

Corrosion behaviour of hot dip zinc and zinc–aluminium coatings on steel in seawater

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Abstract. A comparative investigation of hot dip Zn–25Al alloy, Zn–55Al–Si and Zn coatings on steel was performed with attention to their corrosion performance in seawater. The results of 2-year exposure testing of these at Zhoushan test site are reported here. In tidal and immersion environments, Zn–25Al alloy coating is several times more durable than zinc coating of double thickness. At long exposure times, corrosion rate for the Zn–25Al alloy coating remains indistinguishable from that for the Zn–55Al–Si coating of similar thickness in tidal zone, and is two to three times lower than the latter in immersion zone. The decrease in tensile strength suggested that galvanized and Zn–55Al–Si coated steel suffer intense pitting corrosion in immersion zone. The electrochemical tests showed that all these coatings provide cathodic protection to the substrate metal; the galvanic potentials are equal to $-1,050$, $-1,025$ and -880 mV (SCE) for zinc, Zn–25Al alloy and Zn–55Al–Si coating, respectively, which are adequate to keep the steel inside the immunity region. It is believed that the superior performance of the Zn–25Al alloy coating is due to its optimal combination of the uniform corrosion resistance and pitting corrosion resistance. The inferior corrosion performance by comparison of the Zn coating mainly results from its larger dissolution rate, while the failure of the Zn–55Al–Si coating is probably related to its higher susceptibility to pitting corrosion in seawater.

Keywords. Galvanization by hot dipping; Zn–Al alloy coating; seawater corrosion; pitting corrosion; cathodic protection.

1. Introduction

The investigation of hot dip zinc–aluminum (Zn–Al) alloy coatings started in the 1960s, although galvanized steels have been used successfully for more than 130 years (Horton 1978). The greatest limitation in using galvanized steels in industrial environments is that Zn suffers a large dissolution rate in these environments (Johnsson and Kucera 1982; Townsend and Meitzner 1982). Hot dip aluminized coating has also been used commercially for about 35 years, exhibiting its main advantage over galvanized coating in the excellent barrier protection it provides to the substrate. However, the latter does not provide satisfactory cathodic protection (CP) to the substrate due to the highly insulating oxide film that forms on its surface.

Zn–Al alloy coatings for steel were developed with an anticorrosive performance superior to that of each of the metals used individually. The high corrosion resistance of aluminized coating combined with the excellent CP afforded by galvanized coating to the substrate both contribute to their superior performance (Horton 1978; Zoccola *et al* 1978). Zn–55Al–1.6Si coating, better known as Galvalume, introduced during the 1970s (Borzillo and Horton U.S. Patents 3,343,930; 3,393,089), and Zn–5Al–0.2RE coating, Galfan, developed during the

1980s (Pelerin *et al* 1982), have both proved that the incorporation of zinc and aluminum is quite successful as far as the improvement in corrosion resistance is concerned (Zoccola *et al* 1978; Townsend and Zoccola 1979; Allegra and Zoccola 1983).

A Zn–25Al alloy coating used for marine environments was developed in China in the 1990s, and an industrial production line has been established since then (Li 1999). There are, however, controversies in the existing literature as to the corrosion resistance of these coatings. The corrosion tests conducted in artificial seawater showed that the Zn–25Al alloy coating is superior in corrosion resistance to the galvanized and Zn–55Al–1.6Si coatings (Sun *et al* 1997), which is inconsistent with the results obtained by other workers in atmospheric environments (Townsend and Borzillo 1996). In the present paper, natural exposure tests combined with electrochemical measurements have been applied to evaluate the performance of the Zn (galvanized), the Zn–25Al alloy and the Zn–55Al–Si coated steel wires in seawater.

2. Experimental

The material tested was hot dip Zn–25Al alloy coating that was prepared on the continuous commercial production line. For the purpose of comparison with other

types of coated steels, commercially available galvanized and Zn-55Al-Si coatings were included in the tests. The coating weight, coating thickness and uniformity were measured with standard equipment and tests and shown in table 1.

Two-year tidal zone and immersion zone corrosion tests were performed at Zhoushan corrosion test site representing severe marine environment in China, to evaluate the corrosion resistance of the three types of coatings. The environmental factors of the Zhoushan Seawater Corrosion Test Station are described in table 2. The samples of Zn, Zn-25Al alloy and Zn-55Al-Si coatings for these tests were prepared according to the ASTM G52-76 standard. All 500 mm long samples were ultrasonically degreased with ethanol and weighed before exposure. After exposure to the seawater for a particular time interval, the samples were cleaned to remove corrosion products and reweighed to determine loss of coating due to corrosion. To facilitate direct comparison of coatings with different densities, average thickness losses were calculated from the weight loss measurements.

After the weight measurement, the samples were submitted to tensile testing, according to ASTM A370-77 and ASTM E8-81 test standards, to evaluate the loss of the substrate's tensile strength. The morphology of corroded coating surface after 18 or 24 months of testing was examined with a KYKY-1000B scanning electron microscope.

In the electrochemical tests, corrosion potential as a function of immersion time (12-day testing) and galvanic potential of Zn coating/steel, Zn-25Al alloy coating/steel and Zn-55Al-Si coating/steel couples (330 h testing) were determined. All these tests were performed in seawater. The galvanic current was measured using zero-resistance amperometry. The saturated calomel electrode (SCE) and the platinum electrode were used as reference and counter electrodes, respectively. The galvanized Zn-25Al alloy and Zn-55Al-Si coatings and steel work-

ing electrodes consisting of cylindrical wires, had an exposed surface for tests of 0.96 cm², with the rest of the surface varnish protected. Before the tests, the samples were degreased with ethanol.

3. Results and discussion

After 18 months exposure in tidal zone, the Zn-25Al alloy coating samples were covered with white rust; the Zn-55Al-Si coating samples were also covered with white rust, but several red spots also appeared due to substrate metal corrosion; while the Zn coating samples were totally covered with red rust. The corrosion depths and corrosion rates for the three types of hot dip coatings in tidal zone are given in figures 1 and 2. It can be found that corrosion rates for all three types of coatings decreased with respect to testing time in this zone. However, for galvanized coating initial rate was the highest ($\sim 58 \times 10^{-3}$ mmpy), for Zn-25Al alloy coating the second highest ($\sim 28 \times 10^{-3}$ mmpy), and for Zn-55Al-Si coating the lowest ($\sim 12 \times 10^{-3}$ mmpy). Because of the concomitant decrease in rates of Zn-25Al alloy and Zn-55Al-Si coatings in this environment, the two types of coatings become indistinguishable after about 18 months exposure. At the end of the test (18 months), the corrosion rate of hot dip Zn-25Al alloy and Zn-55Al-Si coatings were the lowest ($\sim 5.1 \times 10^{-3} \sim 5.6 \times 10^{-3}$ mmpy); the corrosion rate of hot dip galvanized coating was the highest ($\sim 20 \times 10^{-3}$ mmpy).

To facilitate comparison of the corrosion resistance of Zn-25Al alloy coating with those of conventional galvanized and Zn-55Al-1.6Si coatings, the ratios of the 18 month corrosion losses for the three coatings in tidal zone, together with those in immersion zone, were calculated as shown in table 3. It can be predicted on the basis of these ratios together with the fact that galvanized coating is twice as thick as either of Zn-25Al alloy and Zn-55Al-1.6Si alloy coatings (table 1) that, the commercially available Zn-25Al alloy coating will outlast galvanized coating by about twice its duration, and lasts to the same extent as Zn-55Al-1.6Si coating in the tidal zone.

In immersion zone, the Zn-25Al alloy coating showed the best corrosion performance, which is in disagreement with the results obtained by other workers in atmospheric environments (Townsend and Borzillo 1996). After 9 months exposure, the Zn-55Al-Si coating samples were heavily covered with white rust, and red rust started to

Table 1. Coating weight, thickness and uniformity.

Coating	Coating weight (g/m ²)	Thickness and uniformity (μm)	
		Metallographic	Gravimetric
Zn	396.6	40 ~ 60	55.6
Zn-25Al alloy	144.9	15 ~ 30	28.6
Zn-55Al-Si	120.7	13 ~ 37	32.2

Table 2. Main environmental factors of Zhoushan Seawater Corrosion Station.

Longitude, latitude	Salinity (mg/L)	Oxygen (ml/L)	pH	Average temperature (°C)	Average tide level (m)
29°59'N, 122°02'E	26	8.82	8.14	17	2.08

appear due to substrate metal corrosion. After immersion in seawater for 18 months, the Zn-55Al-Si coating samples were heavily covered with red rust as shown in figure 3, and at several locations corrosion even reached into the filament. After 12 months of testing, the Zn samples were already exhibiting red corrosion. In contrast, the Zn-25Al alloy coating samples suffered only white corrosion. At the end of the test (24 months), the Zn-25Al alloy coating samples still exhibited only white corrosion as shown in figure 4; while most of the galvanized coating was corroded away and more than 80% of its surface was covered with red corrosion products as shown in figure 5.

The corrosion depths and corrosion rates for the three types of hot dip coatings in immersion zone are given in figures 6-7. It can be readily seen that the corrosion rate for Zn-25Al alloy coating decreased with respect to testing time whereas for Zn and Zn-55Al-Si coatings it decreased in the first few months, and slightly increased with respect to time afterward which implied the corrosion

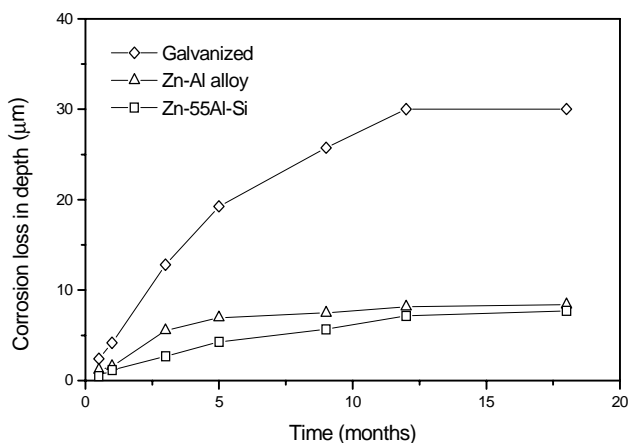


Figure 1. Corrosion depth as a function of time for hot dip coatings in tidal zone.

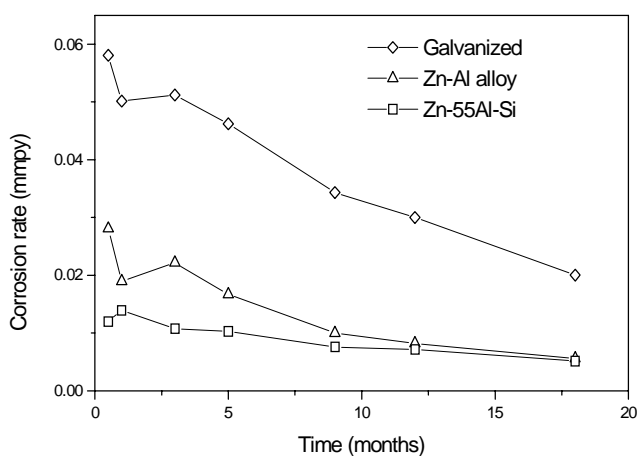


Figure 2. Corrosion rate as a function of time for hot dip coatings in tidal zone.

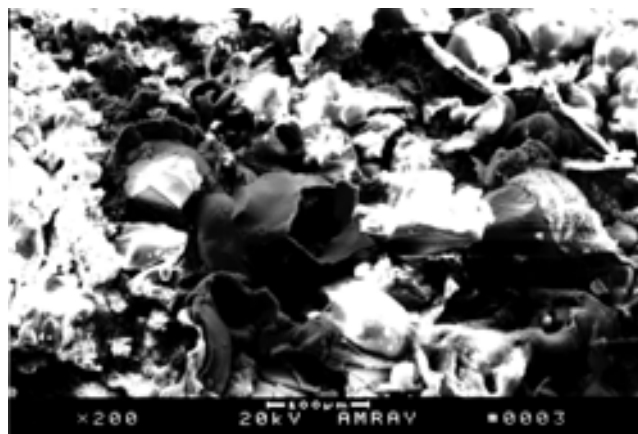


Figure 3. Surface morphology of Zn-55Al-Si coating after immersion in seawater for 18 months (No etching, SEM 200 ×).

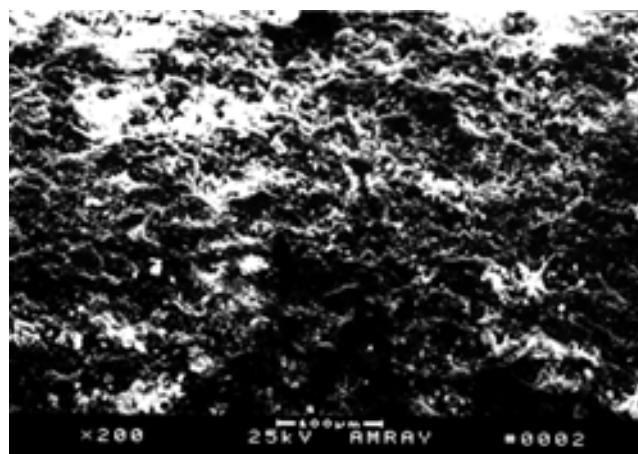


Figure 4. Surface morphology of Zn-25Al alloy coating after immersion in seawater for 24 months (No etching, SEM 200 ×).

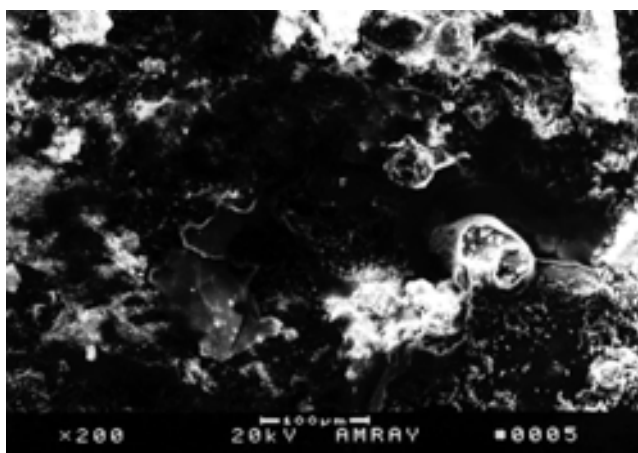


Figure 5. Surface morphology of Zn coating after immersion in seawater for 24 months (No etching, SEM 200 ×).

of the substrate metal. As shown in figure 7, the corrosion resistance of Zn-25Al alloy coating was the highest, its corrosion rate being 7.6×10^{-3} mmpy (after 24 months immersion). The corrosion rates of Zn and Zn-55Al-Si coatings on the other hand were 66×10^{-3} mmpy (after 24 months immersion) and 29×10^{-3} mmpy (after 18 months immersion), respectively. It can thus be predicted that the commercially available Zn-25Al alloy coating will outlast galvanized and Zn-55Al-Si coatings by at least two to three times in immersion zone.

Table 3. 18 months weight losses.

Zone	Ratio of 18 month corrosion losses	
	Galvanized/ Zn-25Al alloy	Zn-55Al-Si/ Zn-25Al alloy
Tidal	3.6	0.92
Immersion	4.8	2.70

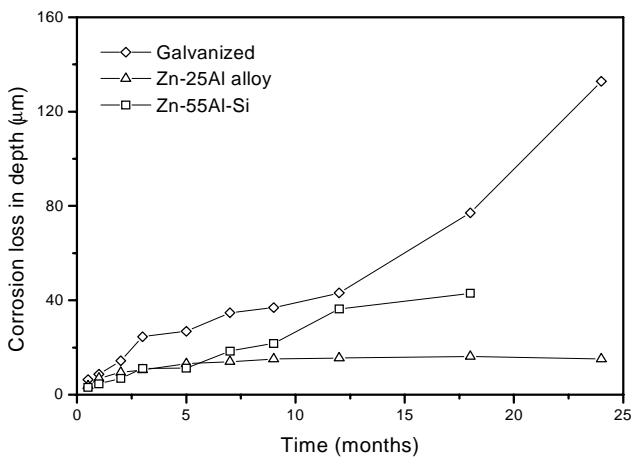


Figure 6. Corrosion depth as a function of time for hot dip coatings in immersion zone.

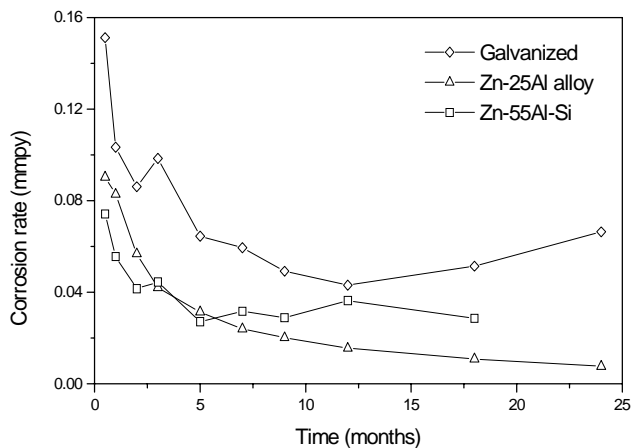


Figure 7. Corrosion rate as a function of time for hot dip coatings in immersion zone.

The best performance of Zn-25Al alloy coating was also confirmed by tensile testing. As shown in figure 8, the tensile strength of Zn-25Al alloy coating samples remained rather constant during immersion test, displaying an average value of 408 MPa. For Zn and Zn-55Al-Si coating samples on the other hand, the initial values of tensile strengths which were of the order of 430 MPa and 429 MPa, respectively decreased with the testing time. The tensile strength reached a value of about 375 MPa for Zn coating after 24 months of testing, and 192 MPa for Zn-55Al-Si coating after 18 months of testing, i.e. about 87% and 45% of their initial values, respectively. This decrease is undoubtedly associated with the more intense attack of the substrate steel, which results from the local corrosion of galvanized and Zn-55Al-Si coated steel, especially the latter.

The corrosion potentials of Zn, Zn-25Al alloy and Zn-55Al-Si coatings are displayed in figure 9. For Zn coating, the corrosion potential stabilized around -1050 mV (SCE); for Zn-25Al alloy coating at around -1030 mV (SCE);

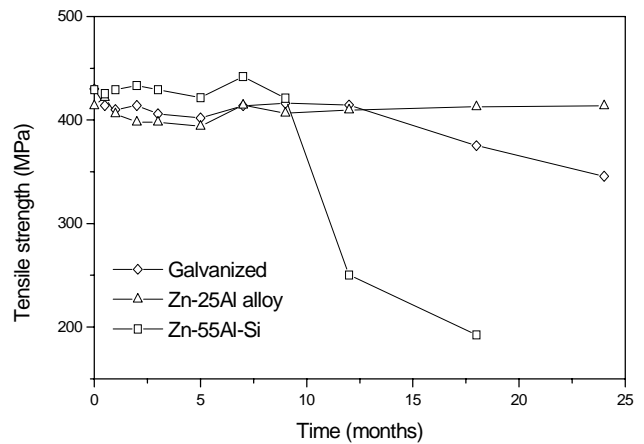


Figure 8. Tensile strength as a function of time for hot dip coatings after removal from seawater.

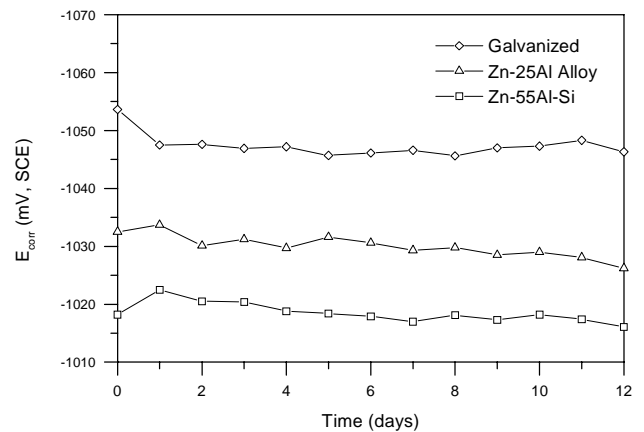


Figure 9. E_{corr} as a function of time for hot dip coatings.

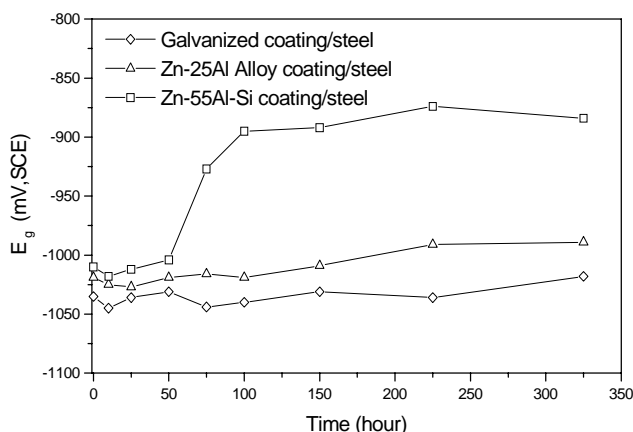


Figure 10. E_g as a function of time for coating/steel couples.

and for Zn–55Al–Si coating, at about -1020 mV (SCE). These values are inside the immunity area of Fe because the equilibrium potential of Fe/Fe^{2+} is within the range of -860 mV (SCE) and thus substantiate the fact that all the three types of hot dip coatings provide cathodic protection to the substrate.

The variation of galvanic potential with respect to testing time in seawater is presented in figure 10 for Zn coating/steel, Zn–25Al alloy coating/steel and Zn–55Al–Si coating/steel couples. The galvanic potential of Zn coating/steel and Zn–25Al alloy coating/steel couples remained reasonably constant with time at around -1050 mV (SCE) and -1025 mV (SCE), respectively. For Zn–55Al–Si coating/steel couple, during the initial 50-hour test, this potential remained around -1020 mV (SCE), which was equivalent to Zn–55Al–Si coating's corrosion potential (figure 9). After this time, however, the galvanic potential sharply shifted to noble direction, then stabilized around -880 mV (SCE). In spite of the positive shift, the potential remained inside the immunity area of iron, ensuring cathodic protection to the substrate. A possible reason for this behaviour could be preferential interdendritic dissolution, during which, after corrosion of the zinc rich phase, the galvanic potential increases to a value typical of the aluminum rich phase. That is, this alloy coating behaves first as Zn and then later as Al. Other workers also reported similar results (Dalledone *et al* 1995).

The galvanic current variation with respect to testing time is presented in figure 11 for Zn coating/steel, Zn–25Al alloy coating/steel and Zn–55Al–Si coating/steel couples. It is evident that at the moment the couples were immersed, the galvanic current was fairly high, of the order of 460 μA for the three couples. Almost immediately it started decreasing, and after 240 h testing, it stabilized around 210 μA for the Zn coating/steel couple, around 180 μA for the Zn–25Al alloy coating/steel couple and 140 μA for the Zn–55Al–Si coating/steel couple. The fact that the galvanic current for Zn coating/steel couple is about 16% higher than that for the Zn–25Al alloy coating/steel couple and 50% for the Zn–55Al–Si coating/steel

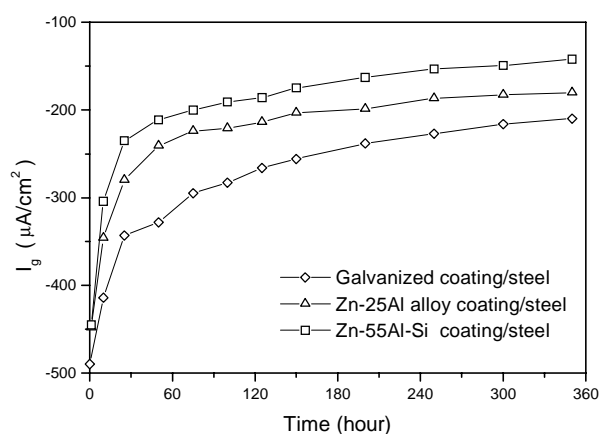


Figure 11. I_g as a function of time for coating/steel couples.

couple is consistent with the galvanic potentials of these couples.

Although galvanized coating provides better sacrificial protection, this coating was consumed after 12 to 18 months exposure because of its larger corrosion rate, and is thus less durable than the Zn–25Al alloy coating. Similar to the Zn–55Al–Si coating, the Zn–25Al alloy coating has a typical two-phase structure comprising a fine network of aluminum rich dendrites and zinc rich interdendritic alloy (Li 1999). The zinc rich interdendritic portion of the coating is preferentially attacked, with the result that the coating behaves much like galvanized coating. That is, the Zn–25Al alloy coating exhibits corrosion potential similar to that of galvanized coating, and provides galvanic protection to steel substrate at exposed coating defects. As corrosion proceeds, however, the protective zinc corrosion products that wash away from ordinary galvanized coating are mechanically retained in the Al rich interdendritic network, thus slowing down further attack. Compared to Zn–55Al–Si coating, the Zn–25Al alloy coating provides satisfactory galvanic protection to steel wire in seawater environment, and thus is more resistant to pitting corrosion and provides protection for longer times. Due to a higher susceptibility to pitting corrosion in seawater, which results from its inferiority in cathodic protection proved by the above electrochemical investigation, the corrosion resistance of the Zn–55Al–Si coating falls down and is inferior to that of Zn–25Al alloy coating (figures 6 and 7). Therefore, the pitting corrosion of the alloy coating may partly account for the behaviour of Zn–55Al–Si coating in seawater, although further work will be necessary to understand its effect more clearly.

4. Conclusions

The results of 2-year seawater corrosion tests of steel wire protected with zinc, Zn–25Al alloy and Zn–55Al–Si coatings at Zhoushan test site demonstrated:

(I) The Zn–25Al alloy coating provides long term protection to steel wire in seawater environment. It was found to

be (a) two to three times more durable than galvanized coating of a double thickness in tidal zone and immersion zone, (b) equivalent to Zn-55Al-Si coating of a similar thickness in tidal zone and (c) two to three times more durable in immersion zone. The surface observation and tensile testing confirmed the best performance of Zn-25Al alloy coating.

(II) The characteristics of the Zn-25Al alloy coating represents a favourable combination of uniform corrosion resistance and pitting corrosion resistance. This combination is a consequence of the alloy microstructure and corrosion mechanism as described. The Zn-55Al-Si coating is inferior in corrosion performance to the Zn-25Al alloy coating owing to a higher susceptibility to pitting corrosion in seawater. Although the galvanized coating provides the best sacrificial protection, its corrosion rate is so high that the coating is consumed after 12 to 18 months exposure, and therefore less durable than the Zn-25Al alloy coating.

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