Influence of chloride ion on depassivation of passive film on galvanized steel bars in concrete pore solution

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HIGHLIGHTS

- The critical chloride value of the passive film on galvanized steel was determined.
- The depassivation mechanism of the galvanized steel bars was interpreted by the PDM.
- The corrosion products mitigated the further corrosion of the galvanized coating.

ARTICLE INFO

ABSTRACT

This work aimed at studying the depassivation mechanism of the passive film on galvanized steel bar in concrete pore solution with different concentrations of chloride ion. The results showed that in a saturated $Ca(OH)_2$ solution, the critical chloride values for the depassivation of the passive films formed on galvanized steel bars and zinc metal specimens were 0.2 M and 0.3 M respectively. When the Cl^- concentration was lower than the critical value, the donor density of the passive film increased and thus the protective property reduced with increasing the concentration of chloride ion, which could be interpreted by the point defect model (PDM). The corrosion products formed on the galvanized steel surface could inhibit the further ingress of the chloride ions and enhance the protective property, while such effect was not obvious for the zinc metal.

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1. Introduction

Hot-dip galvanized steels are becoming widely used in building structures, automobiles and other industrial structures to improve the corrosion resistance of carbon steel exposed to aggressive environments [1–3]. One of the most important applications is the usage in reinforced concrete structures to prolong the service life and large numbers of research studies have been done on the corrosion performance of the galvanized steel in concrete, which is different from the performance in atmosphere environments.

According to the previous studies on the galvanized steel bars in concrete, a critical stage, passivation stage, should be added into the corrosion model [4], which is also called the "initial corrosion" stage of the galvanized steel bars as reported in the literatures [5–7]. The modified model of galvanized steel in concrete is shown in Fig. 1. Many researchers have focused on the passivation process of galvanized steel bars in simulated concrete pore solutions as well as in concrete. Andrade and coworkers [6–8] investigated the influence of pH values of the simulated concrete pore solutions on the initial corrosion of galvanized steel, indicating that the passivation process and the corrosion products varied with the pH value and the passivation mechanism was also proposed. Arenas and Sanchez [9,10] studied the influence of conversion (cerium and lanthanum) coating on passivation of galvanized steel in concrete pore solution and found that the conversion coating changed the early stage corrosion process of the galvanized steel bars in concrete. Tittarelli [11] showed that the presence of oxygen improved the passivation process of galvanized steel bars in concrete and in simulated pore solutions. Therefore, the passivation process of the galvanized steel in concrete could be influenced by many factors, such as pH values of the pore solutions, surface condition and elemental composition of the galvanized coating, oxygen concentration etc.

In addition, a number of studies focusing on the passivation process of the galvanized steel bars with the presence of chloride

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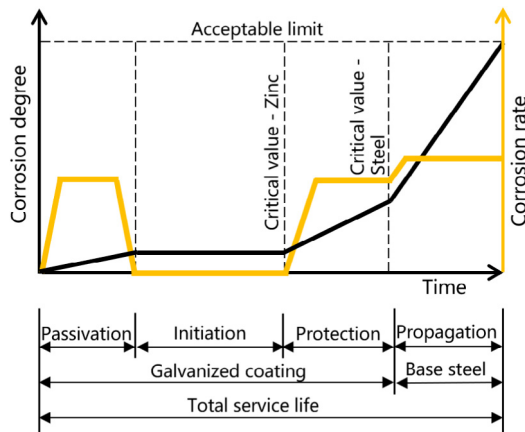
Fig. 1. Corrosion model of galvanized steel bars in concrete during the total service life.

ions have also been reported [12–14]. Ramirez [12] and Haran [15] investigated the behavior of galvanized steel in concrete pore solutions with and without the presence of chloride ions and found that the chloride ion accelerated the breakdown of the passive film. Actually, the galvanized steel was firstly passivated in the fresh concrete mixture without the presence of the chloride ions and then the chloride ions penetrated from the outside to the steel bars only after a long-period of time. Darwin [16] and Bautista [17] simulated the real condition to compare the critical chloride threshold values of galvanized steel and conventional carbon steel in concrete by monitoring the galvanic current. They found that the galvanized steel bars showed a higher critical value than that of the conventional steel and significantly delayed the appearance of high corrosion rates.

However, the depassivation process of the passive film on the galvanized steel could not be considered in the above studies conducted in concrete specimens, due to the complexity of the concrete material. Besides, the corrosion resistant property and the depassivation mechanism of the passive film formed on the galvanized steel bars in concrete was much less separately reported in the previous studies. This aspect is critical to understand the role of the galvanized coating on the anti-corrosion performance of the galvanized steel bars in concrete. Therefore, the present study investigated the influence of the chloride ion on the depassivation mechanism of the passive film formed on the galvanized steel bars in concrete pore solution, which could provide an in depth understanding of the corrosion mechanism of galvanized steel bars in concrete.

2. Experimental program

The galvanized steel specimens (Φ 10 mm $\times$ 30 mm) were cut from the galvanized steel bars which were provided by a supplier in Hong Kong. The substrate carbon steel was a S275J0 (EN 10025-2: 2004) hot rolled steel round bar with a diameter of 10 mm, which was dipped in the zinc bath (445–450 °C) for 4 min resulting in a zinc coating of about 90 μm in thickness. The chemical compositions of the molten zinc bath are shown in Table 1. A copper wire was soldered to one end of the galvanized steel bar and then the

two ends were sealed with silicone sealant leaving an exposed area of 5 cm². A pure zinc (99.9%) metal specimen with a dimension of 10 mm $\times$ 10 mm $\times$ 3 mm was also used in the present work to serve as a reference for the galvanized steel bars, which was commonly used to represent the galvanized steel bars in concrete [11,18–20]. It was also soldered with a copper wire and sealed with the epoxy resin leaving an exposed area of 1 cm².

A traditional three-electrode system conducted by a Multi Autolab M 204 electrochemical work station was used to study the electronic properties of the passive films on the galvanized steel bars in the concrete pore solution. The galvanized steel specimens and the zinc plates were used as the working electrode, a platinum plate was used as the counter electrode and a saturated calomel electrode (SCE) with a Luggin capillary was used as the reference electrode. As reported in the literature [21], the surface finish strongly affected the electrochemical test result. Therefore, in order to gain reproducible results, the specimens were grounded in several steps to 1000 grit using emery paper and then degreased with ethanol. They were dried and kept in a desiccator before test.

A saturated Ca(OH)₂ solution, which contained the highest Ca²⁺ concentration compared with other simulated concrete pore solutions, was used to simulate the concrete pore solution to achieve more continuous passive layers on the galvanized steel bars. It was also commonly used to study the corrosion performance of the galvanized steel bars in concrete [11,15]. For the galvanized steel specimens, the original saturated Ca(OH)₂ solution without any further treatment was used. While, for the zinc metal specimens with a higher purity of zinc, the saturated Ca(OH)₂ solution was bubbled with the oxygen gas (99% purity) for 20 min to provide a high concentration of dissolved oxygen and promote the formation of a compact passive film as reported in the literature [11]. A volume of 400 mL of the electrolyte was used in the electrochemical tests mentioned above to meet the requirement of the electrolyte volume to surface area (V/S) ratio as defined in ASTM G31 [22]. The solutions were all sealed with parafilm throughout the whole test to avoid carbonation and water evaporation. All the specimens were immersed for 20 d to form a fully passivated film on the surface, which is widely known as a $Ca(Zn(OH)_3)_2\cdot2H_2O$ (calcium hydroxyzincate) layer [8,9,11,23].

Afterwards, sodium chloride was added incrementally into the solution, namely 0.05 M, 0.10 M, 0.15 M, 0.20 M, 0.25 M, 0.30 M, 0.35 M, 0.40 M. The time interval between each addition of sodium chloride was approximately 12 h to offer a sufficient reaction time between the chloride ions and the specimens. The open circuit potential (OCP) was measured to monitor the surface condition of the specimens in the concrete pore solution. In order to estimate the corrosion rate [24], linear polarization resistance (LPR) with a scanning rate of 0.167 mV/s was tested from −0.01 mV to 0.01 mV respected to open circuit potential. The Electrochemical Impedance Spectroscopy (EIS) test was carried out periodically to monitor the passive state [25] and provide detailed information of the passive film after the addition of sodium chloride for 12 h. An AC signal amplitude of 10 mV and a frequency range from 100 kHz to 10 mHz were used in the EIS test. The EIS data was analyzed by ZsimpWin software. After the EIS test, the electronic property of the passive film, which can be used as an indicator of the general resistance to corrosion [26] and provides additional information of the passive film on metals, was characterized by the Mott Schottky method when the open circuit potential became steady. The

Table 1
Chemical compositions of the molten zinc bath (% w/w).

Zn	Al	Bi	Cd	Cu	Fe	Ni	Pb	Sn
99.41	0.003	0.007	0.0002	0.011	0.027	0.061	0.481	<0.002