The Electrochemical Behavior & Lifetime Of a Hot-Dip 5-Wt% Al-Zn Coating In Chloride Environments

H.C. Shih, J.W. Hsu, C.N. Sun & S.C. Chung

Batch-type hot-dip zinc and 5-wt% Al-Zn coatings were investigated in the present work for the comparison of their corrosion resistance, electrochemical behavior and microstructures. The 5-wt% Al-Zn coatings possess a prominent electrochemical passivation behavior. Intermetallics formed mainly between iron, aluminum and zinc adhering to the substrate were identified with energy-dispersive X-ray analysis and believed to be responsible for the passivation phenomena as observed in the electrochemical polarization. The 5-wt% Al-Zn coatings exhibited a much better corrosion resistance than the conventional hot-dip galvanized steels under salt spray testing. Although the corrosion potentials of both coatings increased toward the noble potential as the immersion time increases, 5-wt% Al-Zn coatings were always nobler than hot-dip zinc coatings.

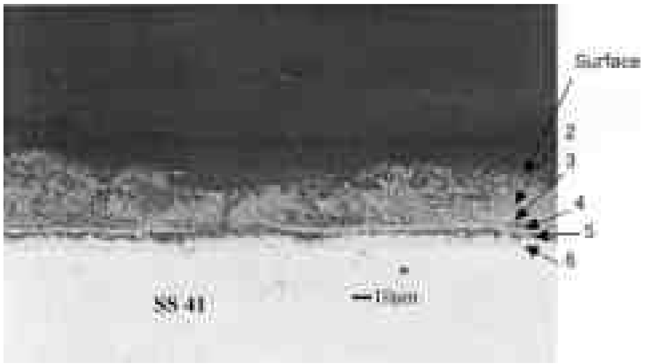

Fig. 1—Cross–sectional morphology of a 5-wt% Al-Zn coating (~60µm) showing the six layers of alloy composition.

Corrosion protection of galvanized steels arises from the barrier action of zinc layer, the secondary barrier action of the zinc corrosion products and the cathodic protection of zinc on the unintentionally exposed part of steel, with the coating acting as a sacrificial anode.

More recently, hot-dip 5-wt% Al-Zn alloy coatings have been found to exhibit a corrosion resistance that is markedly superior to that of hot-dip galvanized steels. Aluminum is added to commercial galvanizing baths to produce ductile coatings by suppressing the growth of brittle Fe-Zn intermetallics. Previous investigators[1-5] who have studied the influence of aluminum additions to the zinc bath on the structure of hot-dipped coatings agreed that small additions of aluminum to the bath delay the reaction between zinc and iron.

Bablik[6] reported that the iron-aluminum compound Fe_3Al inhibits the growth of Fe/Zn phases. Hughes[2] indicated that the inhibition is caused by a thin layer of $FeAl_3$ containing 16 - 27 wt% Zn. The current accepted inhibition mechanism was proposed by Haughton[3] in that a thin layer of Fe_2Al_5 forms on the iron surface in the initial stages of hot dipping, and this layer is responsible for the inhibition of the reaction between iron and molten zinc. In a 5-wt% Al-Zn alloy, localized zinc and aluminum dissolution occurs without dealloying, but gives rise to pits, which may penetrate the full thickness of the coating.[7]

The objective of this study was to investigate the electrochemical behavior and lifetime of 5-wt% Al-Zn coatings and compare them with galvanized steels, and to estimate the phase compositions of the Fe-Al-Zn alloys across the coating thickness from the surface to the interface.

Experimental Procedure

Two types of coated specimens (Zn and 5-wt% Al-Zn coatings) were provided by a local galvanizing shop. Cold rolled structural steel panels of SS41 (50×50×2 mm) were hot-dipped in the pure zinc and aluminum-containing zinc baths. The chemical distribution of the coatings was analyzed by SEM/EDS (JEOL 5410).

Potentiodynamic polarization curves for both the zinc and 5-wt% Al-Zn coatings were derived in an aerated 3% NaCl solution (pH 7). Similar studies were also made for the corrosion current or polarization resistance, based on the linear polarization over a small potential range of ±10 mV with respect to the corrosion potential.[8] A three–electrode cell configuration was employed for the polarization measurements.[9] A saturated calomel electrode (SCE)

Table 1
Chemical Composition of Hot-Dip 5-wt% Al-Zn Coating

Elements	Al	Zn	Fe	O	Oxides and Intermetallics
Layer 1 (Surface)	6.7	65.3	0.7	27.3	Al_2O_3 + ZnO
Layer 2	17.2	64.0	2.8	16.0	$ZnO{\bullet}Al_2O_3$/ZnAl alloy
Layer 3	19.6	63.0	1.8	15.6	$FeAl_3$ or Fe_2Al_5/ZnAl alloy
Layer 4	16.6	63.2	2.6	17.6	Fe_3Al/ZnAl alloy
Layer 5	2.1	82.4	—	15.1	θ-$FeAl_3Zn_{0.4}$/Zn Al alloy
Layer 6	47.7	13.0	31.3	8.0	θ-$FeAl_3Zn_{0.4}$

Table 2
Microhardness of the Surface Coatings on Steel

	Steel (SS 41)	Galvanized Steel	5-wt% Al-Zn Coating
Surface Hardness, HV	153	68	96

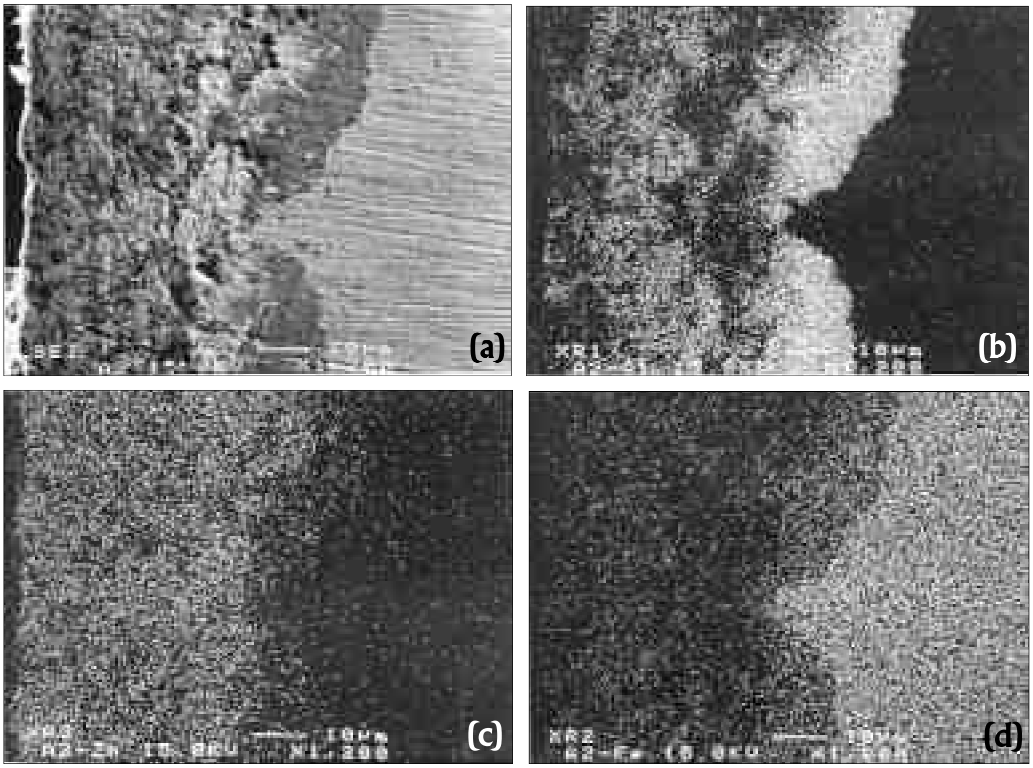

Fig. 2—SEM micrograph (a) and X-ray mappings of Al (b); Zn (c) and Fe (d) for the 5-wt% Al-Zn coated steel.

was used as a reference electrode and a platinum sheet was used as a counter electrode. All polarization work was carried out using a computer controlled measurement system consisting of a potentiostat (EG&G 273). The current was recorded as the potential increased at a scan rate of 1 mV/s. Corrosion potentials for both specimens were monitored at all times during the immersion tests.

Exposure tests were conducted in a salt spray cabinet according to the ASTM B117 procedure. An aerated 3% NaCl solution with a pH value adjusted to 7 was also used for salt spray tests.

Surface hardness was measured by a Vickers microindenter with an applied load of 10 g. The surface hardness was evaluated by taking five indentations on each specimen, and only three middle values were averaged.

Results & Discussion

Microstructures

Figure 1 shows a cross-sectional view of the hot-dipped 5-wt% Al-Zn coating with a thickness of about 60 µm, as observed by SEM/EDS. The composition of the coating surface was found to be the same as that of the galvanizing bath, *i.e.*, 5-wt% Al-Zn.[10] Referring to the Al-Zn, Fe-Al binary[5] and Fe-Al-Zn ternary phase diagrams,[10] there were six alloy layers in the coating, which could be distinguished from one another. The chemical distribution of each layer as semi-quantitatively analyzed by SEM/EDS is shown in Fig. 2 and listed in Table 1. A six-layered structure of the 5-wt% Al-Zn coating, in fact, resulted from the elemental distribution. The outermost layer was mainly composed of a mixture of $ZnO•Al_2O_3$ because of high-temperature oxidation (~500ºC) in air. The innermost layer or the layer immediately adjacent to the steel was the Fe-Al-Zn ternary intermetallic compound, θ-$FeAl_3Zn_{0.4}$. In between were the $ZnO • Al_2O_3$, $FeAl_3$ (or Fe_2Al_5), Fe_3Al and θ-$FeAl_3Zn_{0.4}$ phases alloyed with various solid solutions of Zn-Al alloys. This observation is in general agreement with the results from the Al-Zn, Fe-Al and Fe-Al-Zn phase diagrams.

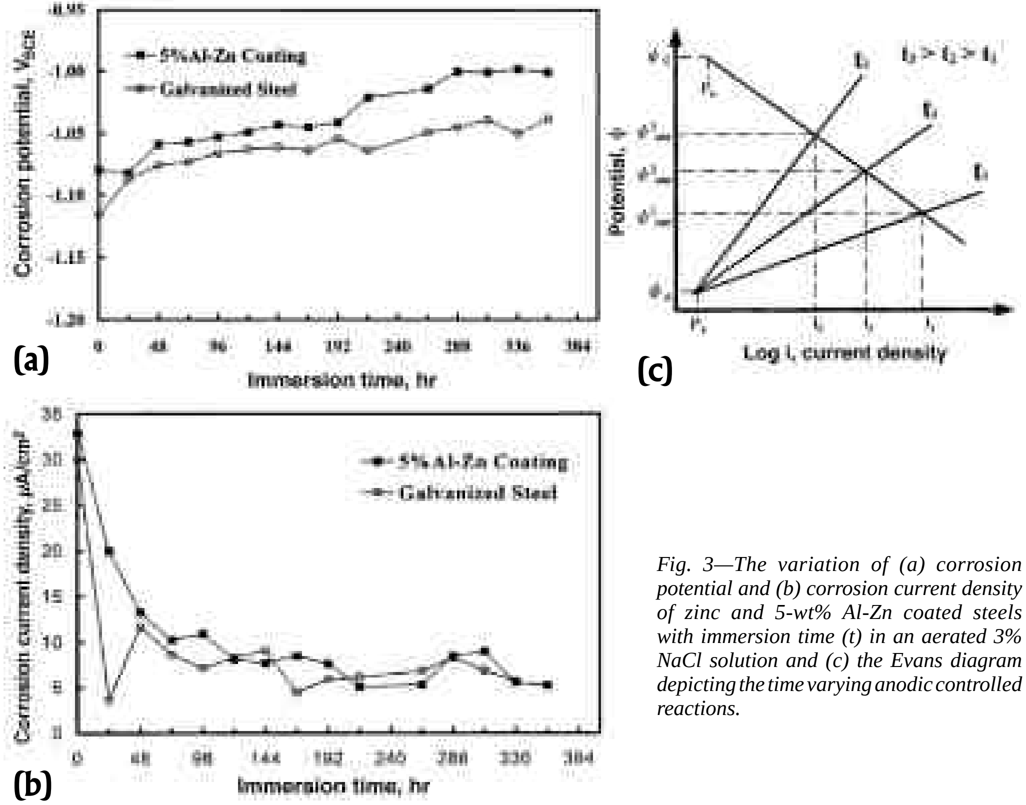

Fig. 3—The variation of (a) corrosion potential and (b) corrosion current density of zinc and 5-wt% Al-Zn coated steels with immersion time (t) in an aerated 3% NaCl solution and (c) the Evans diagram depicting the time varying anodic controlled reactions.

It is worth noting that no Fe/Zn intermetallics were observed in the 5-wt% Al-Zn coatings. The aluminum content (2.1%) in Layer 5 was significantly lower than in the other layers, especially its neighboring layer (Layer 6) and the layer immediate to the steel substrate. The innermost layer was in fact a continuous film of pure single-phase θ-$FeAl_3Zn_{0.4}$, which is the same phase but more or less dispersed in Layer 5, as shown in

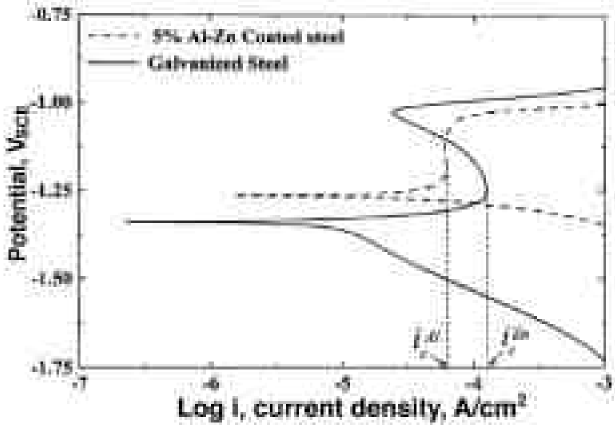

Fig. 4—Potentiodynamic polarization curves of zinc and 5-wt% Al-Zn coated steels in an aerated 3% NaCl solution.

Fig. 1 and Table 1. We believe that the extreme low level of aluminum (2.1%) in Layer 5 was the result of depletion of the aluminum during the formation of higher aluminum content (47.7%) in Layer 6.

The surface hardness of the 5-wt% Al-Zn coatings was about 96 HV, which is 40% more than that for conventional galvanized steel (68 HV), and attributable to the occurrence of Al_2O_3 and intermetallics of Al and Zn, as listed in Table 2.

Corrosion Characteristics

The corrosion potentials of both the zinc and 5-wt% Al-Zn coatings tended to increase toward the noble direction with an exponential decay of the corrosion current density during the first three days of immersion but reached a steady-state thereafter. This clarified the fact that the corrosion process was under anodic control as shown in Figs. 3a and b, and as depicted in Fig. 3c.

It is most likely that a passive film was established on both coated steels during exposure to the environment (3% NaCl), however, the 5-wt% Al-Zn coating tended to exhibit a nobler corrosion potential than that of conventional galvanized steel (Fig. 3a). This may imply that a tenacious oxide film originating from aluminum formed on the surface, and apparently was more effective than all other forms of zinc oxide. After nine days of immersion, a difference of 50 mV in the corrosion potential was developed in which the 5-wt% Al-Zn coating was always more noble than the conventional galvanized steel.

The corrosion current density was measured by polarizing the specimen both anodically and cathodically around the corrosion potential, covering a potential range of 20 mV. Both coatings exhibited a general tendency of an initial exponential decay in corrosion current. Eventually the current approached a steady state of 6 µA/cm^2 after 4 days' exposure (Fig. 3b).

It was apparent that both coatings exhibited a passivity range of about ~200 mV in a chloride environment, as shown in Fig. 4. It is important to note that the 5-wt% Al-Zn coatings tended to have a critical current density (i_c^{Al}) of 7×10^{-5} A/cm^2, which was much lower than that of the galvanized steels, with an (i_c^{Zn}) of 1.5×10^{-4} A/cm^2, indicating an ease of passivation when 5 wt% of Al is alloyed with Zn.

Salt Spray Tests

The exposure tests (50×50 mm) were conducted in a salt spray cabinet. After each exposure of 250 hr, the specimen was retrieved and the degree of corrosion was evaluated. The results of 500, 1250 and 2000 hr salt spray tests are shown in Fig. 5 which indicate a trend of gradual reduction of white corrosion products replaced by yellowish brown rust spots on the galvanized steel.

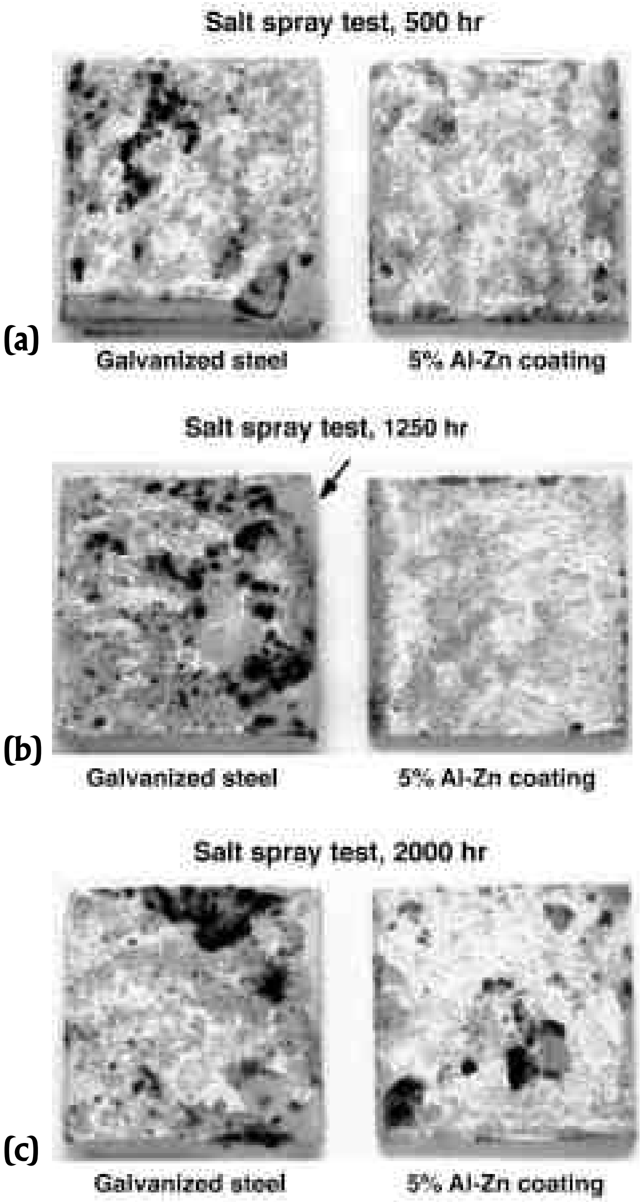

Fig. 5—Surface morphologies of zinc and 5-wt% Al-Zn coatings after salt spray tests for various periods of time: (a) 500, (b) 1250 and (c) 2000 hours.

Physically, at the later stages of the test, the rust scales became loosely attached and eventually easily detached from the zinc-coated steel substrate (arrow in Fig. 5), while 5-wt% Al-Zn coating still remained intact. Figure 6 shows a comparison of the iron rust area between the zinc and 5-wt% Al-Zn coatings after the salt spray tests. The results clearly indicate that the appearance of iron rust for the conventional galvanized steels is much more serious than for the 5-wt% Al-Zn coatings. For instance, coverage of 5% of the surface by iron rust requires 750 hr for conventional galvanized steels but 1700 hr for the 5-wt% Al-Zn coated steel. A doubling of the lifetime can therefore be expected for 5-wt% Al-Zn in chloride-containing environments.

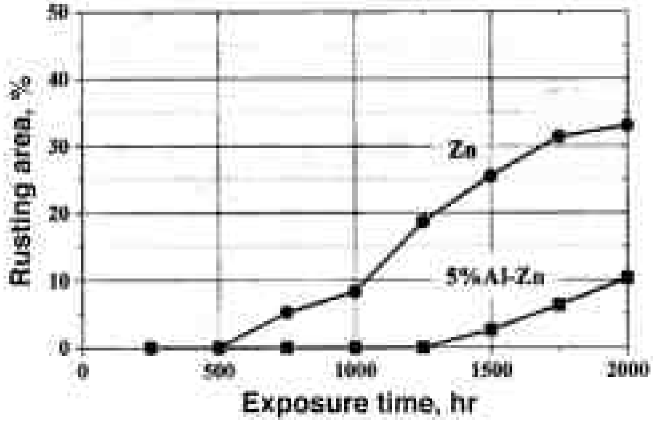

Fig. 6—Degree of corrosion versus exposure time.

Conclusions

1. A six-layered structure of a 5-wt% Al-Zn coating was found to have the following distribution, from the surface to the substrate: $ZnO \bullet Al_2O_3$, $ZnO \bullet Al_2O_3/ZnAl$ alloy, $FeAl_3/ZnAl$ alloy; $Fe_3Al/ZnAl$ alloy; θ-$FeAl_3Zn_{0.4}$/Zn Al alloy and θ-$FeAl_3Zn_{0.4}$.
2. The 5-wt% Al-Zn coating had a higher aluminum content, in the form of an intermetallic compound of θ-$FeAl_3Zn_{0.4}$ film immediately adjacent to the steel substrate.
3. The Fe/Al solid solution and θ-$FeAl_3Zn_{0.4}$ phases exhibited a nobler corrosion potential than all the other Fe/Zn and zinc oxide phases, and particularly at the later stages of corrosion.
4. The θ-$FeAl_3Zn_{0.4}$ film effectively enhanced the adhesion of 5-wt% Al-Zn coatings to the steel substrate.
5. No major intermetallics of Zn and Fe were observed in the 5-wt% Al-Zn coatings.
6. A doubling of the lifetime was expected for the 5-wt% Al-Zn coatings by alloying aluminum to the coating of galvanized steels.

References

1. H. Bablik, *Galvanizing*, 3rd ed., Spon Ltd., London, England, 1950; p. 204.
2. M.L. Hughes, *Proc. Int'l. Conf. on Hot-Dip Galvanizing, Copenhagen, 1950*, Zinc Development Association, Oxford, England, 1953; p. 31.
3. M.A. Haughton, *Proc. 2nd Int'l. Conf. on Hot-Dip Galvanizing, Dusseldorf, 1952*, Zinc Development Association, Oxford, England, 1953; p. 59.
4. A.R.P. Ghuman & J.I. Goldstein, *Metal. Trans.*, **2**, 2903 (1971).
5. Z.W. Chen, R.M. Sharp & J.T. Gregory, *Mat. Sci. Tech.*, **6**, 1173 (1990).
6. H. Bablik, F. Gotzl, & R. Kukaczka, *Werkstoff u. Korros.*, **2**, 1963 (1951).
7. H.N. McMurry, G. Parry, & B.D. Jeffs, *Iron & Steelmaking*, **25**, 210 (March 1998).
8. D.A. Jones, *Principles & Prevention of Corrosion*, 2nd ed., Simon & Schuster, New York, NY, 1996.
9. N.D. Greene, *Experimental Electrode Kinetics*, Rensselaer Polytechnic Institute, Troy, New York, NY, 1965.
10. W.F. Smith, *Structures & Properties of Engineering Alloys*, McGraw-Hill, New York, NY, 1981; p. 162.

Shih

Hsu

Sun

Chung

About the Authors

Han C. Shih is a professor in the Department of Materials Science and Engineering at the National Tsing Hua University. He specializes in corrosion science, materials protection, plasma processing technology and interfacial electrochemistry. He has a PhD from Universität Tübingen, Germany and is the author or co-author of 180 journal papers.

J.W. Hsu is a doctoral candidate at the Department of Materials Science and Engineering at the National Tsing Hua University. He is an expert in materials corrosion and characterization.

C.N. Sun holds an MS from the National Tsing Hua University and is now in military service. He is an experienced specialist in zinc alloys (5-wt% Al) anodizing and metallography studies.

S.C. Chung holds a PhD from the National Tsing Hua University and is now affiliated with Materials Research Laboratories, ITRI, Chutung, Hsinchu, Taiwan. He specializes in the basic corrosion research of galvanized steel and aluminum and zinc anodes.