

Electrochemical Behavior and Protective Property of Al-containing Zinc-Rich Paints

Wen-Ben Chen, Peter Chen*, Hunz-Yin Chen**,
Chung-Min Wu**, and Wen-Ta Tsai

Department of Materials Science and Engineering
National Cheng-Kung University, Tainan, Taiwan

*Shu-Te University, Kaohsiung, Taiwan

**Berlin Company Limited., Kaohsiung, Taiwan

The effect of Al addition on the corrosion performance of zinc-rich paints (ZRP) was investigated. Both electrochemical measurement and salt spray test were employed to evaluate the corrosion performance of ZRP with or without Al addition. The Al content as percentage of the total metallic components in the ZRP, investigated in this study, varied from 0 to 75wt%. The experimental results showed that protective nature of ZRP altered from cathodic protection to barrier former as the Al content was increased beyond 20wt%. The results from salt spray tests also revealed that the corrosion products were modified with the presence of aluminum oxide in the Al-containing ZRP. The amount of zinc white on the painted steel decreased as the Al content in the ZRP increased. The protectiveness, in terms of the time of red rust formation and cathodic protection, was reduced as the Al content was higher than 20wt%.

Keywords : Al-containing zinc rich paint, electrochemical behavior, salt spray, cathodic protection, barrier protection

1. Introduction

The beneficial effect of Al addition on the corrosion performance of hot dip zinc (also called galvanized) coatings has been well recognized.¹⁻⁵⁾ Two most common Al-containing zinc coatings on steels are Zn-5%Al (Galvan) and Zn-55%Al-1.5%Si (Galvalume). Beside cathodic protection, barrier protection also plays important role in enhancing the corrosion performance of the Al-containing zinc coatings, particularly for the coatings with high Al content.

Though the uses of hot dip zinc and zinc alloy coatings have been increased recently, corrosion prevention of steels using zinc-rich paint (ZRP) still exhibits several advantages such as low cost, ease to maneuver etc., over galvanized coating. However, to meet new challenge of severely corrosive environments, new ZRP with better performance against corrosion has to be developed. In this investigation, the development of a new Zn-Al composite paint is attempted. The effect of Al addition on the corrosion performance of ZRP on carbon steel substrate is explored and discussed.

2. Experimental

Different ZRPs were prepared by mixing various amounts of metallic zinc powder and aluminum paste with ethyl silicate binder. The metallic components of the ZRPs investigated in this study are listed in Table 1. The designation, for example 5A-Z, indicated the ZRP contained 5wt% of Al and 95wt% Zn of the total metallic content.

The paints shown in Table 1 were air sprayed onto 15 cm × 10 cm × 2 mm sand-blasted carbon steel specimens. After curing in ambient temperature, these specimens were used for salt spray tests and electrochemical measurement. The salt spray test was performed in accordance with ASTM (American Society for Testing and Materials) method B117-95. The extent of corrosion was evaluated according to ASTM D-610 specification. The electrochemi-

Table 1. Specimen Designation and Contents of Metallic Components in the Zn/Al Paints (wt%)

Specimen designation / Metallic component	ZRP	5A-Z	15A-Z	25A-Z	35A-Z	55A-Z	75A-Z
Al	0	5	15	25	35	55	75
Zn	100	95	85	75	65	45	25

cal measurements include open circuit potential (OCP) measurement and potentiodynamic polarization curve determination in 3.5wt% NaCl solution at 25°C.

X-ray diffraction was used to analyze the corrosion products formed after salt spray tests. Phase identification was accomplished using data from the JCPDS-ICDD files.

The structure and the pigment distribution of the coatings were examined by using a scanning electron microscope (SEM). The corrosion products formed were analyzed by energy dispersive spectroscopy (EDS).

3. Results

3.1 Microstructure

The SEM images of the surface morphology and the cross section of the painted steel were examined. Fig. 1 shows an example of specimen 15A-Z. As can be seen in Fig. 1 (a), the surface of this specimen was covered with spherical Zn particles and Al flakes. The cross section SEM micrograph also reveals the uniform distribution of spherical and flake type of pigments. X-ray mappings of Zn and Al elements in the coating are shown in Fig.

1 (c) and (d), respectively.

3.2 Electrochemical Measurements

The open circuit potential vs time curves for carbon steel and various coated specimens in neutral 3.5wt% NaCl solution at 25°C are shown in Fig. 2. The steady state OCP for carbon steel was about -715 mV(SCE), and that for Al-free ZRP was -1070 mV(SCE). The addition of Al with a content less than 10 wt% caused a decrease of the OCP to about -1100 mV(SCE). As the Al content was gradually increased to 55wt%, the OCP increased to about -960 mV(SCE). The results suggested that galvanic protection of steel might still be established if it was coated with the mixed Zn/Al paints with the Al content as high as 55wt%. As the Al content was increased to 75wt%, a significant increase of the OCP to -620 mV(SCE) was found. Certainly, cathodic protection would be lost with the ZRP coating containing such high Al content.

Potentiodynamic polarization curves of the various specimens, coated with Zn/Al paints, in neutral 3.5wt% NaCl solution are shown in Fig. 3. The results indicated

Fig. 1. (a) SEM image of surface morphology of 15A-Z coating, (b) SEM image of cross section micrograph of 15A-Z coated specimen, (c) Zn X-ray map, and (d) Al X-ray map.

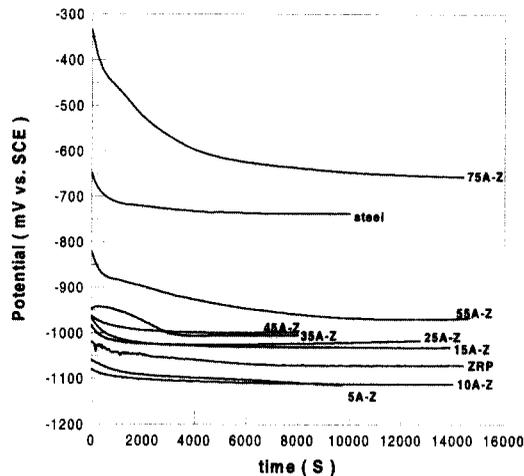


Fig. 2. Potential vs. time curves for steels coated with various Zn/Al paints, in neutral 3.5wt% NaCl solution.

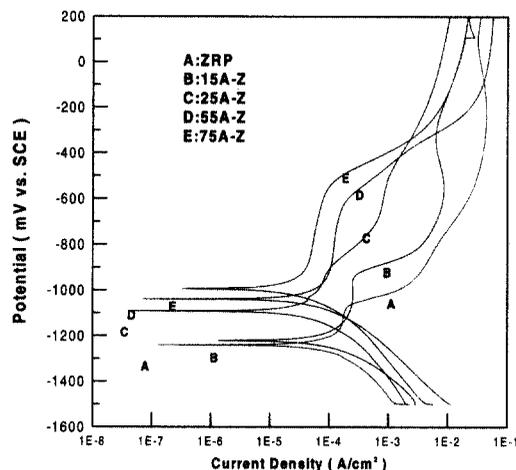


Fig. 3. Potentiodynamic polarization curves for various Zn/Al coated steel specimens, in neutral 3.5wt% NaCl solution.

that the corrosion potential increased with increasing Al content in the paint. A passive region was found in each curve. Clearly, the passive range increased while the passive current density decreased as the Al content was increased. The role of Al as a passivating agent in the ZRP was quite obvious.

3.3 Salt Spray Tests

The results of salt spray tests showed that ZRP without or with appropriate amount Al had superior corrosion protection performance for steel, as compared with hot dip zinc coating. Fig. 4 (4-15) shows the optical micrographs of the specimens coated with hot dip zinc, Al-free ZRP and 15 wt% Al ZRP coatings, respectively, after salt spray for various periods of time. The results showed that red rust appeared on the surface of the hot dip zinc coated steel specimen after 660 h exposure (Fig. 4 (a)). For

Fig. 4. Surface appearances of various specimens after salt spray tests, (a) hot dip Zn, 660 h, (b) ZRP, 2100 h, and (c) 15A-Z, 2100 h.

the specimen coated with Al-free ZRP, no red rust, but with the formation of zinc white, was found after 2100 h of salt spray test. As can be seen in Fig. 4 (c), neither red rust nor zinc white was found on the surface of the specimen coated with Zn/15 wt% Al paint after 2100 h of exposure in the salt spray chamber. The Al-containing

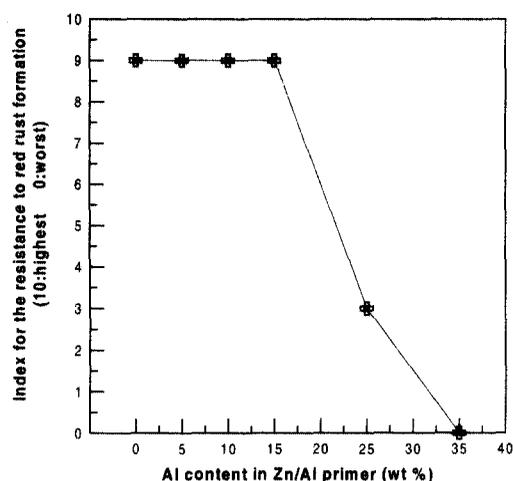


Fig. 5. Index for the resistance to red rust formation for different Zn/Al coated steel specimens, after 2100 h salt spray tests.

ZRP not only had superior corrosion performance to hot dip zinc coating, but also was better than the Al-free ZRP.

The effect of Al content on the corrosion protection performance of ZRP was also investigated. The index for the resistance to red rust formation, according to ASTM D610-95 specification, was used for the evaluation. Fig. 5

Table 2. Summary of surface appearances for various Zn/Al paints after salt spray tests

Specimen	ZRP	5A-Z	15A-Z	20A-Z	25A-Z	35A-Z	55A-Z	75A-Z
Surface appearance								
red rust formation	○	■	○	▲	▲	×	×	×
red rust formation (scratched areas)	■	■	■	▲	×	×	×	×
white rust formation	Y	Y	F	F	N	N	N	N

○: salt spray test > 5000 h - Excellent ■: salt spray test 3000-5000 h - Good
 ▲: salt spray test 1000-3000 h - Fair ×: salt spray test < 1000 h - Poor
 Y: notable amount F: small amount
 N: negligible amount

illustrates the variation of the indexes with Al content in the Zn/Al paints after 2100 h exposure in the salt fog. The results showed that with a low Al content in the ZRP, the area percentage of red rust was less than 0.03%. According to ASTM D 610-95 specification, the index was rated as 9. The excellent resistance to red rust formation was maintained up to 20wt% of Al. Beyond which, the extent of red rust formation increased as indicated by the decrease in index number. The method described in ASTM

Fig. 6. Optical micrographs for the scratched specimens coated with different Zn/Al paints, after 1000 h salt spray test. (a) ZRP, (b) 15A-Z, (c) 20A-Z, (d) 25A-Z, and (e) 35A-Z.

Table 3. X-ray Diffraction Results for ZRP and 15A-Z Before and after 1000 h Salt Spray Test

Specimen	ZRP	15A-Z
As-coated	Zn, ZnO	Zn, Al, ZnO, Al ₂ O ₃
After 1000 h salt spray test	Zn, ZnO, Zn(OH) ₂ , Zn ₇ (CO ₃) ₂ (OH) ₁₀ , Zn ₅ (OH) ₆ (CO ₃) ₂	Zn, ZnO, Zn(OH) ₂ , Zn ₇ (CO ₃) ₂ (OH) ₁₀ , Al, Al ₂ O ₃ , Al(OH) ₃ , Zn Al ₂ O ₄

D 610-95 specification was also used to evaluate the resistance to zinc white formation. Within the range of 0~15wt% Al, the resistance to zinc white formation increased with increasing Al content in the ZRP. Concerning the resistances to both red rust and zinc white formations, Al addition in the amount around 15wt% exhibited the best performance for the ZRP. The results are summarized in Table 2.

Scratched specimens were also used in salt spray tests. Fig. 6 shows the appearances of various Al-containing ZRP after 1000 h exposure in the salt fog. The effectiveness of cathodic protection for the scratched area could be maintained as the Al content was less than 20wt%. For the specimens containing 25 and 35wt% Al, as can be seen in Fig. 6, red rust was formed on the scratched areas, indicating the loss of cathodic protection. The results are also given in Table 2.

The change of surface morphology after salt spray test was examined. The feature of spherical Zn particles disappeared while the shape of Al flake could still be recognized after the tests. The cross sections of the coated steel specimens were also examined after salt spray tests. Fig. 7 shows the SEM micrograph and EDS result for Al-free ZRP after 4000 h of salt spray test. A thick film of corrosion product was formed on ZRP as can be seen in Fig. 7. EDS result revealed that the corrosion product was mainly zinc hydroxide or oxide. Most of the Zn particles inside the ZRP were still remained unattacked (spot A in Fig. 9). However, in some area inside the coating, for example spot B, the ingress of salt water as evidenced by the EDS result of the high chloride content was found. For the Al-containing ZRP, for example 15A-Z, no apparent surface corrosion product was observed. Obviously, surface passivation assisted by Al element prevented the formation of thick zinc oxide or hydroxide. The ingress of Cl⁻ ion was still observed.

X-ray diffraction analyses for the corrosion products formed after salt spray tests are conducted. Table 3 gives the results for ZRP and 15A-Z before and after 1000 h salt spray test. A small amounts of ZnO and Al₂O₃ were identified for both as-coated paints. After salt spray test, Zn(OH)₂, Zn₇(CO₃)₂(OH)₁₀, and Zn₅(OH)₆(CO₃)₂ beside ZnO were formed on the Al-free ZRP. For 15A-Z, ZnO,

wt%	Zn	Cl	O
A	98.69	0.14	1.17
B	80.59	11.65	7.76

Notez : Zn + Cl + O = 100

(b)

Fig. 7. (a) SEM image of cross section micrograph of ZRP after 4000 h salt spray test, (b) EDS results for spots A, B and corrosion product layer in (a).

Zn(OH)₂, Zn₇(CO₃)₂(OH)₁₀, Al₂O₃, Al(OH)₃, and ZnAl₂O₄ were formed after salt spray test. The presence of Al in the ZRP modified the corrosion products formed on the paint surface and retarded the formation of zinc white. The corrosion products formed in salt spray tests were not exactly the same as those formed on the hot dip Zn and Zn/Al coatings exposed in industrial and in marine atmospheres.⁶⁾

After salt spray tests, the OCPs of ZRP coated steel specimens, without or with Al, were measured at various periods of time. For ZRP, the OCP remained as low as -1025 mV(SCE) after 800 h of exposure. Cathodic protection effect could still be maintained even a corrosion product was formed. The time-dependent cathodic protection capability, especially for the ethyl silicate ZRP, has been well addressed by other researchers.⁷⁻⁹⁾ For Al-containing ZRP, however, an increase in OCP was observed for each Zn/Al coated specimen. After 800 h exposure, the OCP could be higher than -700 mV(SCE). According to the X-ray diffraction results, the increase in the OCP was attributed to the formation of passive film such as Al₂O₃, etc. The establishment of barrier effect became more obvious at prolonged exposure in moist saline environment for Al-containing ZRP.

4. Conclusions

The addition of Al into ZRP could retard the formation of zinc white and enhance the barrier effect of the paints. Adequate cathodic protection could still be maintained for the ZRP containing Al up to 20wt%.

Acknowledgement

The authors gratefully acknowledge the support for this work provided by the Department of Economics of the Republic of China under contract 0289010.

References

1. H. E. Townsend and J. C. Zoccola, *Materials Performance*, **18**, 13 (1979).
2. H. E. Townsend, L. Allegra, R. J. Dutton, and S. A. Kriner, *Materials Performance*, **25**, 36 (1986).
3. H. E. Townsend and A. R. Borzillo, *Materials Performance*, **26**, 37 (1987).
4. F. E. Goodwin, in *Zinc-Based Steel Coating Systems: Metallurgy and Performance*, G. Krauss and D. K. Matlock (Eds.), The Minerals, Metals & Materials Society, p. 183, 1990.
5. P. R. Sere, M. Zapponi, C. I. Elsner, and A. R. Di Sarli, *Corrosion Science*, **40**, 1711 (1998).
6. J. J. Friel, *Corrosion*, **42**, 422 (1986).
7. S. Feliu Jr., M. Morcillo, J. M. Bastidas, and S. Feliu, *J. Coatings Technology*, **65**, 43 (1993).
8. S. Feliu, R. Barajas, J. M. Bastidas, and M. Morcillo, *J. Coatings Technology*, **61**, 63 (1989).
9. S. Feliu, R. Barajas, J. M. Bastidas, and M. Morcillo, *J. Coatings Technology*, **61**, 71 (1989).