrete pore solution for 3 days, mild corrosion found on the surface of HDGS, and some white particles are formed. The corrosion degree of CLSPS and ILSPS is lighter. Although a small amount of white particles are attached, the surface uniformity and integrity are not damaged. With the extension of immersion time to 12 days, the corrosion degree of HDGS is significantly increased, and the surface appears serious ablation. The uniformity and integrity of the surface of CLSPS are greatly damaged, and the local parts are severely damaged. The increased corrosion degree leads to wider gaps and more white particles attached to the surface, and the ability to hinder the corrosion medium is reduced. The surface uniformity and integrity of ILSPS is less damaged, and it can still effectively hinder the contact between the corrosive medium and HDGS to play a better protection role. The similar corrosion morphology of lanthanum salt passivation films has also been investigated by Kong [29].



bare HDGS

CLSPF (b) immersed for 12 days

ILSPF

Figure 7. Corrosion morphology of bare HDGS and different lanthanum salt passivation films after immersion in simulated concrete pore solution for different time

4. CONCLUSIONS

(1) Conventional lanthanum salt passivation film and improved lanthanum salt passivation film with complete coverage and special morphological characteristics were prepared on the surface of bare hot-dip galvanized steel by passivation treatment. They are mainly composed of Zn, La, C and O elements with uniform distribution. Compared with conventional lanthanum salt passivation film, the surface of improved lanthanum salt passivation film has finer gaps and better uniformity, and shows better corrosion resistance in simulated concrete pore solution.

(2) Corrosion current density of conventional lanthanum salt passivation film increases slight firstly and then increase greatly with the extension of immersion time. However, the corrosion current density of improved lanthanum salt passivation film gradually tends to be constant. The protection efficiency of conventional lanthanum salt passivation film for hot-dip galvanized steel increases first and then decreases greatly, while the protection efficiency of the improved lanthanum salt passivation film for hot-dip galvanized steel increases slightly. The improved lanthanum salt passivation film has ideal durability, which can protect hot-dip galvanized steel well and improve its corrosion resistance in simulated concrete pore solution.

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