

Characterisation of coating on rebar surface using Hot-dip Zn and Zn-4.9Al-0.1 misch metal bath

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Abstract

The corrosion of rebar is one of the primary causes of premature deterioration of the concrete structure. The ideal option to overcome this situation would be to provide corrosion protection right at the time of manufacturing of the rebar before it is encased in the concrete and hence, warrants the use of corrosion resistance rebar.

The present paper outlines characterisation of coating obtained on rebar surface from pure Zn and Zn-4.9Al-0.1 misch metal bath. The coating was characterised by SEM, EDS, Galvanostatic and XRD techniques. In case of pure Zn bath, distinct phases such as eta, zeta, delta and gamma 1 and gamma were identified in coating where as in case of Zn-4.9Al-0.1 misch metal bath no such distinctive phases were found. The coating obtained from Zn-4.9Al-0.1 misch metal bath was thinner and consisted of outer Al₂O₃ phase followed Zn–Al phase resulting in better ductility compare to the coating obtained from pure Zn bath. Comparative corrosion resistance performances of both types of coating respect to uncoated rebar were evaluated by salt spray and tafel test. were conducted in simulated aggressive chloride and concrete pore solution of coated and The coating obtained form Zn-4.9Al-0.1 misch metal bath was found to be more anodic and showed 1.5-3 times better corrosion resistance in concrete pore solution and 2.5 times better resistance against aggressive chloride attack compare to the coating obtained from pure Zn bath. Both the coatings dissolved in faster rate in highly alkaline environment (pH=13.6) where as dissolution rate decreased with decrease of pH in pore solution. The sacrificial as well as barrier protection of Zn–Al alloy coating was found to be more effective than pure Zn coating. Both types of coated bars showed reduction in bond strength in concrete structure. It is attributed by the faster dissolution of the coating, leading to hydrogen gas evolution thereby creating a gap between the rebar surface and concrete structure.

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1. Introduction

Thermo-mechanical treatment (TMT) is a cost-effective way to produce high strength rebars for concrete reinforcement. The process relies on spraying high-pressure water on the rebar surface immediately after rolling to force formation of martensite [1] at the surface. The residual heat at the core ensures self-tempering of the martensite. In concrete, the alkaline pore solution presents passivate the metal surface so that it does not rust/corrode [2]. Due to carbonation reaction pH of concrete environment fall down [3] and steel comes in passive to active. However, widespread deterioration of concrete structures, most significantly

among the coastline structures is encountered due to the corrosion of the embedded steel, in spite of the alkalinity of the concrete. The influence of Cl⁻ ions to depassivate the steel surface even at high pH levels can be seen as a function of the net balance between two competing processes: stabilization (and repair) of the film by OH⁻ ions, and disruption of the film by Cl⁻ ions [2]. The corrosion of Reinforcing Concrete (RC) structures demonstrates a very complicated form of deterioration [4–10] but the main reason for the decrease in the durability of RC structures is due to the corrosion of the reinforcing bars. The consequence of the corrosion of reinforcements are (i) the decrease of the bar diameter (weakening its mechanical properties); (ii) the spalling and cracking of the concrete cover owing to the expansion associated with the formation of ferrous and ferric oxides; and (iii) the decrease of the steel/concrete bond strength.

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Table 1
Process conditions for coatings obtained on rebar surfaces from pure zinc and Zn-4.9Al-0.1 misch metal baths

Galvanizing bath	Bath composition	Bath temperature (°C)	Dipping time (s)	Cooling media
Pure zinc	Zn:100 %	460–465	45	Normal air
Zn-4.9Al-0.1 misch metal	Zn: 95, Al: 4.9 and misch metal: 0.1 (in wt.%)	420–425	45	Normal air

Additional protective methods could ensure the extended service life of the concrete structure. One way of protecting reinforcing steel from chloride or carbonation corrosion is to coat [11–22] the reinforcing bar.

Sacrificial material such as Zn, Mg and Al would preferentially corrode and thus the reinforcing bar is protected galvanically [23,24]. The coating of steel with zinc is an well established process for enhancing the durability of the steel [25]. However, effectiveness of the coating depends on the environmental pH to which the zinc coating is exposed. A pH below 13.3, the zinc coating provides a passivating coating where as pH above 13.3 zinc coating dissolve continuously until the coating disappears [26]. A series of long term exposure tests have found that galvanized coating delay the onset of corrosion in marine environment but do not prevent it completely [27]. An eleven-year exposure programme in marine environment revealed that the zinc coating suffered 2 to 3 million loss in thickness of the original zinc layer due to corrosion [28]. Zinc is an amphoteric metal, it stable in a specific range of pH 6–12 only [29] and corrosion behavior of galvanized steel in the presence of chlorides is controlled by the medium pH [30].

Ductility of the coating of pure zinc coated material is very poor due to presence of thick brittle phase [31]. Alloying element like copper and cadmium is harmful for ductility of the coating [32]. Addition of nickel in zinc coating reduces the hydrogen evolution reaction as well as increase in the corrosion resistance property against chloride [33]. The minimum requirement of nickel in a zinc-nickel alloy coating is 12 wt. % to enhance corrosion resistance against chloride ions [34].

Alloy making with such composition is a cost prohibitive due to wide difference of their melting temperature.

The addition of 0.18–0.25% Al to the bath leads to the rapid formation of Al–Fe phase (Fe_2Al_5 or Fe–Al–Zn) which inhibits the growth of Fe–Zn intermetallic compounds [35] and therefore improves the mechanical properties of galvanized steel. Fe_2Al_5 - Zn_x grows towards the substrate during galvanizing [36]. Zn–Al alloy have a better corrosion resistance property than pure zinc coating in aggressive chloride environment [37]. 5% Al–Zn coatings are always passive in nature than hot-dip zinc coatings [38]. Al have good resistance capability against chloride where as zinc have good coat ability properties with steel substrate. Zn–Al alloy may be good option to get both the advantages. The passive current densities of Zn–Al alloy in alkaline environments depend on the Zn and Al content [39]. Trace amount of misch addition in Zn–5Al alloy bath is advantageous to get better results [40].

Our objective of this paper is to characterise the coatings obtained on rebar surface from pure zinc and Zn-4.9Al-0.1 misch metal bath.

2. Experimental procedure

The TMT rebar used for the experimental study were 16 mm in diameter. The basic composition of TMT material in weight percent was as follows:

C: 0.12, Si: 0.115, Mn: 0.64, P: 0.023, Cr: 0.026, Ni: 0.011, Mo:0.003, Al: 0.002 the rest being Fe and it was measured using optical emission spectrometer according to standards ASTM E 415-99a [41].

First, the TMT rebar pickled in 18 vol.% HCl solution to remove oxide scale then fluxing treatment carried out in concentrated ZnCl_2 and NH_4Cl mixture solution at 80 °C to prevent temporary oxide formation before galvanizing. The process conditions are shown in Table 1 for coating on rebar surfaces from Zn and Zn-4.9Al-0.1 misch metal baths.

The microstructure of the coating was examined by scanning electron microscopy (SEM. JEOL JXA 6400). An Energy Dispersive Spectroscopy (EDS. KEVEX Super dry detector) was used for determination of chemical composition through

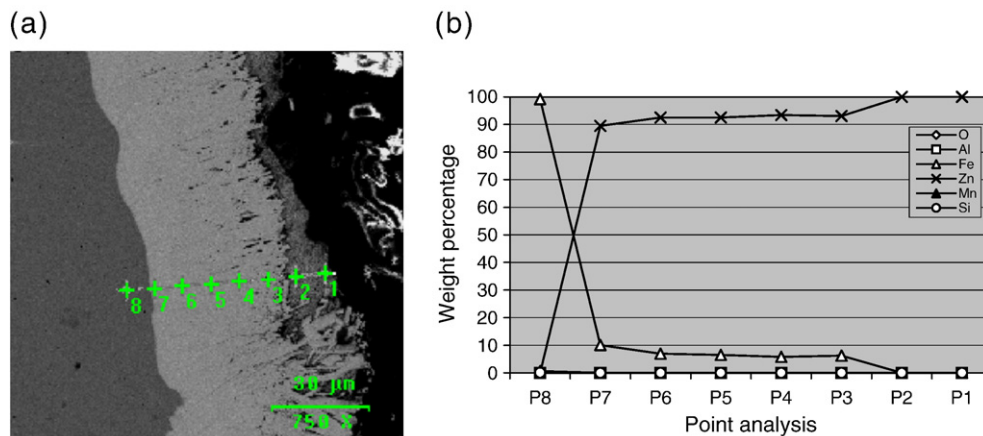


Fig. 1. (a) SEM image and (b) EDS depth profile of the coated layer obtained from pure zinc bath.

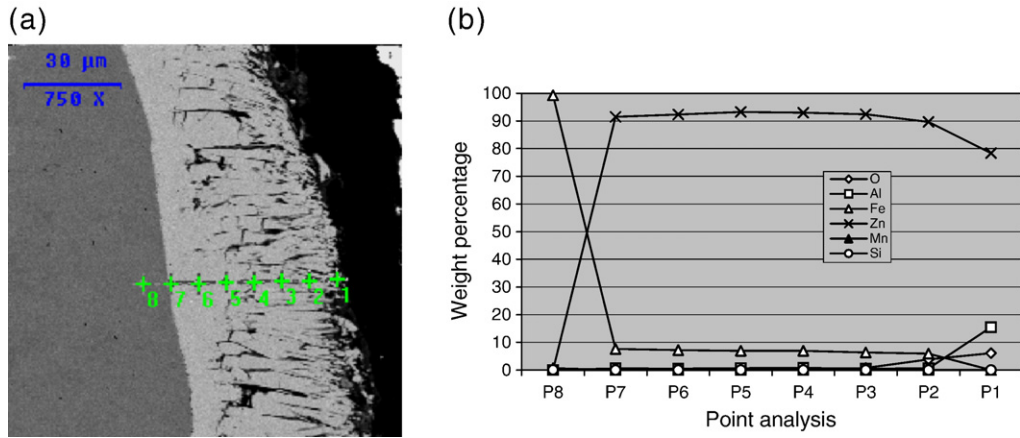


Fig. 2. (a) SEM image and (b) EDS depth profile of the coated layer obtained from Zn-4.9Al-0.1% misch metal bath.

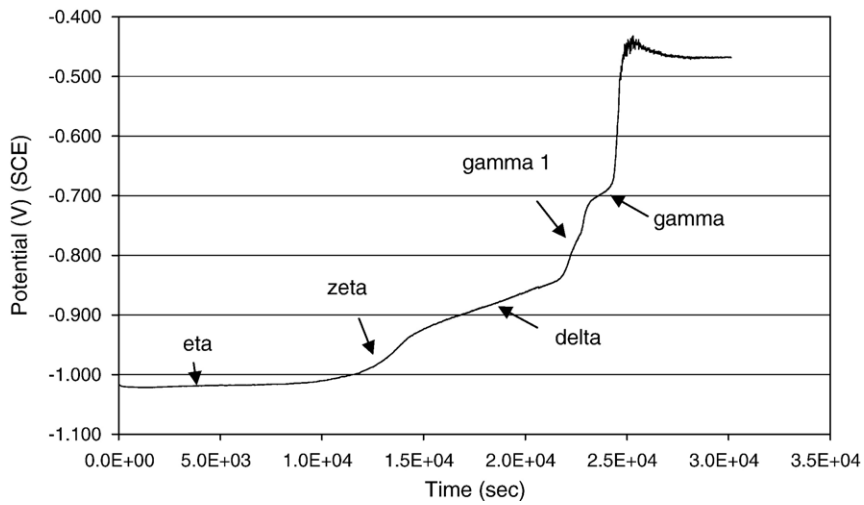


Fig. 3. Determination of different phases formed in coated layer from pure zinc bath by galvanostatic method at constant current of 8 mA/cm².

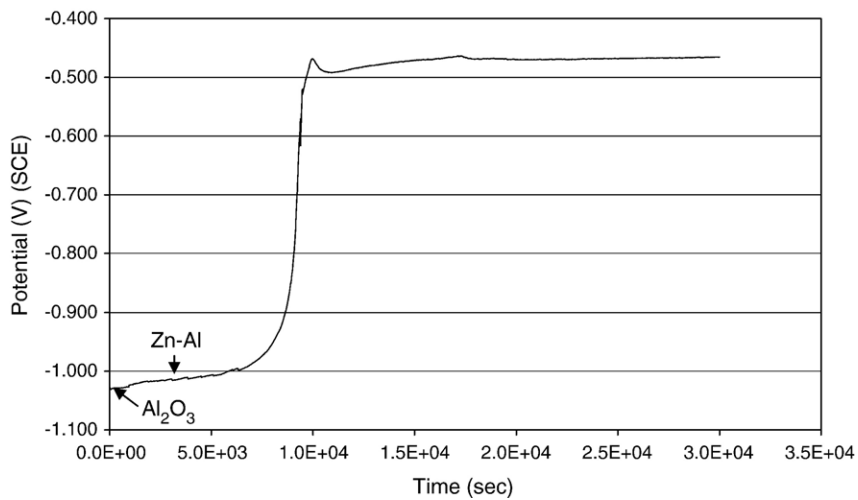


Fig. 4. Determination of different phases formed in coated layer from Zn-4.9Al-0.1% misch metal bath by galvanostatic method at constant current of 8 mA/cm².

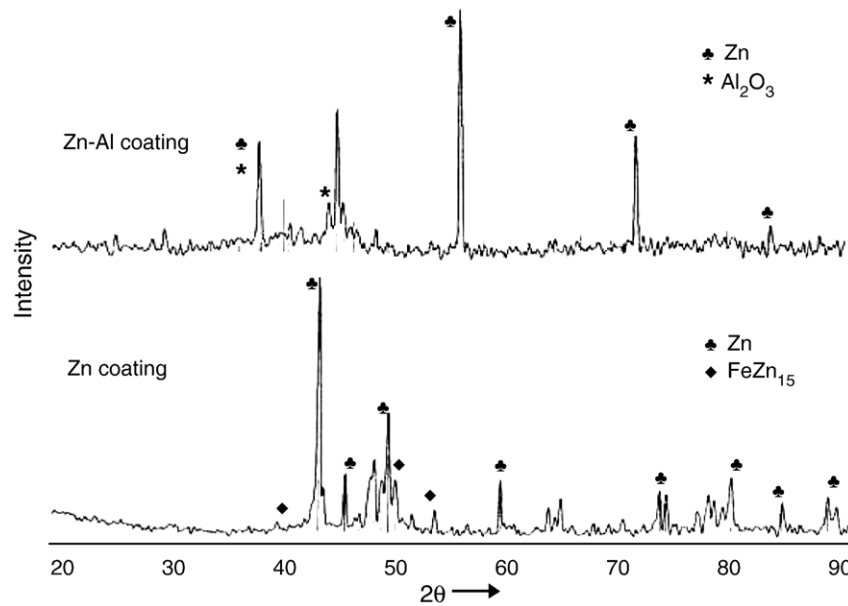


Fig. 5. XRD peaks of outer coated layer for coating obtained from pure zinc and Zn-4.9Al-0.1% misch metal bath.

depth of the coating layer. The structure of the outer coating layer was also determined using X-ray diffraction (XRD, Philips Analytical X-ray B.V. Machine). The galvanostatic study was conducted in an electrolyte solution containing 250 g/l NaCl and 50 g/l ZnSO₄ at a constant current density of 8 mA/cm² to determine the presence of different phases in the coatings. The pH of the electrolyte solution was 5. The salt spray tests of coated and uncoated rebar (10 cm) were conducted in WK111-340 salt spray cabinet (Weiss Technik). ASTM B117-03 was adopted for salt spray test [42]. This practice provides a controlled corrosive environment which has been utilized to generate relative corrosion resistance information for specimens of metals and coated metals in a given test chamber. Dissolution rate of the coated and uncoated rebar surfaces were examined by tafel test in simulated pore solution using Gamry DC105 system. Concrete pore solution was formulated according to the composition described by Christensen [43] and consists of 0.32 mol/L KOH, 0.17 mol/L NaOH and 0.07 mol/L Ca(OH)₂ in distilled water. The pH of this solution was approximately 13.6. Dissolution rate also carried out in pore solution with lower pH to simulate concrete environment in later stages. The scan rate and immersion times for this test were 2 mV/S and 15 min respectively. Coated and uncoated bars were cast in a square concrete block of size 10 cm. Quick setting cement (Convextra GP2) was used for

casting purpose and curing time varied 48–60 h to achieve crushing strength of 200–300 kg/cm² of concrete structure according to the IS specification. The bond strength of rebar surface with concrete structure was evaluated as per IS: 1786 (1985) [44]. After curing of the block, load versus slip was observed with the help of a tensile testing machine (100 KN FUT make tensile testing machine), fitted with an appropriate precession slip measuring device as per IS: 1786 (1985).

3. Results and discussion

3.1. Characterization of coated layer

The SEM images and EDS depth profiles of the coated layer obtained on rebar surfaces from pure Zn and Zn-4.9Al-0.1 misch metal bath are shown in Figs. 1–2. The coating obtained from Zn-4.9Al-0.1 misch metal bath was thinner than the coating obtained from pure Zn bath as evident from both the figures. It is evident from EDS line scan that iron content in the coating decreased from substrate-coating interface to the outer coating surface. The iron content was zero up to certain depth of the coating from the outer surface and it is eta phase. The iron content in the subsequent phases was around 5.5, 7.5, 18 and 25 wt.% which are expected to zeta, delta, gamma 1 and gamma.

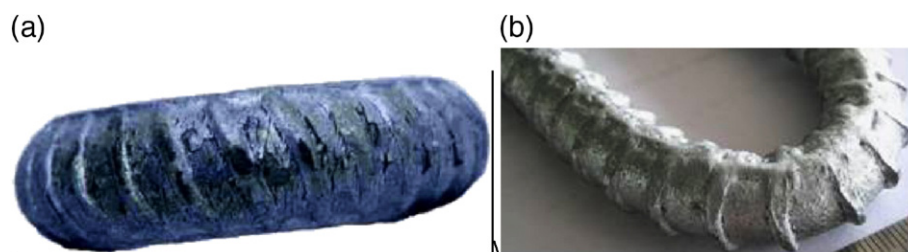


Fig. 6. Appearance of coated surfaces after bending for coating obtained from (a) pure zinc (b) Zn-4.9Al-0.1 misch metal bath under same magnification.

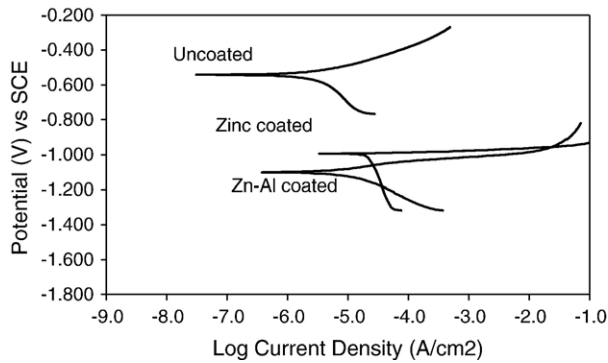


Fig. 7. Tafel analysis of uncoated and both types of coated rebar in simulated concrete pore solution with pH=7.

The presence of all these phases also confirmed by galvanostatic line scan of the coating as shown in Fig. 3 at constant current of 8 mA/cm². It is evident from Figs. 1 and 3 that thickness of eta and delta phase was maximum followed by zeta, gamma 1 and gamma. The thickness of eta and delta was comparable. The coating obtained from Zn-4.9Al-0.1 misch metal bath on the rebar surface was much more uniform as shown in Figs. 2 and 4. The EDS line scan of the coating indicates presence of alumina layer at the outer surface and absence of all the zinc-iron phases such as zeta, delta, gamma 1 and gamma. The galvanostatic line scan also confirmed absence of zinc iron phases in the coating as shown in Fig. 4. Pure zinc phase (eta) followed by zinc-iron alloy phase (zeta) were detected in the coating obtained from pure Zn bath where as Al₂O₃ phase was detected (see Fig. 5) in the coating obtained from Zn-4.9Al-0.1 misch metal bath by XRD technique. Zeta phase didn't detect in the coating obtained from Zn-4.9Al-0.1 misch metal bath.

3.2. Ductility of the coated layer

The bend surface of both types of coated rebar are shown in Fig. 6. The coating obtained from Zn-4.9Al-0.1 misch metal bath was more ductile compare to the coating obtained from pure zinc bath. It is evident from bend surfaces that large numbers of crack were appeared on the coating which was obtained from pure zinc bath where as very limited numbers of crack appeared on the coating which was obtained from Zn-4.9Al-0.1 misch metal bath even after 90° bending.

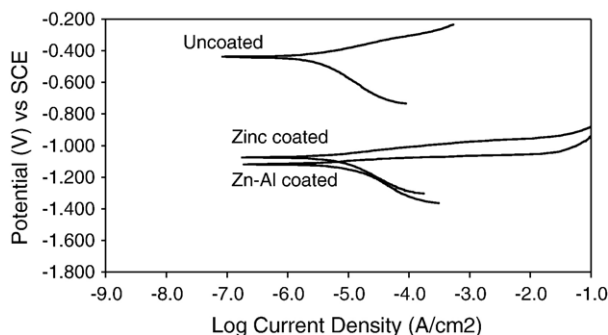


Fig. 8. Tafel analysis of uncoated and both types of coated rebar in simulated concrete pore solution with pH=11.

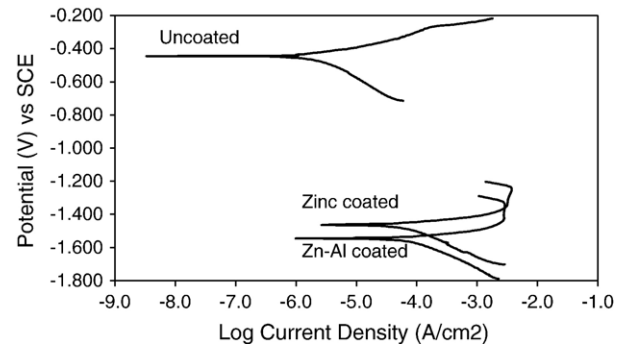


Fig. 9. Tafel analysis of uncoated and both types of coated rebar in simulated concrete pore solution with pH=13.6.

3.3. Electrochemical behavior in simulated concrete pore solutions

The tafel tests were conducted of two types of coated and uncoated rebar for comparative performance in simulated concrete pore solution under varying pH. The coatings obtained from pure zinc and Zn-4.9Al-0.1 misch metal bath were anodic to base steel irrespective of pH of the concrete pore solution as evident from Figs. 7–9. Zinc base coating give barrier as well as sacrificial protection to steel. The anodic nature of both types coating increased with increase in pore solution pH. The coating obtained from Zn-4.9Al-0.1 misch metal bath was more anodic in nature compare to coating obtained from pure Zn bath in simulated concrete pore solutions under varying pH. It is evident from Table 2 that the dissolution of metal or corrosion rate of coated and uncoated rebar sensitive to pH of the concrete pore solution. In neutral (pH=7) pore solution, both types of coating dissolved in slower rate but in comparative sense the coating obtained from Zn-4.9Al-0.1 misch metal bath dissolved in marginally slower than the coating obtained from pure Zn bath. In medium alkaline (pH=11.5) pore solution the coating obtained from pure Zn bath dissolved in faster where as the coating obtained from Zn-4.9Al-0.1 misch metal bath still dissolved in slower rate. The Al₂O₃ phase present on the outer layer of the coating obtained from Zn-4.9Al-0.1 misch metal bath was responsible for slower dissolution. Both types of coating dissolved in very faster rate in highly alkaline (pH=13.6) pore solution. In such highly alkaline environment

Table 2

E_{corr} and corrosion rate of coated and uncoated rebar in simulated concrete pore solution under varying pH

Material history	pH of pore solution	E_{corr} (V)	Corrosion rate (mpy)
Zn coating	7	-0.9947	3.784
Zn-4.9Al-0.1 misch metal coating	7	-1.1013	2.309
Uncoated	7	-0.542	1.399
Zn coating	11	-1.0732	15.052
Zn-4.9Al-0.1 misch metal coating	11	-1.1173	3.237
Uncoated	11	-0.4382	0.351
Zn coating	13.6	-1.4628	24.880
Zn-4.9Al-0.1 misch metal coating	13.6	-1.5456	16.297
Uncoated	13.6	-0.4057	0.09

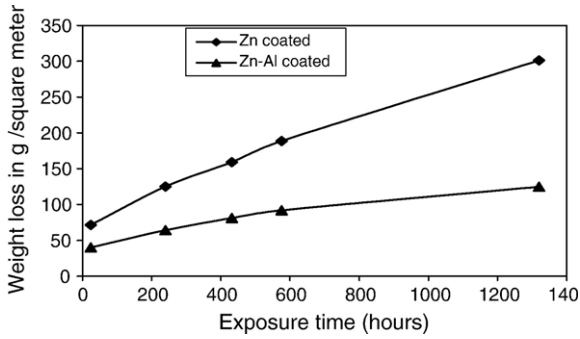


Fig. 10. Weight loss of two types of coated bar in aggressive chloride environments.

the coating obtained from pure zinc bath dissolved around 1.5 times faster than the coating obtained from Zn-4.9Al-0.1 misch metal bath. On the other hand uncoated rebar behave in opposite manner; dissolved faster in neutral pore solution and its dissolution rate gradually felt down with increase of pH in pore solution. Also, free corrosion potential of uncoated rebar was changed in opposite manner respect to coated rebar and it gradually increased with increase in pore solution pH. Free corrosion potential and corrosion rate of uncoated and both types of coated rebar in concrete pore solutions are shown in Table 2.

3.4. Electrochemical behavior in aggressive chloride environments

Fig. 10 shows the metals dissolution of both coated and uncoated rebar in aggressive chloride environment. It is evident from this figure that coated materials were much more resistance to chloride attack compares to uncoated rebar. Metal loss of the coating obtained from Zn-4.9Al-0.1 misch metal bath was around 2.5 times slower due chloride attack than the coating obtained from pure Zn bath. It is attributed by the presence of aluminum oxide phase on the outer surface of the coating which resists chloride attack.

3.5. Pull-out test results

The comparative bond strength of both types coated as well as uncoated rebar with concrete structure is shown in Fig. 11. It is evident from this figure that both the coated rebar showed drop in concrete bond strength compare to uncoated rebar. The drop in bond strength was maximum for the coating obtained from pure Zn bath. It is attributed by the faster dissolution of the coating in highly alkaline concrete environment leading to hydrogen gas evolution there by creating a gap between the rebar surfaces and the concrete structure. Hydrogen gas effect for drop in concrete bond strength gradually felt down with elapse of time.

4. Conclusions

1. Thinner coating obtained from Zn-4.9Al-0.1 misch metal bath compare to the coating obtained from pure Zn bath. Clearly distinct phases such as eta, zeta, delta and gamma 1 and gama were detected in the coating obtained from pure zinc bath where as Al₂O₃ followed by Zn–Al phases detected in the coating obtained from Zn-4.9Al-0.1 misch metal bath. The Zn-Fe intermetallics was absent in the coating obtained from Zn-4.9Al-0.1 misch metal bath.
2. The coating obtained from a pure zinc bath showed limited ductility where as the coating obtained from Zn-4.9Al-0.1 misch metal bath showed improved ductility. It is attributed by the absence of brittle zeta phase in the coating obtained from Zn-4.9Al-0.1 misch metal bath.
3. The free corrosion potential increased with increase in pore solution pH of uncoated rebar where as decreased with increase in pore solution pH of both types of coated rebar. Both types of coating dissolved in faster rate in highly alkaline (pH=13.6) pore solution. The coating obtained from Zn-4.9Al-0.1 misch metal bath dissolved in slower rate than coating obtained from pure zinc bath. The difference in coating dissolution was around 1.5–3 times in neutral and medium alkaline pore solution where as difference in metal

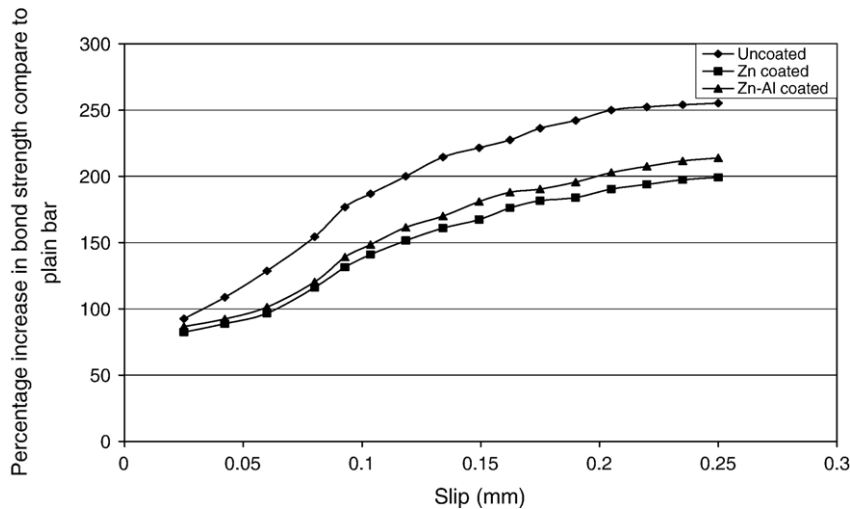


Fig. 11. Percentage increase in bond strength with concrete structure of uncoated and both types of coated rebar compare to plain bar.

dissolution was only 1.5 times in highly alkaline (pH= 13.6) pore solution. The coating obtained from Zn-4.9Al-0.1 misch metal bath showed 2.5 times better resistance against aggressive chloride attack than the coating obtained from pure zinc bath. The sacrificial as well as barrier protection of Zn–Al alloy coating was found to be more effective than pure Zn coating.

4. Both types of coated rebar showed drop in bond strength with concrete structure compare to uncoated rebar. It is attributed by the faster dissolution of the coating leading to hydrogen gas evolution thereby creating a gap between the rebar surface and concrete structure which give poor bonding.

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