Self-Healing Effect by Zinc Phosphate and Calcium Silicate Included in Organic-Inorganic Composite Coating on 55% Al-Zn Coated Steel Sheet^{*1}

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Improved corrosion resistance of steel sheets plated with zinciferous metal, and particularly 55% Al-Zn alloy coated steel sheets, has become necessary in recent years. However, 55% Al-Zn alloy coated steel sheets are susceptible to surface cracks during forming due to the hardness of the metallic coating. This research examined various non-chromate corrosion-preventive compounds for organic-inorganic composite coatings and found that a composite coating containing a mixture of $\text{Zn}_3(\text{PO}_4)_2$ and CaSiO_3 provided the highest corrosion resistance among all the additives tested. The corrosion mechanism was investigated by post-test analysis of the specimens by SEM, AFM, TEM and EDX, revealing that an amorphous surface layer, which was approximately 30 nm thick and contained Ca, Cr, P, Si, C, and O, had newly formed on the steel surface exposed after deformation of the coating. It is presumed that Ca^{2+} and HPO_4^{2-} were formed by dissolution of the CaO component in CaSiO_3 and hydrolysis of $\text{ZnO}_3(\text{PO}_4)_2$, respectively, and reacted to form an insoluble Ca-phosphoric acid compound which inhibited corrosion of the metal exposed by cracks. [doi:10.2320/matertrans.M2010290]

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1. Introduction

Maintenance-free building materials with long-term durability are required to overcome corrosion problems due to acid rain caused by air pollution and spray from snow-melting agents and encourage residential and commercial construction in coastal regions, exemplified by waterfront development. Use of 55% Al-Zn alloy coated steel sheets has greatly increased as a substitute for the conventional hot-dip galvanized steel sheets. The 55% Al-Zn alloy coating on these steel sheets has a dendrite structure with an α phase of Al solid solution and a β phase of Zn solid solution and exhibit excellent corrosion resistance due to the passivation effect of Al and the sacrificial anticorrosion effect of Zn.¹⁾ Horton²⁾ investigated the correlation between the Al content in hot-dip Zn-Al alloy coated steel sheets and corrosion resistance and found that the corrosion resistance of 55% Al-Zn alloy coated steel sheets is two to five times higher than that of hot-dip galvanized steel sheets in various environments.

In general, a chromate coating containing organic resin is applied to 55% Al-Zn coated steel sheets to improve corrosion resistance.^{3,4)} Improvement is achieved through the self-healing effect of Cr(VI) chemical species (hereafter, Cr(VI)) and the barrier effect of Cr(III) chemical species (hereafter, Cr(III)), as well as the barrier effect of the organic resin itself. However, as this alloy coating is harder than the zinciferous coatings, severe forming of 55% Al-Zn alloy coated sheets causes surface cracks deep enough to reach the steel substrate. Even assuming a chromate coating containing an organic resin is applied, rust is initiated at the formed area

and the appearance of the product is markedly degraded. Although use of this sheet had been limited to applications requiring comparatively light forming, demand for applications which require severe forming, such as roofing and siding, is increasingly steadily due to its design properties and functionality.

Previous reports have demonstrated that the self-healing effect which prevents corrosion at coating defects contributes to the corrosion-resistance provided by the chromate coatings⁵⁻⁹⁾ and a correlation exists between the Cr(VI) content and corrosion resistance.¹⁰⁻¹²⁾ Theoretically, the post-forming corrosion resistance of 55% Al-Zn coated steel sheets can be improved by increasing the Cr(VI) content, but there are practical limits to increases in Cr(VI), as Cr(VI) is a water-soluble substance that causes unacceptable environmental pollution when eluted, and also causes yellow discoloration of the coating. Thus, a new approach to improving post-forming corrosion resistance without using Cr(VI) had been required. Chromate-free coatings are also needed for steel sheets plated with zinciferous metal, which are widely used in electric appliances, in order to comply with environmental regulations such as the RoHS Directive. It is no exaggeration to say that the search for substances with self-healing effects as substitutes for Cr(VI) is the most critical issue for the development of chromate-free coatings.

In order to improve the post-forming corrosion resistance of 55% Al-Zn coated steel sheets, the authors carried out an experimental study of the self-healing effect by adding different corrosion inhibitors other than Cr(VI) to the organic-inorganic composite coating used on this type of sheet. The results showed that extremely high corrosion resistance superior to that of Cr(VI) can be obtained by adding calcium silicate to zinc phosphate.^{13,14)} The contributions of these two compounds to corrosion resistance were investigated quantitatively, and the mechanism responsible for improvement of post-forming corrosion resistance was

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Table 1 Corrosion-preventive additives used for this work.

Type	Compounds
A	$\text{Zn}_3(\text{PO}_4)_2$
B	$\text{Zn}_3(\text{PO}_3)_2$
C1	88 mass% $\text{Zn}_3(\text{PO}_4)_2$ + 12 mass% CaSiO_3
D	PbO
E	BaCrO_4

examined by analyzing the composition and structure of the corrosion products on the surface of formed sections after the corrosion test.

2. Experimental

2.1 Corrosion-preventive additives

The inorganic corrosion-preventive additives used in this study are shown in Table 1.^{15,16)} Zinc phosphate (A), zinc phosphite (B), and a mixture (C1) of calcium silicate and zinc phosphate were employed as precipitation-type corrosion-preventive additives. Lead oxide (D) and barium chromate (E) were tested as passivation-type corrosion-preventive additives.

2.2 Specimens

Organic-inorganic composite coatings were prepared using a chromate treatment solution to which acrylic resin and phosphoric acid had been added. The basic composition was acrylic resin, Cr, and phosphoric acid in the ratio of 75 : 1 : 2 (mass ratio). The corrosion-preventive additives were also added to the acrylic resin in the ratio of 25 or 50 : 100 (mass ratio). Cr was added as a partially-reduced chromic acid solution, which was prepared by reducing Cr(VI) to Cr(III) by adding cane sugar to a chromic acid solution (20 g/l) until a Cr(III)/(VI) mass ratio of 30/70 was achieved. These solutions were diluted so as to obtain a Cr coating weight of 20 mg/m² as metallic Cr. Specimens were prepared by coating the diluted solutions on 55% Al-Zn coated steel sheets (sheet thickness: 0.5 mm, zinc coating weight: 75 g/m² on one side) with a bar coater, followed by drying (peak metal temperature: 120°C).

The organic-inorganic composite coating containing additives C1 consisting of a mixture of zinc phosphate and calcium silicate exhibited the highest corrosion resistance in this study. Therefore, with this additive, specimens were prepared using different ratios of zinc phosphate and calcium silicate in order to investigate the contributions of the two compounds. Treatment solutions were also prepared using chromic acetate(III) as the Cr source in the above basic composition in order to elucidate the corrosion mechanism when the self-healing effect of Cr(VI) was excluded. Specimens were prepared by coating the solutions on electro-galvanized steel sheets (sheet thickness: 0.5 mm; zinc coating weight: 20 g/m² on one side), followed by drying (peak metal temperature: 120°C). Under these preparation conditions, the ratio of corrosion-preventive additives (60% zinc phosphate + 40% calcium silicate) to acrylic resin was 25 : 100 (mass ratio).

2.3 Evaluation of corrosion resistance

The specimens described above were subjected to 5T bending, in which the specimen was bent 180° while leaving a gap 5 times the sheet thickness, or scratching of the surface with a cutter reaching the steel substrate, after which the edges were sealed with either black tar epoxy resin or transparent adhesive tape. A salt spray test conforming to JIS Z2371 was performed, and the extent of rust generation was investigated. The corrosion resistance of the 5T bent sections was estimated using a rating scale of 0–5 points corresponding to the area of rust on the ridge, 5 points indicating no rust and 0 points indicating rust covering the entire section. Scores were given using the average rating for two specimens having the same coating composition.

2.4 Surface and cross-sectional analysis of structure and composition

An organic-inorganic composite coating containing the corrosion-preventive additives zinc phosphate and calcium silicate, which exhibited the best corrosion resistance in the above-mentioned salt spray test, was prepared on an electro-galvanized steel sheet as described in section 2.2. The specimen was subjected to surface and cross-sectional analysis after the salt spray test. For comparison, a specimen coated with an organic-inorganic composite coating without corrosion-preventive additives was subjected to the same analysis.

2.4.1 Surface analysis

In order to assess the extent of damage of 55% Al-Zn alloy coating caused by bend forming, secondary electron (SE) images of the surface of the 5T bent section were taken by FE-SEM (Hitachi S-510). The specimen coated with an organic-inorganic composite coating without corrosion-preventive additives was observed at an accelerating voltage of 25 kV after gold vapor deposition.

For examination of the morphology of the corrosion products, SE images were taken with an in-lens detector (LEO, presently Carl Zeiss LEO1530) at an accelerating voltage of 1 kV. No electrically conductive material was evaporated onto the specimen surface. Under these conditions, surface substances such as thin oxide layers could be visualized by the difference in the electrical conductivity of the specimen surface layers.¹⁷⁾

The composition of the corrosion products was investigated through in-depth elemental analysis by AES (PHI SAM-660) under conditions of primary electron-beam energy: 3 keV, beam current: 10 nA and analysis area: 3 μm. Sputtering was performed using by an Ar⁺ ion gun with a sputtering rate of 5 nm/min for a SiO₂ layer.

2.4.2 Cross-sectional analysis

Cross-sectional analysis of the composition and structure of the corrosion products were carried out by FE-TEM (FEI CM20FEG) and EDX (EDAX Phoenix). TEM samples were prepared by the microsampling method using an FIB device (Hitachi Hi-Tech FB2000A).¹⁸⁾ To prevent damage by the ion beam, the specimens were introduced into the FIB device after carbon coating by vacuum deposition, and a protective carbon layer was further formed on the sampling area by chemical vapor deposition (CVD). TEM samples were cut out using a Ga ion beam and were removed from the

specimens after joining to a W probe by CVD. The samples were then fixed on a Mo grid, again using CVD, and thinned with a Ga ion beam. TEM observation and EDX analysis were carried out at an accelerating voltage of 200 kV.

3. Results

3.1 Evaluation of corrosion resistance

An SE image of the 5T bent section before the corrosion test is shown in Fig. 1. Numerous cracks of various sizes were observed. The interior of the cracks where the steel sheet was exposed is considered to be the initiation site of corrosion.

The results of an evaluation of the corrosion resistance of the 5T bends after a 120 h salt spray test are shown in Fig. 2. The specimen with the organic-inorganic composite coating with lead oxide (additive D), which was expected to have a passivation effect by pH control in corrosive environments,

showed lower post-forming corrosion resistance than the specimen without corrosion-preventive additives. However, the specimens with the other corrosion-preventive additives showed improved corrosion resistance. In particular, the post-forming corrosion resistance of the specimen using additives C1 (zinc phosphate and calcium silicate) was superior to that of the specimen using barium chromate, in which Cr(VI) was expected to have a passivation effect.

To investigate the relative contributions of zinc phosphate and calcium silicate in additive C1, which exhibited the best corrosion resistance in the formed specimens, the corrosion resistances of organic-inorganic composite coatings containing various ratios of zinc phosphate and calcium silicate were evaluated in a scratching test. Figure 3 shows the appearances of the specimens after a 240 h salt spray test. The coatings prepared by mixture of the two compounds (i.e., additives C1-C3) suppressed rust generation at the scratched section, and their protective effect increased as the content of the additives increased. In particular, no rust was observed in the scratched section of the specimen using additive C3, in which the ratio of the corrosion-preventive additives (33% zinc phosphate + 67% calcium silicate) to the acrylic resin was 50 : 100 (mass ratio), indicating the extremely high corrosion resistance of the specimen. Although a greater corrosion resistance effect was seen in the specimen using only zinc phosphate (A) than in the specimen without corrosion-preventive additives, that effect was very small in comparison with the specimens using both zinc phosphate and calcium silicate (C1-C3). In the specimen using only calcium silicate (C4), rust was not limited to the scratched section but extended over the whole area; thus, the corrosion resistance with this additive was inferior to that with no corrosion-preventive additive.

Fig. 1 Appearance and SE image of 5T bent section of 55% Al-Zn coated steel sheet (Accelerating voltage = 25 kV).

corrosion-preventive additives		Appearance of 5T bent section 10mm	Corrosion resistance of 5T bent section (Rating after 120h of salt spray test)					
			0	1	2	3	4	5
A	$\text{Zn}_3(\text{PO}_4)_2$							
B	$\text{Zn}_3(\text{PO}_3)_2$							
C1	$\text{Zn}_3(\text{PO}_4)_2 + \text{CaSiO}_3$							
D	PbO							
E	BaCrO_4							
	Non-additives							

Fig. 2 Corrosion resistance of 5T bent section of 55% Al-Zn coated steel sheets with chromate coating containing various corrosion-preventive additives after 120 h of salt spray test.

Fig. 3 Appearance of 55% Al-Zn coated steel sheets with chromate coating containing different ratio of Zn₃(PO₄)₂ and CaSiO₃ after salt spray test for 240 h.

Fig. 4 Appearance of Zn coated steel sheets with Cr(III) coating with additives C2 after salt spray test for various times.

Comparing the results of the scratch test (Fig. 3) and 5T bending test (Fig. 2) with additive C1 (zinc phosphate and calcium silicate), although the degree of corrosion is larger in the scratch test than in the 5T bending test, this difference can be attributed to the fact that exposed steel area is larger and the test time is twice as long in the scratch test. In both corrosion tests, the specimens using additive C1 displayed higher corrosion resistance than the specimen using only additive A (zinc phosphate). While the size of the defects differs in the two tests, these results suggest that the scratch test is an appropriate method for evaluating corrosion resistance after forming.

In order to elucidate the mechanism responsible for improved post-forming corrosion resistance by a coating containing a mixture of zinc phosphate and calcium silicate, a specimen in which chromic acetate(III) was added as Cr was prepared on an electrogalvanized steel sheet. A salt spray test was performed using scratched specimens. The appearance of the specimens after the test is shown in

Fig. 4. More severe corrosion was observed in the electrogalvanized steel sheet without corrosion-preventive additives than in the 55% Al-Zn coated steel sheet (Fig. 3) with Cr(VI) addition but without the corrosion-preventive additives. That is, the specimen without corrosion-preventive additives showed white rust after 24 h and red rust after 144 h at the scratched section. In contrast, the specimen with additive C2 (zinc phosphate and calcium silicate) retained a metallic gloss on the inside of the scratched section and showed no rust on the scratched section for more than 200 h. Thus, the additives zinc phosphate and calcium silicate also improved the post-forming corrosion resistance of an electrogalvanized steel sheet, although the organic-inorganic composite coating on the sheet included Cr(III) instead of Cr(VI). The composition of the electrogalvanized coating is more homogeneous than that of the 55% Al-Zn coating, which comprises a dendrite structure of α phase (Al solid solution) and β phase (Zn solid solution). This means the corrosion characteristics of electrogalvan-

Fig. 5 SE images of scratched section of Zn coated steel sheets with Cr(III) coating after salt spray test for 24 h (Accelerating voltage = 1 kV).

ized coatings are virtually independent of the observation position. Therefore, in the following, electrogalvanized steel sheets were used as the substrate material for surface and cross-sectional analysis.

3.2 Surface and cross-sectional analysis

3.2.1 Surface analysis

Figure 4 showed the specimens of electrogalvanized steel sheets after the salt spray test. After 24 h, specimens were observed by ultra-low accelerating voltage SEM to assess the state of corrosion in the interior of the scratches. SE images of the surfaces of the scratched sections are shown in Fig. 5. In the specimen with additive C2 (zinc phosphate and calcium silicate), the contrast in the scratched section is brighter than that in the specimen without corrosion-preventive additives when observed under low magnification. This suggests that electrification (resulting from accumulation of positive charge due to use of a low accelerating voltage electron beam) is low in this section, that is, surface electroconductivity is high.¹⁷⁾ In the image at higher magnification, minute scratch marks are observed in the specimen with the additive C2. This indicates that the metal is exposed or the corrosion products, assuming they exist, are extremely thin in the scratched section of the specimen with additive C2. In contrast, since the scratched section of the specimen without the corrosion-preventive additives showed a dark contrast, electroconductivity was considered to be low. In this case, the existence of relatively thick corrosion products with a porous structure on this surface is conceivable. AES depth profiles of the scratched sections of the two specimens are shown in Figs. 6 and 7. In the specimen without corrosion-preventive additives, which showed white rust in Fig. 4, a film comprising mainly Zn and O and also

Fig. 6 Depth profiles at the bottom of scratched section of Zn coated steel sheet with Cr(III) coating after salt spray test for 24 h.

containing Cr had formed, and Cl was concentrated in the outermost layer. A film thickness of approximately 200 nm was estimated from the sputtering rate of SiO_2 , assuming the position at which the O concentration is half that at the surface is the interface between the film/metal substrate. In contrast, the film that formed on the specimen using additive C2, in which the scratched section retained its metallic gloss after the salt spray test (Fig. 4), comprised mainly Ca, C and

O, and also contained Si, P, Zn, and Cr but no Cl. This film was as thin as approximately 30 nm. Thus, the composition and thickness of the corrosion product layers formed in the scratched section after the salt spray test differed significantly, depending on whether additive C2 was used or not.

3.2.2 Cross-sectional analysis

The scratched section of the specimen using additive C2 after the salt spray test was cut into a slice by the FIB micro-

sampling method, and cross-sectional microstructural analysis was performed by TEM. A bright field image is shown in Fig. 8, and EDS spectra and electron diffraction patterns are shown in Fig. 9. An amorphous surface layer containing Ca, Cr, P, Si, and other elements with a thickness of approximately 30 nm had formed on the steel surface. These results are consistent with those obtained by SEM and AES. The Ga and Mo components in the EDS spectra are thought to be due to contamination during the FIB micro-sampling, as a Ga ion beam and Mo grid were used.

4. Discussion

The corrosion reaction of a metal M in a neutral aqueous solution is as follows:¹⁹⁾

Furthermore, M^{z+} and OH^{-} react as follows:

According to Meyer¹⁹⁾ who investigated the mechanism of corrosion-prevention of iron by zinc phosphate, when zinc phosphate exists in the corrosive environment shown above, the hydrolysis reaction (4) of zinc phosphate occurs due to alkalization by reaction (2):

In other words, the corrosion-preventive action of zinc phosphate is the result of the formation of a protective layer, triggered by the corrosion reaction of the metal.

The effect of adding calcium silicate is considered in terms of its constituent oxides, SiO_2 and CaO . SiO_2 is a typical additive in chromate coatings and is widely used as it greatly enhances the corrosion resistance of such coatings.²⁰⁾ The corrosion-preventive mechanism of SiO_2 has been actively investigated and is thought to be as follows:

- (1) Suppression of the oxygen reduction reaction by promoting the formation of basic zinc chloride²¹⁾
- (2) Suppression of the anodic reaction by fixation of Zn^{2+} ion by the silanol group²²⁾
- (3) Suppression of the anodic reaction by formation of a SiO_2 film²³⁾
- (4) Barrier effect by formation of silicate zinc²⁴⁾

However, none of these studies explained how SiO_2

Fig. 7 Depth profiles at the bottom of scratched section of Zn coated steel sheet with Cr(III) coating containing additive C2 after salt spray test for 24 h.

Fig. 8 Cross-sectional TEM image of scratched bottom section of Zn coated steel sheet with Cr(III) coating containing additive C2 after salt spray test for 24 h.

Fig. 9 EDS spectra and electron diffraction patterns of newly formed thin film on scratched bottom section after salt spray test for 24 h.

improves post-forming corrosion resistance. Moreover, as the dissolution reaction of Zn is involved in all of the mechanisms mentioned above, SiO₂ cannot be considered the primary factor in improving post-forming corrosion resistance.

CaO forms Ca(OH)₂ in aqueous solutions by the following reactions:

Since the solubility of Ca(OH)₂ is 0.097 g/100 g (0°C),²⁵⁾ pH will increase to 12.4 if 100% of the dissolved Ca(OH)₂ is ionized. The dissolution rates of Zn and Al increase when the solution pH is higher than approximately 12–13²⁶⁾ and 11,²⁷⁾ respectively. Therefore, it is thought that the specimen using only calcium silicate was dissolved as a result of the high alkalization of the specimen surface by dissolution of the CaO component, and for this reason, its corrosion resistance was lower than that of the specimen without the corrosion-preventive additives (Fig. 3).

In the case of the specimen with the additives zinc phosphate and calcium silicate, reaction (6) is thought to promote the hydrolysis reaction (4), and the HPO₄²⁻ and Ca²⁺ which are formed by reactions (4) and (6), respectively, react to form a Ca-phosphoric acid compound. This Ca-phosphoric acid compound forms various structures, depending on the ratio of Ca and phosphoric acid. Insoluble compounds such as hydroxyapatite Ca₁₀(PO₄)₆(OH)₂ are formed when the Ca ratio is high.²⁸⁾ As a result, a dense, extremely thin layer consisting of an insoluble Ca-phosphoric acid compound is thought to have formed, and this substance inhibited the corrosion reaction of the exposed part of steel sheet under the corrosive environment. A large amount of C detected by AES analysis in Fig. 7 is considered to derive from CaCO₃, which may be formed by reaction of the Ca²⁺, which remained after corrosion was arrested by the formation of the above-mentioned insoluble Ca-phosphoric compound, with CO₂ dissolved from the air. The specimen without corrosion-preventive additives was covered with a thick layer of corrosion products consisting mainly of Zn and O, and it can be presumed that this layer is less protective against corrosion due to its porous structure. It should be noted that this discussion is based on surface and cross-sectional analysis of specimens using an electrogalvanized steel sheet substrate. In the future, it will be necessary to investigate the mechanism by which post-forming corrosion resistance is improved with 55% Al-Zn coated steel sheets, while also considering the contribution of the sacrificial anodic action of the plating.

5. Conclusion

With the aim of improving the post-forming corrosion resistance of 55% Al-Zn coated steel sheets, the authors attempted to induce a self-healing effect by adding corrosion inhibitors other than Cr(VI) to the organic-inorganic composite coating formed on the sheet using a chromate solution containing acrylic resin, phosphoric acid additives, and other chemical compounds. Inorganic compounds with various

corrosion-preventive actions were added to the coating, and post-forming corrosion resistance was investigated. The mechanism responsible for improved post-forming corrosion resistance was investigated with specimens using an additive consisting of a mixture of zinc phosphate and calcium silicate, which exhibited extremely high corrosion resistance. The following results were obtained.

- (1) The 55% Al-Zn coated steel sheets on which an organic-inorganic composite coating containing zinc phosphate and calcium silicate was formed exhibited an extremely high corrosion inhibition effect in the salt spray test, surpassing that provided by Cr(VI). The effect was very small with the specimen using only a zinc phosphate additive, and the corrosion resistance of the specimen using only calcium silicate was lower than that with no corrosion-preventive additives.
- (2) Use of the zinc phosphate and calcium silicate additive also resulted in extremely high post-forming corrosion resistance of electrogalvanized steel sheets with an organic-inorganic composite coating containing chromic acetate(III) as Cr, which was studied in order to exclude the self-healing effect of Cr(VI). An amorphous surface layer, which was approximately 30 nm thick and contained Ca, Cr, P, and Si, newly formed on the interior of the formed section where the steel sheet was exposed.
- (3) When CaO in calcium silicate comes into contact with water, it forms Ca(OH)₂ creating an alkaline environment on the steel sheet by forming Ca²⁺ and OH⁻ which promotes the hydrolysis reaction of zinc phosphate. It is thought that an insoluble Ca-phosphoric acid compound was formed by reaction of the Ca²⁺ and HPO₄²⁻ resulting from these reactions, and this compound inhibited the corrosion reaction.

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