

Electrochemical Roles of Anti-corrosive Pigments in Sacrificial Corrosion Protection of Painted Galvanized Steel and their Relation to Organic Coating Delamination

Takahito AOYAMA,^{1)*} Izumi MUTO,¹⁾ Takao KANAI,²⁾ Kensei YUASA,³⁾ Yu SUGAWARA¹⁾ and Nobuyoshi HARA¹⁾

1) Department of Materials Science, Tohoku University, 6-6-02, Aramaki, Aoba-ku, Sendai, 980-8579 Japan.

2) Intellectual Property Division, Nippon Steel & Sumitomo Metal Corporation, 20-1 Shintomi, Futtsu, 293-8511 Japan.

3) Kimitsu Works, Nippon Steel & Sumitomo Metal Corporation, 1 Kimitsu, 299-1141 Japan.

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The effect of anti-corrosive pigments on the delamination of an organic film on a Zn coated steel was investigated using a cyclic wet-dry corrosion test (according to ISO 16539 Method A). The organic film was made from a mixture of polyvinyl butyral-co-vinyl acetate (PVB) ethanol, and a pigment. SrCrO_4 or Na_2HPO_4 was added as a pigment. The delaminated area around a deep scratch on the specimen with the SrCrO_4 -containing film was smaller than those of the Na_2HPO_4 -containing and pigment-free films. The corrosion rate and potential of the Zn layer coupled with the steel were estimated on the basis of the iR -drop in the films and the polarization curves of the Zn and steel electrodes. Also, the electrode potentials of the Zn under the PVB films were measured by scanning Kelvin probe force microscopy. From these results, it was confirmed that the delamination of the PVB films on galvanized steels was mainly caused by the anodic reaction of the Zn layer. The galvanic coupling of the delamination fronts at the interface of the Zn layer and the PVB film to the steel substrate at the scratches, inhibits the oxygen reduction reaction on the steel, in effect preventing Zn corrosion.

KEY WORDS: galvanized steel; cut edge corrosion; organic coating; cyclic corrosion test; Kelvin probe force microscopy; potential distribution measurement; polarization measurements; galvanic coupling.

1. Introduction

Prepainted galvanized steels have excellent corrosion resistance in atmospheric environments and are widely used in architectural applications. A protective organic coating acts as a barrier against corrosion in atmospheric environments, and the galvanic reaction between the Zn layer and the steel substrate provides sacrificial corrosion protection against red rust formation at the cut edges. To improve resistance against cut edge corrosion and the delamination of the paint layer, anti-corrosive pigments are added to organic coatings.

Strontium Chromate (SrCrO_4) is well known as an effective anti-corrosive pigment, and is commonly added to organic coatings.^{1,2)} Chromates are reserved in paint layers and are eventually released^{3–9)} before being electrochemically reduced to chromium oxyhydroxide at corrosion sites, which acts as a corrosion inhibitor.^{10–12)}

Atmospheric corrosion at and around the cut edges and scratches of painted galvanized steels is associated with several processes: 1) the galvanic corrosion of the Zn layer coupled with the steel substrate, 2) the release of

anti-corrosive pigments from organic coatings, 3) the corrosion prevention by the pigments, 4) the delamination of organic coating, and 5) the formation of white and red rust. McMurray *et al.* investigated the relationship between the variation of inhibitor pigmentation and the electrochemical activities of the Zn layer and the steel substrate using the scanning vibrating electrode technique (SVET).¹³⁾ Zin *et al.* assessed the galvanic reactions between Zn and steel using a model cell of cut edges.¹⁴⁾ They demonstrated that chromate initially acts as an anodic inhibitor for Zn corrosion, and after a few hours, it prevents the cathodic reaction on the steel. Muto *et al.* reported that chromate inhibited the oxygen reduction reaction on the steel substrate, providing the conditions for the Zn layer to act as a sacrificial anode.¹⁵⁾ While it is generally accepted that the galvanic cell at cut edges and/or scratches bring about red rust formation and the delamination of paint layers, the inhibition mechanisms of rust formation and organic coating delamination by chromate are still unclear.

Because of the toxicity of chromates, an extensive search has been underway for alternative pigments. As yet, however, no alternative pigments which could replace chromates in coating layers have been fully developed.^{16,17)} The difficulty in developing these alternatives lies largely in the inhibition mechanisms of cut-edge corrosion and organic

* Corresponding author: E-mail: takahito.aoyama.t7@dc.tohoku.ac.jp
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coating delamination by pigments: they are still unclear. It follows then that a better understanding of how pigments improve corrosion resistance will likely assist in the development of alternatives.

In this study, to elucidate the mechanism of corrosion protection by anti-corrosive pigments, we focused on the organic coating delamination initiated at scratches in atmospheric corrosion conditions. The corrosion potential distributions at galvanized steel/organic coating interface were measured using Kelvin force microscopy. The results were then compared with the conventional electrochemical polarization curves of Zn and steel surfaces.

2. Experimental

2.1. Specimens

A Zn coated (galvanized) steel sheet without any post-treatment was used in this study. A galvanized steel sheet of 0.5 mm in thickness, with a Zn layer (approximately 0.049 mm in thickness) on both sides was used as the starting material. The galvanized steel was cut into 12 mm × 12 mm squares, and then the back side of the specimens with *ca.* 100 μm was ground with 1500-grit silicon carbide paper to remove the Zn layer.

2.2. Cyclic Corrosion Test Methods

To simulate marine atmospheric environments, a cyclic wet-dry corrosion test (ISO 16539 Method A) was performed. **Figure 1** shows the changes in temperature and relative humidity (RH) with time during the cyclic corrosion test. The patterns shown in Fig. 1 is derived from the diurnal variation of temperature and relative humidity on the stainless steel panel exposed to an outdoor environment in Japan.¹⁸⁾ The dew point of water vapor (absolute humidity) in the air during the cyclic wet-dry corrosion test was kept at 301 K to simulate the summer season in Japan.^{19,20)}

Figure 2 shows the schematic illustration of the sample preparation procedure prior to the cyclic wet-dry corrosion test. An organic coating made of polyvinyl butyral-co-vinyl acetate (PVB) was applied to the specimen surface.²¹⁾ PVB (molecular weight 70 000–100 000) was obtained from the Aldrich Chemical Company. A 15 mass% PVB-ethanol solution was prepared, and then either SrCrO_4 or Na_2HPO_4 was added as the anti-corrosive pigment. The Phosphate

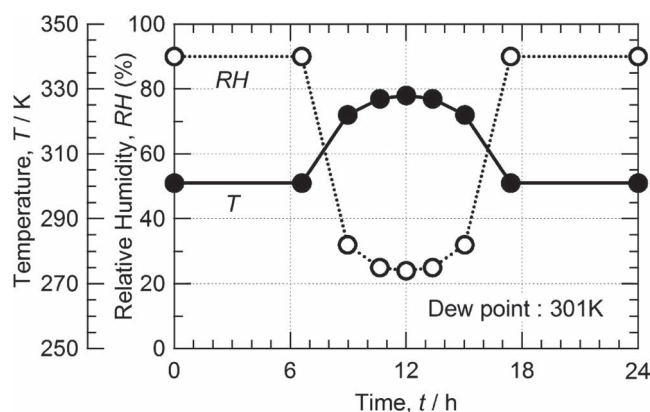


Fig. 1. Temperature and relative humidity patterns during one cycle of cyclic wet-dry corrosion test.

was considered as an alternative to the chromate.²²⁾ The concentrations of SrCrO_4 and Na_2HPO_4 were adjusted to 500 ppm (w/v) and 350 ppm (w/v), respectively, where the w/v stands for weight/volume. The molarity of SrCrO_4 and Na_2HPO_4 was the same value ($2.46 \times 10^{-3} \text{ M}$). Three types of the PVB-ethanol solutions were prepared for coating: 1) pigment-free coating, 2) coating containing SrCrO_4 , and 3) coating containing Na_2HPO_4 . Prior to coating, two parallel strips of polyimide adhesive tapes were attached to the specimen surface. The specimen was coated with PVB-ethanol solution using polyimide tape (69 μm in thickness) to ensure a uniform film thickness, as shown in Fig. 2(a). Subsequently, the PVB-ethanol solution was cured in the air at 353 K for 1 h (Fig. 2(b)). An approximately 100 μm deep knife scratch of about 5 mm in length was made on a central region of the specimen surface. Visual inspections were carried out to confirm that the scratch had completely penetrated the film. After that, with the exception of the test area, the surface of the specimen was covered with an acid proof tape to expose 5 mm × 11 mm as shown in Fig. 2(c). Therefore, an electrolyte layer of diluted synthetic sea water formed as shown in Fig. 2(d). Diluted synthetic sea water (ASTM D 1141) was used as the electrolyte. The amount of chloride ion deposition on the test area was set at 0.25 g m^{-2} by controlling the concentration and volume of the diluted synthetic sea water. The chloride ion concentration of the diluted synthetic seawater was 500 ppm (w/v), and the initial thickness of the electrolyte layer was adjusted to 500 μm . The test conditions employed in this study have been shown to be appropriate for reproducing and accelerating the atmospheric corrosion of Zn alloys.^{19,20)}

2.3. Kelvin Probe Force Microscopy

A Kelvin probe force microscope (Multimode 8, Bruker) and a single-crystal Si covered with Pt-Ir tip (SCM-PIT, Bruker) were used. After the cyclic corrosion test, KPFM potential maps were measured on the specimen surface without performing any cleaning or drying. The KPFM images were obtained at a scan rate of 0.957 Hz. The

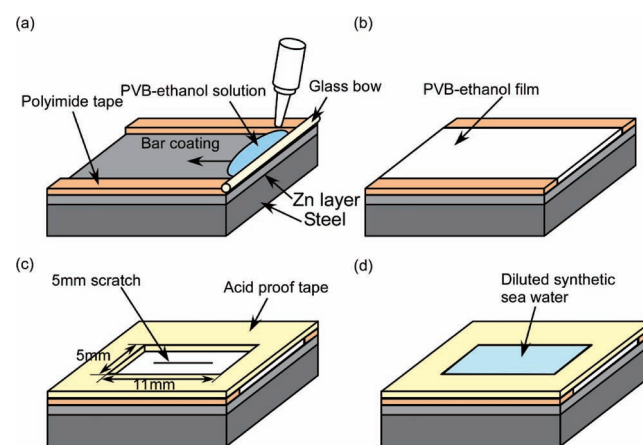


Fig. 2. Preparation procedure of specimens for cyclic wet-dry corrosion test. (a) Bar-coating of PVB films and Polyimide tapes used to ensure film thickness uniformity, (b) curing the PVB film in the air at 353 K for 1 h, (c) scratching the surface and masking by an acid proof tape, and (d) formation of an electrolyte layer of diluted synthetic sea water. The amount of chloride ion deposition was 0.25 g m^{-2} .

measurements were performed at 298 K and *ca.* 35% RH. The boundary between the corroded and un-corroded areas was selected by optical microscopy, and then the KPFM measurements were conducted in the areas around the delamination fronts through the PVB film. The scan area of the KPFM measurements were $100\ \mu\text{m} \times 100\ \mu\text{m}$. After the KPFM measurements, the PVB film was peeled off, and then scanning electron microscopy (SEM) observations were made using a JEOL JSM-7100F. Prior to SEM observations, the specimen surface was rinsed with pure water and dried in a N_2 stream.

2.4. Polarization Measurements

The galvanized steel, the same as that used for the cyclic corrosion test, was used for polarization measurements. For comparison, polarization curves of the steel substrate were measured after the Zn layer was removed by mechanical polishing with 600-grit silicon carbide paper. Potentiodynamic polarization curves were taken for the Zn layer and the steel substrate in diluted synthetic sea water with and without the anti-corrosive pigment (SrCrO_4 or Na_2HPO_4). The chloride ion concentration of the diluted synthetic seawater was adjusted to 500 ppm (w/v). The concentration of SrCrO_4 and Na_2HPO_4 were 500 ppm (w/v) and 350 ppm (w/v), respectively. These solutions were prepared from deionized water and analytical grade chemicals. Anodic and cathodic polarization curves were measured in deaerated and air-saturated conditions, respectively. With the exception of the electrode area (*ca.* $10\ \text{mm} \times 10\ \text{mm}$), the surfaces of the samples were covered with epoxy resin and subsequently with paraffin. The measurements were performed at 298 K in a conventional three electrode cell. The counter electrode was a Pt plate, and the reference electrode was an Ag/AgCl (3.33 M KCl) electrode. Unless otherwise specified, all potentials cited in this paper were with respect to the Ag/AgCl (3.33M KCl) electrode (0.206 V vs. standard hydrogen electrode at 298 K). The potential scan rate was $23\ \text{mV min}^{-1}$.

3. Experimental Results and Discussion

3.1. Delamination Resistance of PVB Films

To clarify the effect of the anti-corrosive pigments on the delamination resistance of the PVB films, a cyclic wet-dry corrosion test was carried out. **Figure 3** shows the surface appearances of the specimens before and after 2 cycles with the amount of chloride ion deposition of $0.25\ \text{g m}^{-2}$. After the corrosion test, corroded dark areas appeared around the scratch. These dark areas were thought to correspond to the delamination areas of the PVB film, which were caused by the corrosion of the Zn layer. A distinct dark area was initiated at the scratch and spread to the periphery. In this study, since no red rust was generated at or around the scratches, the Zn layer effectively provided sacrificial corrosion protection. The predominant cathodic reaction on the scratch was oxygen reduction, and an anodic reaction appeared to occur on the Zn. Since the Zn layer was covered with the PVB film, the interface between the Zn layer and the PVB film acted as an anodic site, which brought about the delamination of the film. Because the size of the dark area of the SrCrO_4 -containing film was smaller than those of

Zn / Cl⁻ : $0.25\ \text{g m}^{-2}$ (2cycles)

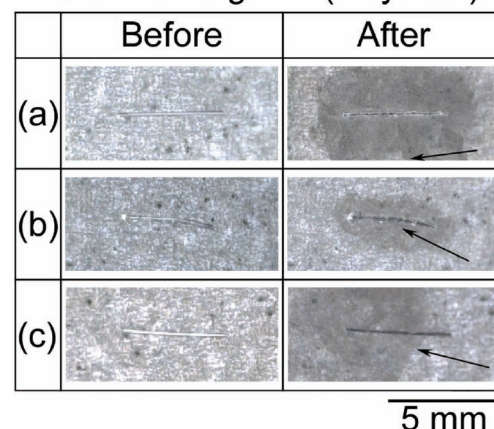


Fig. 3. Surface appearances of galvanized steels covered with PVB films before and after 2 cycles in the cyclic corrosion test with a chloride ion deposition of $0.25\ \text{g m}^{-2}$. (a) Pigment-free, (b) SrCrO_4 -containing, (c) Na_2HPO_4 -containing films. The arrows indicate the mapping positions of the KPFM measurements.

the Na_2HPO_4 -containing and pigment-free films. It is most likely that the SrCrO_4 -containing film had a higher corrosion inhibition effect against Zn corrosion than that of the Na_2HPO_4 -containing and pigment-free films.

3.2. Polarization Behaviors

To ascertain the effect of anti-corrosive pigments on the electrochemical properties of the Zn layer, polarization measurements were performed. **Figure 4** exhibits the effects of SrCrO_4 and Na_2HPO_4 on the polarization behavior of the Zn (galvanized steel surface) in diluted synthetic sea water (500 ppm Cl^-). Both deaerated and air saturated solutions were used for the anodic and cathodic polarization measurements, respectively. When the anti-corrosive pigments were added into the solution, the anodic and cathodic current densities for the Zn layer were suppressed when both SrCrO_4 and Na_2HPO_4 were added. The polarization curves of the Zn layer in the SrCrO_4 solution were similar than those in the Na_2HPO_4 solution, but the delamination resistance of the SrCrO_4 -containing film was higher than that of the Na_2HPO_4 -containing film as seen in Fig. 3. The polarization behaviors of Zn alone provide no clear clues about the mechanism of the delamination resistance of the PVB films.

The galvanic reaction between the Zn layer and the steel substrate is an important point affecting delamination. We have therefore focused on the corrosion potential. A comparison of Figs. 4(a) and 4(b) indicates that the corrosion potentials of the polarization curves moved to the noble direction with the addition of the pigments. One of the differences between the SrCrO_4 and the Na_2HPO_4 was the higher corrosion potentials in the SrCrO_4 -containing solution. The shifting of the corrosion potentials of the Zn layer due to the addition of pigment were probably related to the prevention of the delamination of the PVB film.

Figure 5 shows the effects of the SrCrO_4 and Na_2HPO_4 on the polarization behavior of the steel substrate in diluted synthetic sea water (500 ppm Cl^-). The deaerated and air saturated solutions were also used for the anodic and cathodic polarization measurements, respectively. The

anodic and cathodic current densities for the steel substrate were also suppressed when both SrCrO_4 and Na_2HPO_4 were added. Another important difference between SrCrO_4 and the Na_2HPO_4 was that the decreases in current densities due to SrCrO_4 were much larger than when Na_2HPO_4 was added. At around -0.5 V, the cathodic current densities in the Na_2HPO_4 solution was *ca.* 0.1 A m^{-2} , which was the

almost same as that in the solution without Na_2HPO_4 . On the other hand, it is clear that SrCrO_4 inhibited oxygen reduction effectively in the potential region above *ca.* -0.9 V. Below *ca.* -0.9 V, hydrogen gas evolution occurs, with no alteration in the current densities due to the pigment additions noted.

Above *ca.* -0.9 V, the cathodic current densities on the steel substrate were lower due to the pigments, leading to an increase in the corrosion potentials. As seen in Figs. 5(a) and 5(b), the potential shift caused by SrCrO_4 was larger than that caused by Na_2HPO_4 .

3.3. Effect of Pigments on Galvanic Reactions

The key to understanding the effect of the anti-corrosive pigments on the delamination resistance of the PVB films is very likely, the galvanic reaction between the oxygen reduction rate on the steel and the corrosion rate of the Zn layer. A comparison between the anodic polarization of the Zn and the cathodic polarization of the steel substrate is shown in Fig. 6. The polarization curves in this figure were selected from Figs. 4 and 5. For simplicity, a 1:1 area ratio for the Zn and the steel was assumed, allowing the cathodic polarization curve on the steel and the anodic polarization curve on the Zn to be shown in the same figure without the need to correct the area ratio. As a first approximation (Case 1), the intersection of the polarization curves corresponded to the corrosion rate of the Zn (indicated as point Case 1). The corrosion current densities of the Zn layer were estimated from the results in Fig. 6, and are listed in Table 1. The order of the Zn corrosion rate was pigment-free >

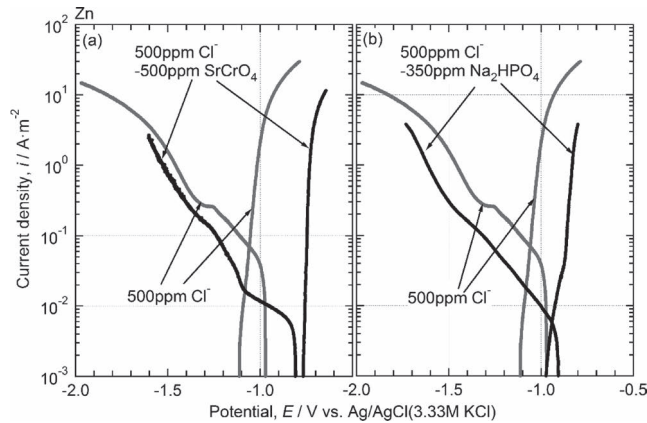


Fig. 4. Polarization curves of Zn in diluted synthetic sea water at 298 K (500 ppm Cl^-). (a) Solution with and without SrCrO_4 , (b) solution with and without Na_2HPO_4 .

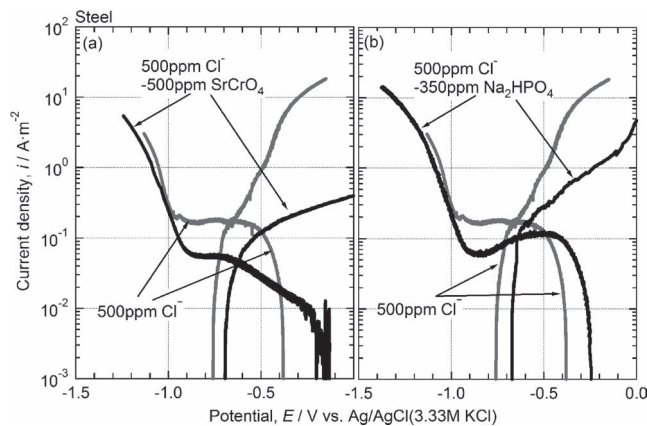


Fig. 5. Polarization curves of steel in diluted synthetic sea water at 298 K (500 ppm Cl^-). (a) Solution with and without SrCrO_4 , (b) solution with and without Na_2HPO_4 .

Table 1. Corrosion rates of Zn layer under galvanic coupling with steel (A m^{-2}).

	500 ppm Cl^-	500 ppm Cl^- with 350 ppm Na_2HPO_4	500 ppm Cl^- with 500 ppm SrCrO_4
Zn Corrosion rate without considering iR -drop	0.52	6.0×10^{-2}	5.2×10^{-2}
Zn Corrosion rate with considering iR -drop	7.0×10^{-3}	6.5×10^{-3}	6.0×10^{-3}

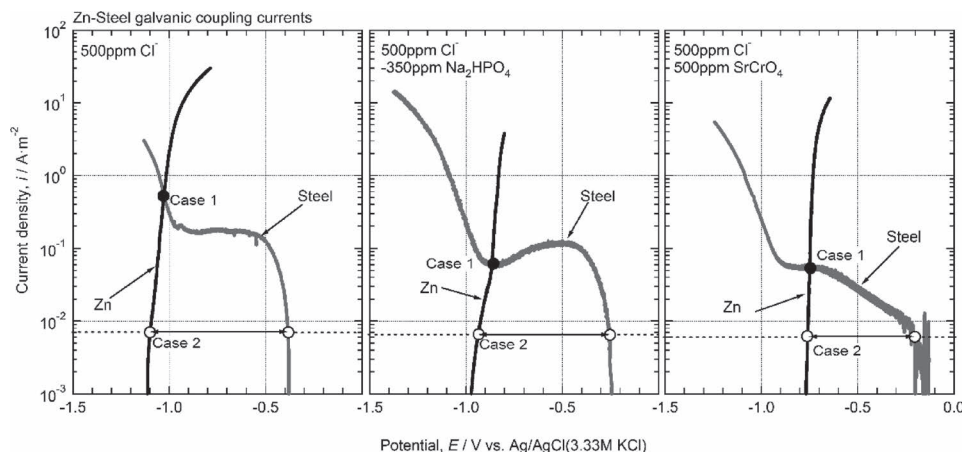


Fig. 6. Comparison between the anodic polarization of the Zn and the cathodic polarization of the steel substrate. The curves were selected from Figs. 4 and 5. The arrows indicate the estimated galvanic current densities between the steel substrate and the delamination front of the Zn covered with the PVB film.

$\text{Na}_2\text{HPO}_4 > \text{SrCrO}_4$, which was consistent with the trend in the size of the PVB delamination areas shown in Fig. 3.

In the actual situation (Case 2), the specimen surface was covered with the PVB film, with an iR -drop between the anodic and cathodic sites, separating the electrode potentials of the Zn and steel surfaces. Sykes and Xu applied the electrochemical impedance spectroscopy to measure the electrical resistance of the PVB film which formed on a Zn–Fe galvanic couple (bi-electrode) immersed in 1 mass% NaCl solution.²³⁾ They demonstrated that the electrical resistance between the anode and the cathode was around 1 M Ω . In this study, we used this value to roughly calculate the iR -drop: the arrows in Fig. 6 indicate the estimated coupling current densities for Case 2. The corrosion rates, which are summarized in Table 1 clearly show that the order of the corrosion rates of the Zn layer was pigment-free $> \text{Na}_2\text{HPO}_4 > \text{SrCrO}_4$. As such, the delamination resistance of the PVB films was likely be related to the galvanic corrosion rate of Zn, even under the delamination conditions at the interface of the Zn layer and the PVB film. If this assumption is correct, the order of the corrosion potential of the Zn layer under the PVB films would be (less-noble) pigment-free $< \text{Na}_2\text{HPO}_4 < \text{SrCrO}_4$ (noble). To verify the assumption, the corrosion potentials of the Zn layer under the PVB films were measured using KPFM.

3.4. KPFM Potential at the Interface

After 2 cycles in the cyclic wet-dry corrosion test with a chloride ion deposition of 0.25 g m^{-2} , KPFM potential maps were obtained without performing any cleaning or drying prior to the measurements. Before KPFM measurements, the corroded area was selected, and an image was taken using optical microscopy. After KPFM measurements, the PVB film was gently peeled off, and then an SEM/EDS analysis was carried out.

Figure 7 shows the optical microscopy image, KPFM potential map, SEM image, and EDS maps of the galvanized

steel covered with a pigment-free PVB film. The position of the measurement area was indicated by the arrow presented in Fig. 3(a). As seen in Fig. 7(a), the interference color which was appeared on the Zn under the PVB film suggested that small gaps (micro-crevices) were formed due to delamination. It is likely that the micro-crevices between the Zn and the PVB film were induced by corrosion of the Zn. In addition to this, strong O and Cl signals were detected by EDS analysis. It was confirmed that the black colored area around the scratch (see Fig. 3) was the delaminated region of the PVB film, and that delamination was caused by the anodic reaction of the Zn. Since KPFM potential is inversely proportional to corrosion potential, an inverse KPFM potential is shown in Fig. 7(b).^{24–26)} As indicated by the arrows, it is clear that the corrosion potentials of the area (A1) located on the left side of the Zn corroded region were lower than those of the un-corroded area (A2). The delamination front may be to the left of the Zn corroded area in this case. The corrosion potential of the area on which the strong O and Cl signals were detected was higher than that of the area A1. Although the details remain uncertain, the electrical insulation properties of the Zn corrosion products were thought to affect the KPFM potentials.

An optical microscopy image, the KPFM potential map, an SEM image, and EDS maps of the specimen covered with the SrCrO_4 -containing the PVB film are shown in **Fig. 8**. The position of the mapping area was also indicated by the arrow presented in Fig. 3(b). Also in this case, the interference color and the signal of O were observed; however, no accumulation of Cl was generated. The discussion presented so far suggests that the SrCrO_4 suppressed the corrosion rate of the Zn, resulting in little if any accumulation of Cl^- ions at the anodic site, since Cl^- ions migrated toward anodic sites to maintain electrical neutrality. As shown in Fig. 8(b), the potentials of the corroded areas indicated by the arrows (B1) were around -0.50 V (vs. Pt-Ir), which was higher than that of the specimen covered with the pigment-

Zn coated steel pigments-free (after corrosion test)

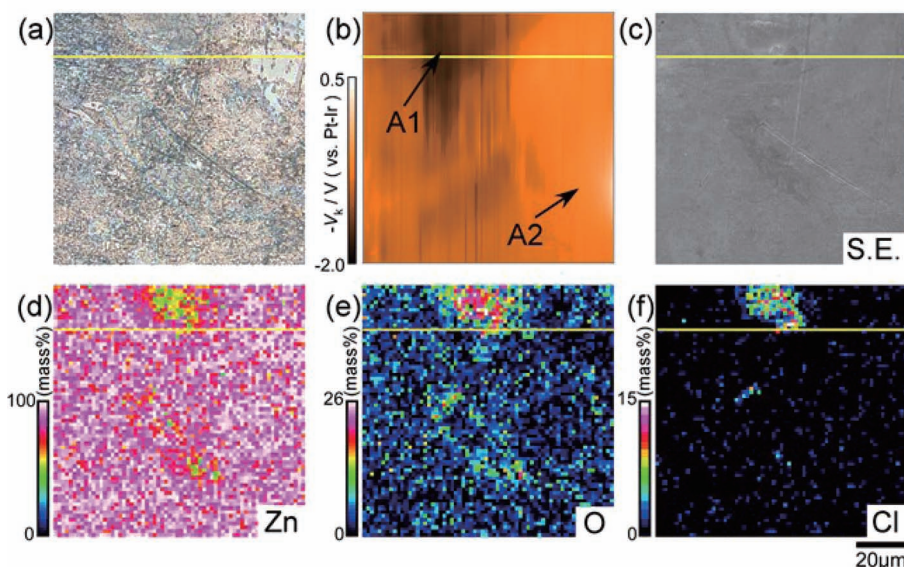


Fig. 7. (a) Optical microscopy image, (b) KPFM potential map, (c) SEM image, and EDS maps of (d) Zn, (e) O, and (f) Cl the specimen covered with the PVB film without the pigments. The mapping position is indicated by the arrow in Fig. 3(a). The scan directions in KPFM potential map were along the vertical axis (top to bottom). The yellow line indicates the position of line profile analysis.

free film.

The optical microscopy image, the KPFM potential map, an SEM image, and EDS maps of the specimen covered with the Na_2HPO_4 -containing PVB film are shown in **Fig. 9**. The position of the mapping area is also indicated by the arrow presented in Fig. 3(c). Both interference color and an O signal were observed. In this case, at the position indicated by the white arrow in Fig. 9(f), a small amount of Cl accumulation was detected by the EDS analysis, suggesting that the Zn corrosion rate in this case was slightly higher than that in the case of the SrCrO_4 -containing film. However, the Cl concentration for the pigment-free film was much higher,

implying that the order of the Zn corrosion rate under the PVB film was pigment-free > Na_2HPO_4 > SrCrO_4 .

Finally, to clarify the assumption that, the delamination resistance of the PVB films was roughly determined by the corrosion current densities of the Zn galvanically coupled with the steel (scratched area), a comparison of the corrosion potentials of the Zn was conducted. **Figure 10** shows the line profiles of the KPFM potentials for the specimens. The scanning positions are indicated by the yellow lines in Figs. 7–9. As seen in Fig. 10, the corrosion potentials of the corroded areas were (less-noble) pigment-free < Na_2HPO_4 < SrCrO_4 (noble). This is evidence that the

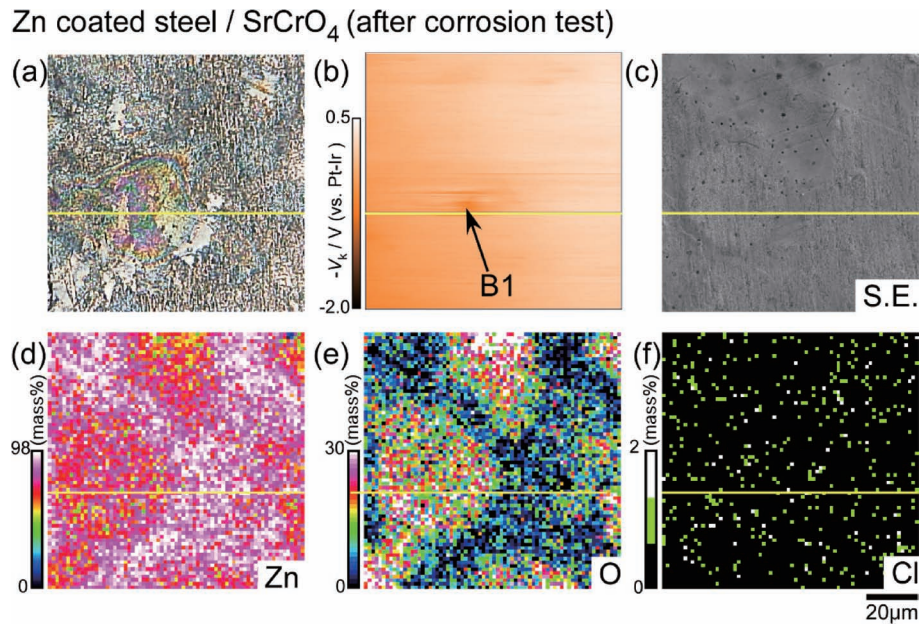


Fig. 8. (a) Optical microscopy image, (b) KPFM potential map, (c) SEM image, and EDS maps of (d) Zn, (e) O, and (f) Cl of the specimen covered with the PVB film with SrCrO_4 . The mapping position is indicated by the arrow in Fig. 3(b). The scan directions in KPFM potential map were along the horizontal axis (left to right). The yellow line indicates the position of line profile analysis.

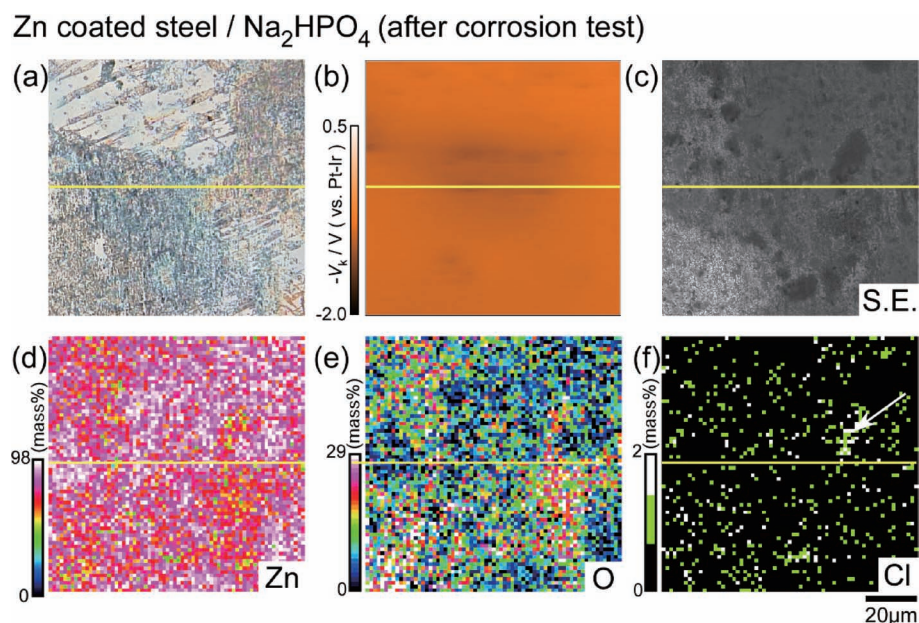


Fig. 9. (a) Optical microscopy image, (b) KPFM potential map, (c) SEM image, and EDS maps of (d) Zn, (e) O, and (f) Cl of the specimen covered with the PVB film with Na_2HPO_4 . The mapping position is indicated by the arrow in Fig. 3(c). The scan directions in KPFM potential map were along the horizontal axis (left to right). The yellow line indicates the position of line profile analysis.

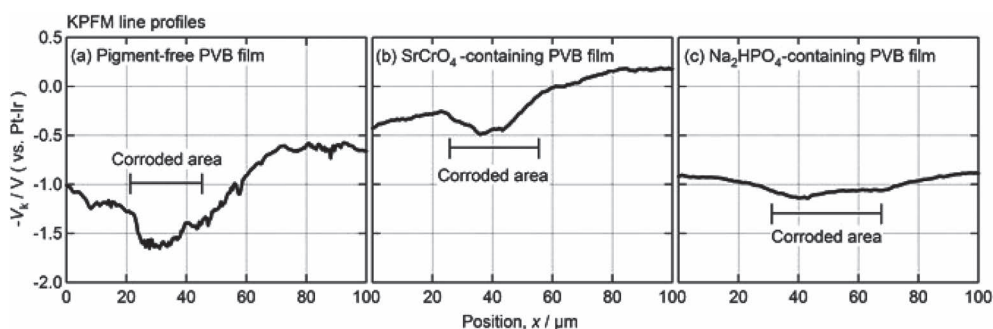


Fig. 10. Line profiles of inverse KPFM potential of the Zn covered with the PVB film. (a) pigment-free PVB film, (b) SrCrO_4 -containing PVB film, and (c) Na_2HPO_4 -containing PVB film. The positions of line scan are presented in Figs. 7–9.

assumption is correct; the delamination of the PVB films on galvanized steels is caused by the anodic reaction of the Zn layer. The delamination fronts at the interface of the Zn layer and the PVB film were galvanically coupled to the steel substrate at the scratches. As can be seen in Fig. 6, can be concluded that the oxygen reduction reaction on the steel has to be inhibited in order to prevent the delamination introduced by cut edges and/or scratches. In addition, the electrode potential of the Zn must be less than the onset potential of steel dissolution to prevent red rust generation. The other important point for an anti-corrosive pigment is that Zn electrode potential must not rise excessively.

4. Conclusions

(1) In the cyclic wet and dry corrosion test with the amount of chloride ion deposition of 0.25 g m^{-2} , corroded dark areas (delamination) were initiated at the scratch which spread to the periphery. The corroded areas of the SrCrO_4 -containing film were smaller than those of the Na_2HPO_4 -containing and pigment-free films.

(2) The anodic and cathodic current densities for Zn were suppressed by SrCrO_4 and Na_2HPO_4 in polarization measurements. Shifts in the corrosion potentials in the noble direction were also observed, with larger changes for SrCrO_4 .

(3) In the case of the steel substrate, SrCrO_4 more effectively inhibited the oxygen reduction as a cathodic reaction than Na_2HPO_4 . Both pigments resulted in an increase in the corrosion potentials, with the addition of SrCrO_4 resulting in a larger potential shift than the addition of Na_2HPO_4 .

(4) The galvanic coupling current densities of the Zn layer covered with the PVB films with and without the pigments were estimated on the basis of the iR -drop in the films and the polarization behaviors of the Zn and the steel. The estimated order was (high) pigment-free > Na_2HPO_4 > SrCrO_4 (low). If the delamination of the PVB films was induced by Zn corrosion, the order of the corrosion potential of the Zn layer under the PVB films would be (less-noble) pigment-free < Na_2HPO_4 < SrCrO_4 (noble).

(5) The inverse KPFM potentials of the Zn under the PVB films were measured. The order of the electrochemical potentials at the corroded interface of the Zn and the PVB film was (less-noble) pigment-free < Na_2HPO_4 < SrCrO_4

(noble).

(6) The delamination of the PVB films on galvanized steels was mainly caused by the anodic reaction of the Zn layer. The delamination fronts at the interface of the Zn layer and the PVB film was galvanically coupled to the steel substrate at the scratches. Anti-corrosive pigments clearly affected the galvanic reaction between the Zn and the steels substrate.

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