

Effect of rebar coating on corrosion resistance and bond strength of reinforced concrete

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Abstract

The objective of this study is to assess the corrosion resistance of zinc-coated and coating effect on the bond strength between concrete and reinforcing steel. Potentiodynamic polarization method was utilized to determine the corrosion rates of carbon steel and zinc in both pH 12 solution and 3.5 wt% NaCl solution. In addition, cylindrical specimens were cast and exposed to 3.5% NaCl solution and a direct current density (0.5 mA/cm^2) was applied to accelerate the corrosion process. Open circuit potential (OCP), direct current polarization resistance were obtained to evaluate the rebar corrosion.

Potentiodynamic polarization curves show that the corrosion rate of zinc is higher than carbon steel in pH 12 solution but lower in 3.5% NaCl solution. The bond strength of uncoated rebar is 5–10% less than zinc-coated rebar before aqueous immersion test. The bond strength decreases with an increase in corrosion rate for uncoated rebar and zinc-coated rebar. After 14-days accelerating corrosion process, the reduction ratio of bond strength for zinc-coated rebar is less than uncoated rebar.

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1. Introduction

Corrosion of reinforcing steel in concrete may reduce bond strength and steel cross section area and thus affects the serviceability and durability of concrete structures [1–3]. The most widely used measures for avoiding corrosion of rebar includes hot-dip galvanizing and epoxy-coated systems. Both coating systems can minimize the corrosion risk in most exposure conditions [4–7]. Zinc-coated steel has been widely used for over 100 years. Zinc acts as sacrificial anode in the corrosion cell and generates much less volume change of corrosion products than carbon steel, so it can diminish the deterioration of reinforced concrete. According to Ramirez's

results [8], galvanized steel has a higher critical chloride threshold than bare steel. However, Unz [9] indicated that in high chloride ion solution, pitting corrosion occurs in the zinc substrate regardless of any existing passivation films. Therefore, whether zinc is stable in highly alkaline medium such as concrete pore solution, and whether bond strength of zinc-coated steel is diminished should be deliberated.

2. Experimental program

2.1. Corrosion of zinc specimens and carbon steel specimens

The zinc used in this study was composed of 99.7% Zn and 0.3% Al and the carbon content of steel was 0.36%. The zinc specimens and carbon steel specimens

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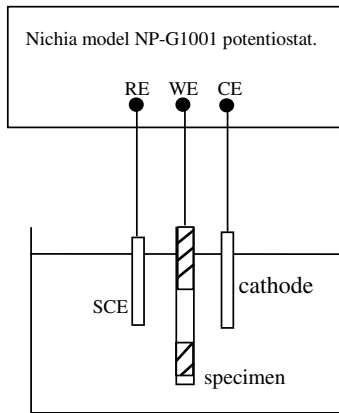


Fig. 1. Schematic representation of the potentiodynamic polarization measurement system.

were metallographically ground. Test specimens with an area of 1×1 cm were immersed in 3.5% NaCl and pH 12 solutions, respectively. Potentiodynamic polarization measurement set-up is illustrated in Fig. 1. The corrosion was evaluated by potentiodynamic polarization and open circuit potential (OCP) measurement using a Nichia (model NP-G1001) potentiostat. The potential scan range was from -200 mV below OCP to 1000 mV above OCP and the scan rate was 1 mV/s. The corrosion current density (i_{corr}) can be estimated from Stern–Geary equation

$$i_{\text{corr}} = \left[\frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \right] \times \frac{1}{R_p} = \frac{B}{R_p}, \quad (1)$$

where i_{corr} is the corrosion current density, and β_a , β_c are the anodic and cathodic Tafel slopes, respectively. R_p is the polarization resistance ($\Omega \text{ cm}^2$). For iron, the constant, B , is assumed to be 26 mV in evaluating corrosion rate of steel for actively corroding system and 52 mV for passively system. In addition, for galvanized coating values of B were used 52 and 6 mV under passive and active corrosion condition, respectively [10]. To calculate corrosion current density, the total surface area of rebar embedded in concrete is considered. After the corrosion current density is obtained, the instantaneous corrosion rate (r) can be calculated from Faraday's law as follows:

$$r = \frac{i_{\text{corr}}}{n} \times \frac{a}{F}, \quad (2)$$

where F is Faraday's constant ($96,500$ C/equivalent), n is the number of equivalent exchange, and a is the atomic weight.

3. Corrosion of reinforced concrete

3.1. Materials and specimen preparation

Concrete mixtures with a maximum aggregate size of 9 mm and a slump of 150 mm were used. The cement content was 405 kg/m^3 and the water cement ratio was 0.6 . Concrete mix design was listed in Table 1. The compressive strength of concrete at 28 days was 32 MPa. The chemical compositions of reinforcing steel were listed in Table 2.

The dimension of concrete cylinder was 10 cm diameter and 20 cm height. A 12.7 mm diameter rebar was embedded in the center of the cylindrical specimen. In order to control consistent failure mode, the embedded length of 100 mm was kept. Hot-dip zinc coating is a process in which metal is immersed in a liquid bath of zinc to obtain a protective coating. Based on the previous study [11], the temperature of liquid bath was kept at 468 °C. Rebar was dipped in the bath for 1 min (Z1), 2 min (Z2) and 3 min (Z3), respectively, to obtain various coating thickness.

After demolding, the specimen was cured in water for 7 days, then stored at 25 °C and 70% RH until the age of 56 days.

3.2. Testing method

For accelerating corrosion process, the specimens were immersed in 3.5% NaCl solution and impressed current was applied. Corrosion measurement set-up is illustrated in Fig. 2. The rebar was used as a working electrode. Saturated calomel electrode was used as a reference electrode and the titanium mesh as counter electrode. A current density of 0.5 mA/cm^2 was applied to the uncoated rebar and zinc-coated rebars. Every 24 h, the impressed current was cut-off, and OCP and linear polarization resistance were measured using a Nichia model NP-G100/ED potentiostat.

Table 1
Mix design for concrete (w/c = 0.6)

Materials	Mix proportions (kg/m ³)
Water	243
Cement	405
Sand	777
Aggregate	843

Table 2
Chemical compositions of reinforcing steel

Element wt%	C 0.36	Cu 0.23	Si 0.20	Mn 0.61	P 0.04	S 0.03
	Ni 0.36	Cr 0.23	Mo 0.20	Sn 0.61	Fe balance	

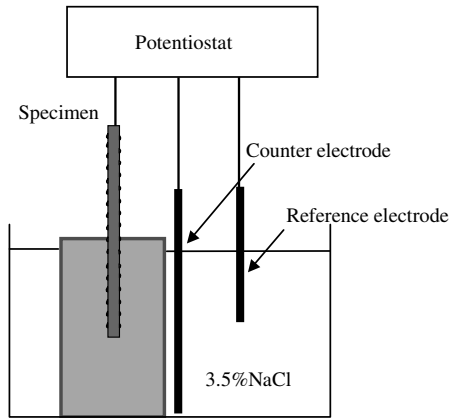


Fig. 2. Schematic representation of the electrochemical system.

4. Pull-out test

After finishing the electrochemical measurements, the specimens were removed from the tanks for pullout test that was conducted following the specification of ASTM C 234-91a [12]. The pullout test was carried out using universal testing machine. Two linear variable displacement transducers (LVDTs) were used to measure the slips at both ends, and the stroke rate was kept at 1.27 mm/min. Pull-out test set-up is illustrated in Fig. 3.

5. Results and discussion

5.1. Zinc coating observation

There were four thin layers formed in the coating: the 1st layer (outside layer) is zinc, the 2nd layer is zeta (ζ) phase, the 3rd layer is delta (δ) phase, and the 4th layer (inside layer) is steel substrate, as illustrated in Fig. 4(a). The zinc and iron contents of each layer were using by EDS and tabulated in Table 3. The hot-dip coating was mainly an iron-zinc alloy and iron content de-

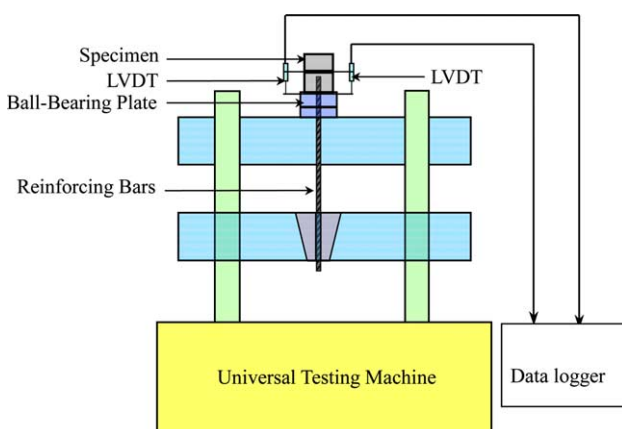


Fig. 3. Schematic representation of the pull-out test system.

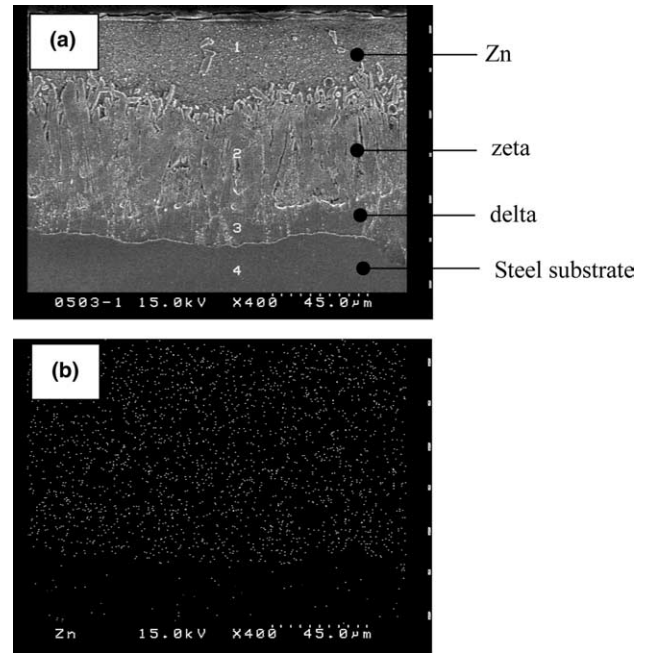


Fig. 4. Microstructure of hot-dip galvanized coating: (a) scanning electron micrograph of hot-dip coating; (b) X-ray map showing Zn on the coating.

Table 3
Composition of coating layer (wt%)

Layer	Zinc	Iron
Zinc	99.70	0
ζ	93.76	6.24
δ	89.77	10.23

creased from inner layer to outer layer. X-ray mapping shows that the zinc was uniformly distributed in the coating as shown in Fig. 4(b). Fig. 5 shows the change of coating thickness with hot-dip time. With an increase of hot-dip time, there was no significant change in the thickness of zeta (ζ) and delta (δ) layer, and total thickness was about 100 μm . The zinc thickness increased with increasing hot-dip time. According to ASTM A90-01 [13], the specimens were immersed in hydrochloric acid–antimony trichloride solution and the coating was stripped out. Based on weight loss and exposure area, the zinc weight per unit area was 891, 925, and 1090 g/m^2 (or zinc coating thickness was 127, 132, and 156 μm) for 1, 2, and 3-min hot-dip time, respectively.

6. Galvanized materials' inhibit behavior

The polarization curves of zinc and carbon steel are represented in Fig. 6. The values of the corrosion current density and the corrosion potential for carbon steel and galvanized materials in pH 12 solution and 3.5% NaCl water solution are listed in Table 4. The test result

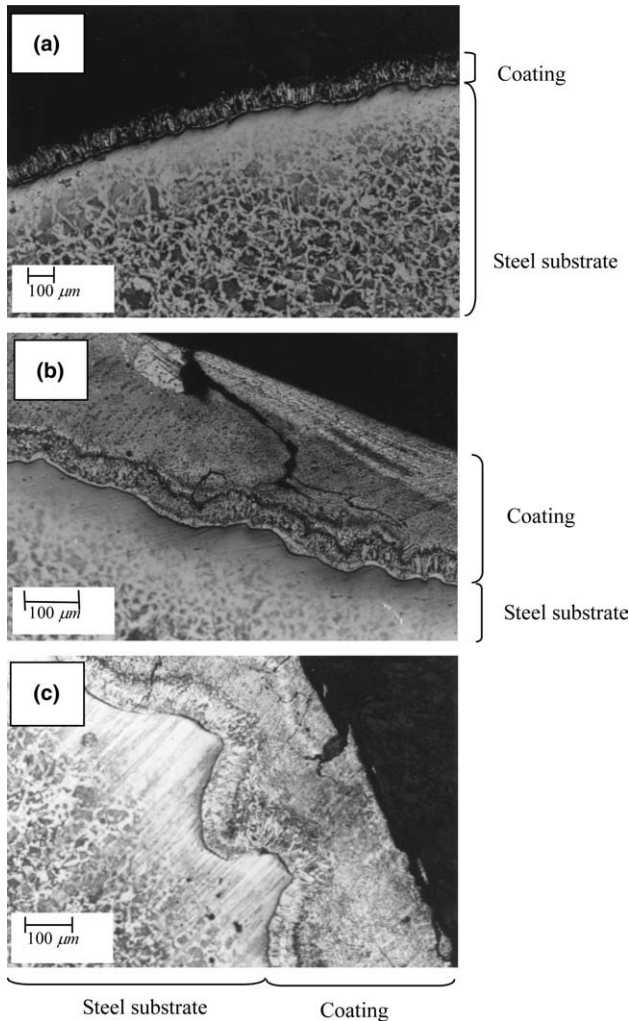


Fig. 5. Effect of hot-dip time on coating thickness: (a) 1 min; (b) 2 min; (c) 3 min.

shows that the corrosion potential of the zinc is obviously lower than that of the carbon steel in both kinds of solutions. From the viewpoint of electrochemistry, this means that galvanized materials are more active than carbon steel. The test result shows that when the galvanized material is put in an environment where pH 12, its corrosion rate is about 2.63 times that of carbon steel in the same environment. Because carbon steel can be passivated in an alkali environment and causes lower corrosion rate. In 3.5% NaCl, corrosion rate of carbon steel is slightly higher than that of galvanized materials. The passive film of steel is easier to damage in chloride-containing solution.

7. Electrochemical measurements

7.1. Open circuit potential

Fig. 7 show the potential-time behavior of zinc-coated rebar and rebar, respectively. Initially, the open

circuit potential value of the zinc-coated rebar is between -373 and -465 (mV, SCE), obviously lower than the uncoated rebar's open circuit potential -70 (mV, SCE). The hot-dip time has no significant effect in OCP in all acceleration tests.

The result shows that within 6 days of the accelerated corrosion, the open circuit potential of the rebar drops rapidly from -70 to -483 (mV, SCE). When the open circuit potential reaches about -600 (mV, SCE), cracks on the surface of the concrete can be found.

The open circuit potential of zinc-coated rebar is approximately between -400 and -900 (mV, SCE); the hot-dip time does not reflect much in the value of the open circuit potential, when the open circuit potential is about -850 (mV, SCE), the tensile stress of the resulting zinc-coated rebar corrosion will create cracks on the surface of the concrete. The potential reaches steady value after 16 days test for all specimens.

7.2. Corrosion rate measurement

The relationship between corrosion rate and accelerated corrosion time are shown in Figs. 8(a)–(d). After 1 day of accelerated corrosion test, the corrosion rate of the zinc-coated rebar is 2.4 times that of the uncoated rebar in the concrete pore solution. The corrosion rate of rebar in concrete pore solution is measured by linear polarization resistance method and calculated from Stern–Geary equation. Before 6 days of accelerated corrosion, the corrosion rate of the rebar is about $12 \mu\text{m}/\text{year}$. Within 12 days after the 6 days of accelerated corrosion, the corrosion rate increases distinctly from 12 to $56 \mu\text{m}/\text{year}$ abruptly, and causes cracks that can be observed visually. This may be because within 6 days of accelerated corrosion, the amount of chloride ions has not reached to the critical value, therefore only a part of the passive protective film on the rebar has been damage, thereafter, the amount of chloride ions has reached to the critical value. This means that the passive protective film on the rebar has been totally spoiled, and thus the corrosion rate of the rebar increases abruptly.

The corrosion rate of the zinc-coated rebar increased linearly with the time elapsed. The slope could be $Z3 > Z2 > Z1$, which means that the thicker the zinc layer, the greater the corrosion rate is increased as time elapses. However, different from the uncoated rebar, zinc-coated rebar does not show distinct two stage corrosion rates. This indicates that zinc-coated rebar is uniform corrosion and allows a larger amount of chloride ions than the uncoated rebar.

7.3. Characteristics of the interface between rebar and concrete

The aim of this test is to accelerate the chloride ions' penetration into the surface of the rebar. As the

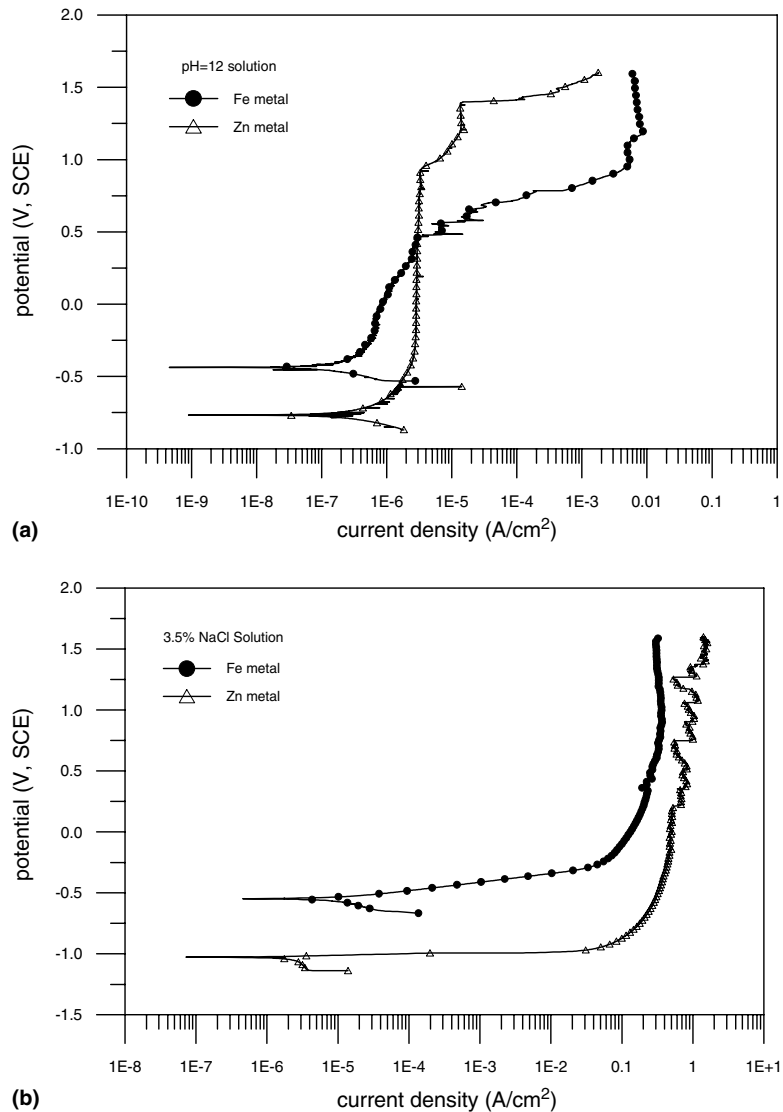


Fig. 6. The potentiodynamic polarization curves: (a) in pH 12 solution; (b) in 3.5% NaCl solution.

Table 4

The values of OCP and corrosion rate using potentiodynamic polarization method

	3.5% NaCl solution		pH 12 solution	
	Carbon steel	Zinc	Carbon steel	Zinc
OCP (V, SCE)	-0.56	-1.04	-0.43	-0.77
Corrosion rate ($\mu\text{m}/\text{year}$)	50	32	3.0	7.8

rebar (diameter 1.27 cm) is imbedded in the center of the test cylinder (diameter 10 cm), the thickness of the protective coating can be deemed as 4.4 cm, with a fixed current (0.5 mA/cm²), an accelerated corrosion test is carried out for 6, 14 and 18 days, respectively. Next, chloride ion titration tests are carried out with concrete powder samples taken from the surface of steel bars, this sampling method avoids the test data

to be effected by coarse aggregate. The result of the electric field acceleration test on concrete powder shows that the chloride ion content at the surface of the steel bar reaches 0.11% (in sample wt%) after 6 days.

The correlation between corrosion rate and chloride content at rebar/concrete interface is plotted in Fig. 9. In this test, within the first 6 days of accelerated corrosion, chloride ions do not increase rapidly on the surface of the rebar. After 6 days of accelerated corrosion, the chloride ion content on the surface of the rebar starts to increase rapidly, and the corrosion rate has the same tendency as that of the ion content. Hence, it can be judged that after 6 days of accelerated corrosion, the chloride ion on surface of the rebar exceeds a certain critical value, thereby the passive protective film on the surface of the rebar is damaged. Consequently, the

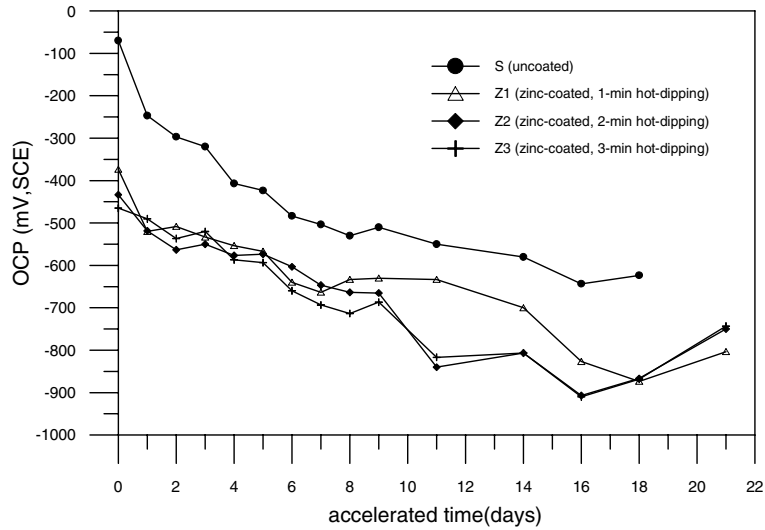


Fig. 7. Corrosion potential as a function of hot-dip time for the reinforcing steel in concrete.

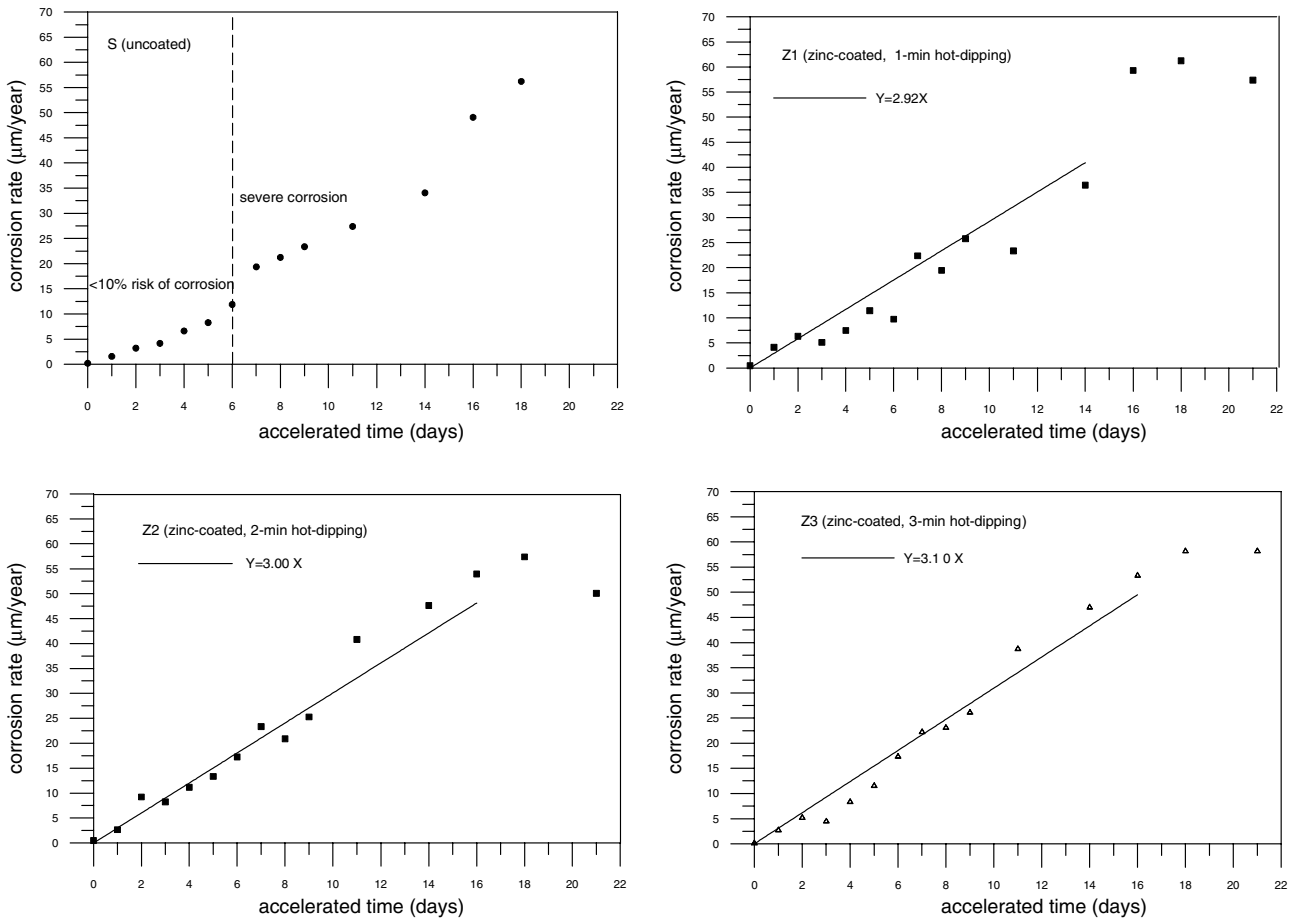


Fig. 8. Corrosion rate as a function of hot-dip time for the reinforcing steel in concrete.

chloride ions' catalytic action accelerates the corrosion rate of the rebar. The critical value obtained in this research is 0.07% (expressed in sample wt%) and can be considered as the threshold for active corrosion.

7.4. Bond strength

Test results show that galvanized reinforcement has higher interfacial bond strength (about 5–15%) than

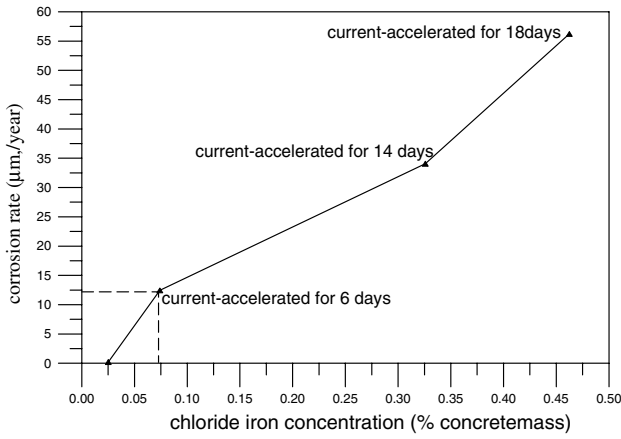


Fig. 9. Chloride concentration–corrosion rate relationship for the reinforcing steel in concrete.

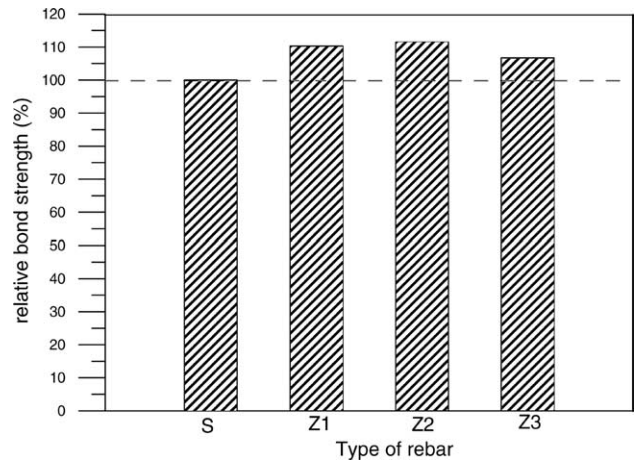


Fig. 10. Effect of different type of rebar on bond strength.

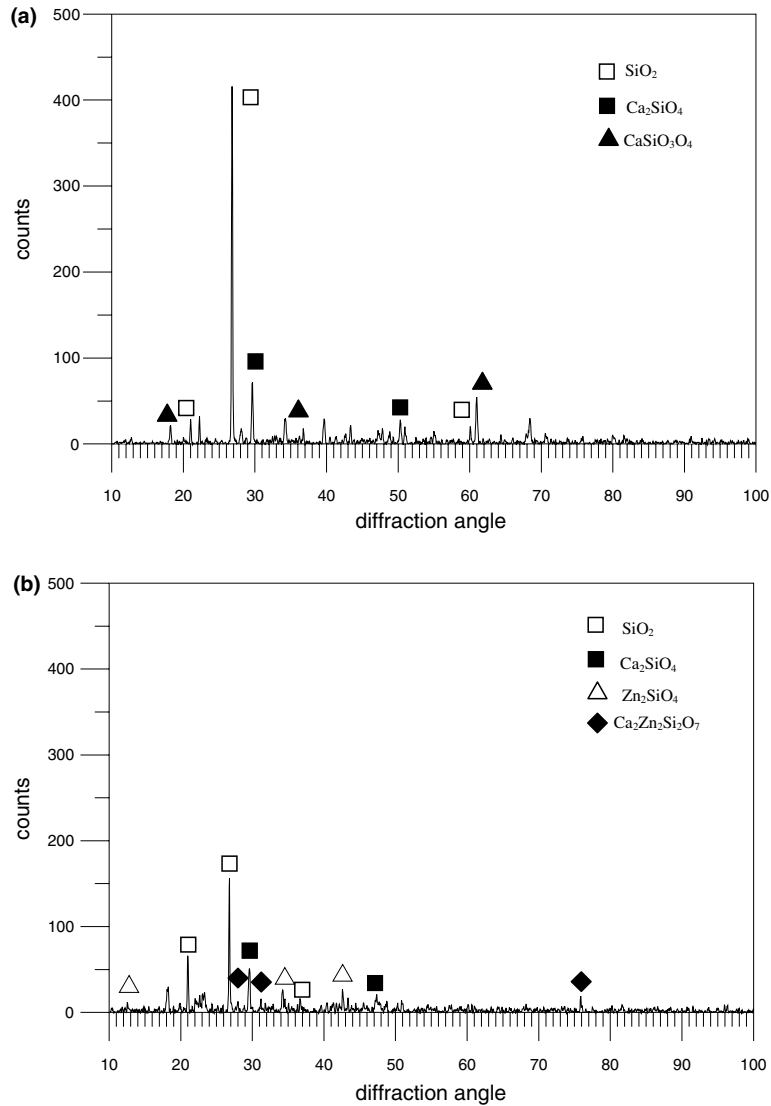


Fig. 11. X-ray pattern of chemical composition of concrete that formed on: (a) uncoated; (b) zinc-coated rebar surface.

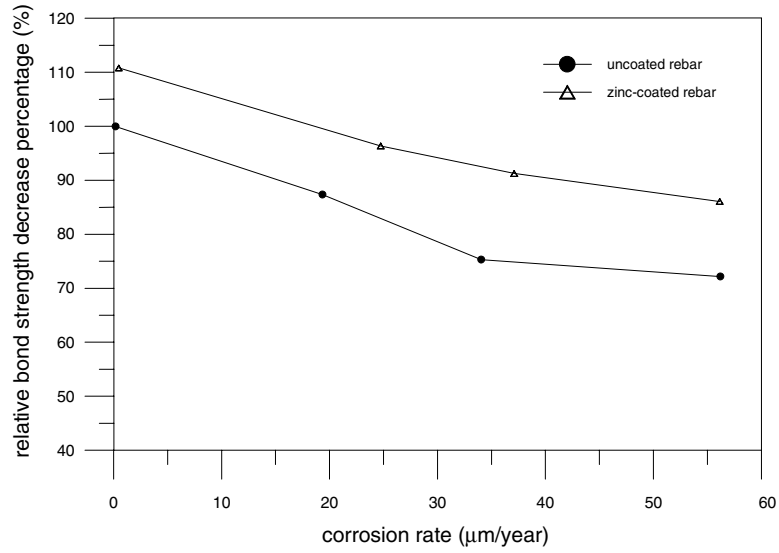


Fig. 12. Effect of corrosion rate on bond strength.

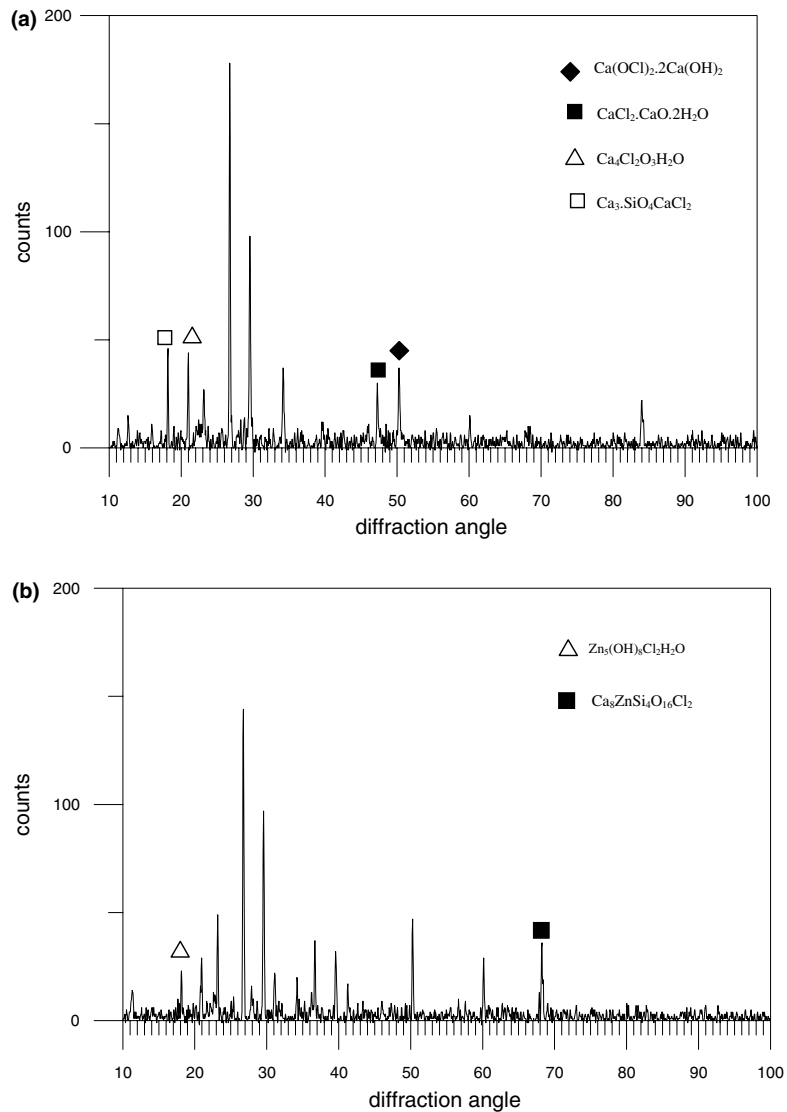


Fig. 13. X-ray pattern of chemical composition of concrete after corrosion that formed on: (a) carbon steel; (b) zinc-coated steel surface.

uncoated rebar as shown in Fig. 10. The coating thickness has little effect on interlock force and friction force between concrete and rebar.

It was found during concrete hydration, ZnO and Zn(OH)₂ elements in the zinc-coated rebar reacts with hydration compound to produce calcium zincate salt which passivates the rebar, and the calcium zincate salts may retard the hydration process and thus reduce the bond strength at early age (7–14 days). However, at age of 56 days, SiO₂ and Ca₂SO₄ were found in the uncoated rebar/concrete interface and ZnSiO₄ and Ca₂Zn₂Si₂O₇ were found in the zinc-coated rebar/concrete interface as shown in Fig. 11. It indicates that the chemical adhesion improvement may increase the bond strength between zinc-coated rebar and concrete.

7.5. Corrosion affects on bond strength

The bond strength is also affected by corrosion as shown in Fig. 12. After 14 days of accelerated corrosion, the reduction ratios of bond strength are 25.8% for uncoated rebar and 18.0% for zinc-coated rebar. The corrosion rates are 37.6 μm/year for zinc-coated rebar and 34.0 μm/year for uncoated rebar. The corrosion products in the rebar/concrete interface reduce the interlock and friction effects and thus decrease the bond strength. It is more prominent in uncoated rebar/concrete interface due to the volume increase of corrosion product than in zinc-coated rebar/concrete interface where zinc coating acts as a sacrificial anode and a barrier to prevent steel from corrosion. The volume change of zinc corrosion product is slightly to affect the interlock force between rebar and concrete, and thus the reduction of bond strength is minimized.

7.6. Compound analysis with the X-ray diffraction

The chemical compounds in the rebar/concrete interface were observed by X-ray diffraction. Before corrosion test, SiO₂ and 2CaOSiO₄ were detected in the uncoated rebar/concrete interface and Ca₂ZnSiO₇ and ZnSiO₄ were found in the zinc-coated rebar/concrete interface. In zinc coating surface, ZnO reacts with SiO₂ and Ca²⁺ to form ZnSiO₄ and Ca₂SiO₃, which is a insoluble white powder. ZnSiO₄ and Ca₂SiO₃ may combine to form Ca₂ZnSiO₇. After chloride ions penetrate into concrete cover, CaCl₂ and ZnCl₂ were observed in the rebar/concrete interface as shown in Fig. 13. CaCl₂ is a highly soluble material, which could cause a loose structure in the interface between the rebar and the concrete, thus it reduces the bond strength.

8. Conclusions

From results of potentiodynamic polarization results, the corrosion rate of zinc coating material is higher in pH 12 solution and lower in 3.5% NaCl solution than that of carbon steel. After 6-days accelerated corrosion process, the chloride ion concentration in the rebar/concrete interface is about 0.07 wt% which considered as the threshold value for the significant increase of corrosion rate. Before corrosion test, the bond strength of zinc-coated rebar is 5–10% higher than uncoated rebar. The zincates compound analyzed by the X-ray diffraction can increase the chemical adhesive force of the interface. The bond strength of rebar/concrete interface decreases as the corrosion rate increases. After 14-days accelerated corrosion process, the reduction ratio of bond strength for uncoated rebar is higher than zinc-coated rebar although the corrosion rate of uncoated rebar is less than zinc-coated rebar. Insignificant volume change of zinc corrosion product does not affect the interlock force between zinc-coated rebar and concrete.

References

- [1] Yoon S, Wang K, Weiss WJ, Shah SP. Interaction between loading, corrosion, and serviceability of reinforced concrete. *ACI Mater J* 2000;97(6):637–44.
- [2] Fu X, Chung DDL. Effect of corrosion on the bond between concrete and steel rebar. *Cem Concr Res* 1997;27(12):1811–5.
- [3] Almusallam AA, Al-Gahtani AS, Aziz AR, Rasheeduzzafar. Effect of reinforcement corrosion on bond strength. *Constr Build Mater*. 1996;10(2):123–9.
- [4] Kayali O, Yeomaus SR. Bond of ribbed galvanized reinforcing steel concrete. *Cem Concr Comp* 2000;22:459–67.
- [5] Malik AU, Andijani I, Ahmed S, Al-Muaili Fahd. Corrosion and mechanical behavior of fusion bonded epoxy (FBE) in aqueous media. *Desalination* 2002;150(3):247–54.
- [6] Darwin AB, Scantlebury JD. Retarding of corrosion processes on reinforcement bar in concrete with an FBE coating. *Cem Concr Comp* 2002;24(1):73–8.
- [7] Erdogdu S, Bremner TW, Kondratova IL. Accelerated testing of plain and epoxy-coated reinforcement in simulated seawater and chloride solutions. *Cem Concr Res* May 2001;31(6):861–7.
- [8] Ramirze E, Gonzalez JA, Bautista A. The protective efficiency of galvanizing against corrosion of steel in mortar and in Ca(OH)₂ saturated solutions containing chlorides. *Cem Concr Res* 1996;26(10):1525–36.
- [9] Unz M. Performance of galvanized reinforcement in calcium hydroxide solution. *ACI J Proc* 1978;3:91–9.
- [10] Haran BS, Popov BN, Petrou MF, White RE. Studies on galvanized carbon steel in Ca(OH)₂ solutions. *ACI Mater J* 2000;97(4):425–31.
- [11] Marder AR. The metallurgy of zinc-coated steel. *Prog Mater Sci* 2000:191–271.
- [12] ASTM C234-91a, Standard test method for comparing concretes on the basis of the bond developed with reinforcing steel. ASTM; 2000.
- [13] ASTM A 90-01, Standard test method for weight of coating on iron and steel articles with zinc or zn-alloy coatings. ASTM; 2001.