Corrosion Behavior of Galvanized Steel with Organic Coatings Containing Metallic Powders

Hiroyuki Ogata^{1)*} and Hiroki Habazaki²⁾

¹⁾ *Planning Department, Functional Materials Solution Division, JFE Techno-Research Corp.*

²⁾ *Division of Applied Chemistry, Faculty of Engineering, Hokkaido University*

* **Corresponding Author** : 1 Kawasaki-cho, Chuo-ku, Chiba, 260-0835, Japan
E-mail: h-ogata@jfe-tec.co.jp

Recently, the authors reported the improved corrosion resistance of the electro-galvanized steel coated with epoxy resin organic layers by the simultaneous additions of flaky Al and particulate Ni powders for the use in fuel tanks. In order to understand the roles of Ni and Al powders in the coatings on the corrosion behavior of the coated electro-galvanized steel, the electro-galvanized steel was coated with epoxy resin layers containing either Ni or Al powders, and their corrosion behavior was examined by the corrosion immersion tests in aqueous solution containing formic acid, acetic acid and NaCl, potentiodynamic polarization measurements, electrochemical impedance spectroscopy (EIS), and oxygen gas and water vapor permeation measurements. Both Ni and Al powders in the organic coatings accelerated the corrosion. The potentiodynamic polarization curves disclosed the increased anodic and cathodic currents and the EIS study showed the reduced coating resistance by the addition of Ni or Al powders. Findings in this study suggested that the improved corrosion resistance of the coatings containing both Al and Ni powders were not simply explained by the corrosion behavior of the coated steel containing only Ni or Al powders and a possible synergistic effect of Ni and Al powders in improving the corrosion resistance is discussed.

Key words : corrosion, organic coating, metal powder, galvanized steel, degraded gasoline resistance

1. Introduction

Terne (Pb-Sn alloy) coated steel sheets have been widely used for automotive fuel tanks.¹⁾ In order to reduce the harmful substances of Pb and Cr (VI), environmentally-benign galvanized steel sheets with organic coatings were developed. The coatings consist of a thin organic film of approximately 1 μ m thickness on the outer surface of tank and a 3- μ m-thick organic film containing metallic powders (particulate Ni and flaky Al powders) on the inner surface (fuel side) of tank. The outer organic film secures the lubrication property and the corrosion resistance, and the inner organic film containing metallic powders is formed to satisfy both weldability and inner surface corrosion resistance.²⁾

Corrosion protection properties of organic coatings containing metallic powders were examined in the decades. Epoxy coatings containing 10 vol% Al powders were prepared on carbon steel and galvanized steel, and their corrosion behavior was examined in 3% NaCl using electrochemical impedance spectroscopy (EIS).^{3,4)} It was reported that the Al powders improved the corrosion resistance of carbon steel because of cathodic protection and precipitation of corrosion products of Al. The corrosion products filled the pores of organic coating, improving the barrier nature of the coating. In contrast, the corrosion protection of the coating on the galvanized steel was less satisfactory and hence severe corrosion was reported. Nikravesh et al. added micaceous iron oxide

(MIO) and Al powders to epoxy-polyamide coatings on a mild steel for corrosion protection, and they reported that the powders improved the corrosion resistance and the Al powders were more effective than MIO in improving the corrosion resistance in NaCl solution.⁵⁾ Cathodic disbonding of polymer coating was also improved by the addition of MIO and Al powders. Arman et al. reported that partial replacement of Zn-rich epoxy coating with MIO and lamellar Al powders improved the corrosion resistance of steel.⁶⁾ However, in this case, they reported that the MIO-loaded coating showed better corrosion protection compared with the Al-loaded coating. Thus, the corrosion behavior of powder-containing organic coatings appears to be rather complex.

Inside of automobile fuel tanks is a corrosive environment, containing aqueous solution including formic acid, acetic acid and sea salt. These organic acids are derived from oxidation of alkenes, which are main components of gasoline.⁷⁾ Thus, fuel tank materials must have sufficient corrosion resistance as well as weldability, which is required to introduce welding process of the coated galvanized steel to construct fuel tanks. As discussed above, the epoxy coatings containing both Ni and Al powders, showing satisfactory weldability and corrosion protection properties, have been commercially used for fuel tank,²⁾ but the corrosion protection characteristics were still unclear. Recently, we examined the corrosion behavior of a galvanized steel coated with epoxy resin films containing various concentrations of particulate Ni and flaky Al powders in an aqueous solution

containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C.⁸⁾ We found that the particulate Ni powder in the epoxy resin coating accelerated corrosion because of galvanic corrosion between a Ni and a Zn layer and increased gas diffusion owing to the presence of voids in the epoxy resin around Ni powders. However, the addition of flaky Al powders together with Ni powders improved the corrosion resistance. The simultaneous addition of Ni and Al powders appeared to suppress the galvanic corrosion and the improved gas barrier properties due to the labyrinth effect of the flaky Al powders was also likely to improve the corrosion resistance.

In the present study, for a better understanding of the role of the Ni and Al powders on the corrosion behavior of electro-galvanized steel coated with epoxy resin films, the Ni and Al powders were added to the organic epoxy resin films separately and the corrosion behavior of the coated electro-galvanized steel was examined by corrosion immersion tests, SEM-EDS observations of the corroded specimens, potentiodynamic polarization and EIS studies, and gas permeation measurements in more details. The separate addition of Al powders reduced the corrosion resistance of the coated galvanized steel as well as the addition of Ni powders. A synergistic role of the simultaneous additions of Ni and Al powders on the corrosion resistance of the organic coatings is discussed in this study.

2. Experimental

2.1 Specimen materials

Electro-galvanized steel sheet with a trivalent chromium process (TCP) coating was used in this study. The coated steel sheet specimen was prepared by Standard Testpieces Co. and a NIPPON HYOMEN KAGAKU, Tryner TR-177AB Cr(III) coating solution was used for the TCP coating. Approximately 40 g m⁻² of Zn was deposited on the cold-rolled steel sheet, which was 0.8 mm thick. The TCP coating of approximately 40 mg m⁻² was formed by a dipping method. After the TCP coating, the specimen was heat-treated at 100°C for 10 s. Epoxy resin (ADEKA, EM0718) coatings containing either particulate Ni powders of 3-7 μm size (Vale Japan, Nickel Powder Type123) or flaky Al powders of 18 μm in long diameter, 5 μm in short diameter and 1 μm thickness (Toyo Aluminium, Aluminum Paste 1700NL) were prepared by a bar coating method. After heat treatment at 150°C for 15 s, the coating thickness was approximately 3 μm. The amount of Al powders added to the epoxy resin changed from 0 to 40 phr and the amount of Ni powders added to epoxy resin changed from 0 to 70 phr. Here, "phr" is used as an abbreviation for "per hundred resin". For example, the notation showing that Ni addition was "40 phr" means that 40 parts of Ni by weight was added to 100 parts of epoxy resin.

2.2 Corrosion tests

Fig. 1 shows the schematic illustration of the corrosion tests. The coated specimens were cut to 30 mm x 80 mm in size for the corrosion tests and the backside and edges of the specimens were masked with protective tape to expose an area of 20 mm x 70 mm. A corrosive aqueous solution (pH 3.2) containing 100 ppm of formic acid, 100 ppm of acetic acid and 83 ppm of NaCl was used in this study. This solution was set in a glass container so as to immerse about 2/3 area of the specimen, and the container was sealed with a plastic wrap to prevent a decrease of the volatile component in the corrosive solution. The corrosion tests were performed in an electric furnace to keep the solution temperature at 40 ± 1°C. After immersion for 350 h, the specimens were removed, washed with water and dried under hot air. The corroded specimens were then photographed, and the corrosion resistance was evaluated by obtaining the corroded area ratio by binarization.

Fig. 1 Schematic illustration of the corrosion tests.

2.3 Surface and cross-sectional observations

For cross-sectional observations of the coated specimens before and after the corrosion tests, the specimens were embedded in resin after Pt-Pd alloy vacuum deposition on the surface, and then polished mechanically. Surface and cross-sections were observed using a Hitachi, S-4800 field emission gun scanning electron microscope (SEM) operated at an accelerating voltage of 5.0 kV. When performing elemental mapping by EDS, the accelerating voltage of 15.0 kV was used.

2.4 Analysis of amount of metal eluted into corrosive solution

The corrosive solutions after the corrosion tests were analyzed using a Thermo Fisher Scientific, ELEMENT 2 type inductively coupled plasma mass spectrometer (ICP-MS) to quantify the dissolved amounts of Ni, Fe and Al. The analysis of the dissolved Zn was performed using a Shimadzu, ICPS-8100 inductively coupled plasma optical emission spectrometer (ICP-OES). The analytical conditions for ICP-MS and ICP-OES were summarized in Table 1.

Table 1 Conditions used for ICP-MS and ICP-OES analyses.

	ICP-MS	ICP-OES
Analyzed elements	Al, Ni, Fe	Zn
Plasma output (W)	1250	1200
Ar carrier gas rate (L min ⁻¹)	0.80	0.80
Measured mass number (m/z)	27 (Al), Fe (56), 60 (Ni)	-
Measured wavelength (nm)	-	206.191 (Zn)
Internal standard	Sc (m/e = 45)	-
Integration time (s)	0.25	5
Number of scans	9	-

2.5 Measurements of oxygen and water vapor permeability of coatings

For the oxygen gas and water vapor permeation measurements, epoxy resin coatings containing Ni or Al powders were painted on a polyimide film (Kapton 500H manufactured by Du Pont-Toray Co. Ltd.) of 125 μm thickness by a wire bar coating method. We used an O-well, Omegatrans gas permeation measurement system for both oxygen gas and water vapor permeation measurements. The oxygen permeability of the metallic powder-containing resin layer was measured by the method described below under the condition of a measurement area of 40 mm ϕ , 40°C, 90% RH and 100 kPa of oxygen.

- (i) Measurement of oxygen permeability of polyimide film (125 μm): Permeability rate A
- (ii) Measurement of oxygen permeability of polyimide film (125 μm) + Metallic powder-containing resin layer (30 μm): Permeability rate B

The oxygen gas barrier nature was evaluated from the difference of the permeability rates A and B ($\Delta\text{OPR} = \text{A}-\text{B}$). The water vapor permeability was also measured under the same condition with the oxygen permeability and the difference of the water vapor permeability ($\Delta\text{WPR} = \text{A}-\text{B}$).

2.6 Electrochemical polarization measurements

Electrochemical anodic and cathodic polarization curves of the coated specimens were measured using a Hokuto-Denko, HZ-5000 electrochemical system. A three electrode cell with a Pt counter electrode, an Ag/AgCl (saturated KCl solution) reference electrode and an aqueous electrolyte containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl ppm at pH 3.2 and 20°C was used. Prior to the polarization, the coated specimens were immersed in the electrolyte for 15 min to obtain relatively stable open-circuit potential. The potential sweep rate was 1.0 mV s⁻¹.

2.7 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) was also used in this study to elucidate the corrosion behavior. The EIS measurements were performed in the electrolyte same as the immersion tests and polarization measurements, but the electrolyte temperature was 20°C. The EIS data were obtained using an Ivium, Compactstat potentiostat/galvanostat with FRA facilities at an open circuit potential with an AC amplitude of 10 mV (rms). The obtained data were analyzed using a ZSimpWin software.

3. Experimental results

3.1 Corrosion tests

Fig. 2 shows the surface appearance of the corroded specimens with various amounts of Ni powders after the corrosion tests for 350 h. The corrosion of the Ni-free specimen was less significant and the corroded area ratio estimated from the image analysis was only 8.3%. The addition of Ni powders increases the corroded area, reaching to 100% (entire surface) at 70 phr Ni. In particular, the severe corrosion is also found in the vapor-exposed area in addition to the entire corrosion of the immersed area when the Ni content is increased to 70 phr. Thus, the corrosion of the coated electro-galvanized steel

Sample name	(A)	(B)	(C)	(D)
Ni (phr)	0	20	40	70
Corroded area ratio (%)	8.3	54.1	71.4	100
Corrosion appearance after immersion for 350 h				
Liquid phase Evaluation area				

Fig. 2 Surface appearance of the samples (A) to (D) immersed in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h (Online version in color.).

is highly accelerated by the addition of Ni powders. In contrast, when Al powders are added, the corroded area is not clearly observed (Fig. 3). However, compared with the non-corroded region of the Al-free sample, the Al-added specimens show slightly light appearance uniformly on the entire surface, suggesting possible uniform formation of corrosion products, which is discussed later in detail.

The corrosion of the coated specimens was further examined by SEM observations. Fig. 4 shows surface and cross-section of the electro-galvanized steel with the epoxy coating containing 20 phr Ni. The specimen was immersed in the corrosive solution for 350 h, but the observed region in Fig. 4 was beneath the protective tape mask. Thus, no severe corrosion was found in this region, but the presence of many small voids in the zinc layer suggested the corrosion of the Zn layer even beneath the mask (Fig. 4 (a)). The epoxy coating on the Zn layer is $\sim 3 \mu\text{m}$ thick, but the thickness increases to the size of powders around the particulate Ni powders of 5–6 μm in diameter. The surface observation of the coated specimen (Fig. 4 (b)) discloses that Ni powders are not completely covered with the epoxy resin and partly exposed to the corrosive solution. Since the Ni powders (5–6 μm in diameter) are larger than the thickness of the coating ($\sim 3 \mu\text{m}$), many Ni powders appear to contact with a Zn layer, generating galvanic couple in the corrosive environment. The plus sign position in Fig. 4 (b) was analyzed by EDS, and the EDS spectrum, shown in Fig. 4 (c), reveals the presence of Ni.

Surface of the coated specimen containing 20 phr Ni after immersion in the corrosive solution for 350 h was also observed, and Fig. 5 (a) shows an example of the obtained SEM images. Powdery corrosion product is formed in the square area and the powders are rich in Zn as seen in the EDS spectrum (Fig. 5 (c)) of the area 1 in Fig. 5 (b). The corrosion product is formed near the Ni

Fig. 4 Scanning electron micrographs of (a) cross-section and (b) surface of the sample (B) beneath the corrosion protection immersed in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h and (c) EDS spectrum of the marked point in (b).

Fig. 5 (a,b) Scanning electron micrographs of surface of the sample (B) with 20 phr Ni immersed in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h and EDS spectra of the marked (c) area 1 and (d) point 2 in (b).

Sample name	(E)	(F)	(G)	(H)
Al (phr)	0	5	15	40
Corroded area ratio (%)	8.3	0	0	0
Corrosion appearance after immersion for 350 h				
□ Liquid phase Evaluation area				

Fig. 3 Surface appearance of the samples (E) to (H) immersed in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h (Online version in color.).

powder, which is confirmed by the EDS analysis (Fig. 5 (d)) of the plus sign position 2 in Fig. 5 (b). Because of the absence of corrosion products in other region of Fig. 5 (a), the corrosion of Zn layer was accelerated by the Ni powder due to the galvanic couple between Ni and Zn.

Cross-sections of corroded regions of the same specimen were also observed by SEM (Fig. 6). A large corrosion product (areas 1 and 2) of $>20 \mu\text{m}$ size is developed above the Ni powder (area 3). The corrosion product in the areas 1 and 2 consists mainly of Zn species, as shown in Figs. 6(b) and 6(c). The EDS spectrum of the area 3 (Fig. 6(d)) clearly indicates that the particle of the area 3 is Ni. Because of severe

Fig. 6 (a) Scanning electron micrograph of a cross-section of the sample (B) with 20 phr Ni immersed in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h and EDS spectra of the marked areas (b) 1, (c) 2 and (d) 3 in (a).

Fig. 7 (a,b) Scanning electron micrographs of cross-section of the sample (F) with 5 phr Al immersed in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h and EDS spectra of the marked (c) point 1 and (d) area 2 in (b).

corrosion of this observed region, the epoxy coating was detached from the galvanized steel substrate; embedded resin is present beneath the coating in Fig. 6.

Fig. 7 shows SEM images and EDS spectra of a cross-section of the coated specimen containing 5 phr Al. A flaky Al powder is located near the top of the epoxy coating. In contrast to the coated specimen containing Ni powders (Fig. 6), no large corrosion products are developed above the coating. However, corrosion of the Zn layer proceeded and no continuous Zn layer remained on the steel substrate. The corrosion products are located only beneath the epoxy coating and consist mainly of Zn with Al content being rather low as shown in EDS spectra of the point 1 and area 2. Since Ni-containing coatings produced the large corrosion products above the epoxy coating (Fig. 6), the morphology of the corroded surface of the Al-containing coating is largely different from that of the Ni-containing coating.

Fig. 8 Change in the amount of dissolved (a) Zn and (b) Ni and Al with metal powder content in coating during immersion in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h.

Dissolved amounts of Zn, Ni and Al during the corrosion tests were measured by ICP analysis and the results are shown in Fig. 8. Both the Ni and Al additions increase the dissolved amount of Zn (Fig. 8(a)), confirming the accelerated corrosion of the Zn layer by the metallic powders. The corrosion acceleration is larger for the Ni addition in comparison with the Al addition. The dissolved amount of Zn is almost saturated at and above 20 phr Ni probably because of complete corrosion of the Zn layer, while the dissolved Zn increases with an increase in the Al content. The dissolved amounts of Zn are always below 10% of Zn in the electro-galvanized steel, the remaining Zn is probably precipitated as corrosion products. For the Ni-containing coatings, the dissolved amount of Ni was always low even at high Ni contents (Fig. 8(b)). The Ni powders become a cathodic site in the Ni/Zn galvanic couple, suppressing the dissolution of Ni. When Al is added to the coating, the Al powders dissolve together with Zn, and dissolved Al increases with the Al content (Fig. 8(b)).

Approximately 33% of Al added to the coating was dissolved into the solution at 40 phr Al. Fe dissolved in the corrosive solution was below a detectable limit in the present study.

3.2 Measurements of oxygen and water vapor permeability of coatings

Fig. 9 shows the effect of the amount of Ni and Al powders added to the coating on the oxygen gas and water

Fig. 9 Correlation between (a) the oxygen gas (b) water vapor barrier property and metal powder content in coating with an inset in (a) showing scanning electron micrograph of a cross-section of the coating with 70 phr Ni.

vapor permeability of the coatings. The oxygen gas barrier nature of the coatings decreases with an increase in the Ni content, although the water vapor barrier nature is almost unchanged by the Ni addition. The reduced barrier nature to oxygen gas by the addition of Ni may be associated with the presence of voids around the spike-shaped Ni powders, as shown in the inset SEM image of Fig. 9 (a). In contrast, the barrier nature of the coatings to both oxygen gas and water vapor is largely enhanced by the addition of Al powders.

3.3 Polarization measurements

For a better understanding of the corrosion behavior of the coated specimens, the coated specimens were potentiodynamically polarized in the corrosive solution at 20°C. Fig. 10 (a) shows the potentiodynamic polarization curves of the coated specimens containing Ni powders. The cathodic current density increases largely with an increase in the Ni content; the coated specimen with 70 phr Ni shows nearly three orders of magnitude higher cathodic current density in comparison with the coated specimen free from Ni. The anodic current density in the vicinity of the corrosion potential also increases with the content of Ni. Thus, the corrosion current density increases with the Ni content. The increase in the anodic current density is less than the cathodic current density,

Fig. 10 Potentiodynamic polarization curves of the electro-galvanized steel with epoxy coatings containing (a) Ni and (b) Al powders measured in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 20°C.

resulting in shift of the corrosion potential by ~50 mV to a noble direction by the addition of Ni. The anodic current density becomes almost constant above -0.5 V vs Ag/AgCl, and the steady state anodic current density also increases with an increase in the Ni content. Fig. 10 (b) shows the polarization curves of the coated specimens containing Al powders. Again, both cathodic and anodic current densities increases with an increase in the Al content, but the increase is less significant in comparison with the Ni addition

3.4 Electrochemical impedance spectroscopy

Fig. 11 shows Bode plots of the coated specimens with Ni and Al powders and Fig.12 shows equivalent circuits used to fit the measured spectra of Fig.11. The impedance at low frequency region decreases with an increase in the Ni and Al content, indicating the reduced coating resistance by the metal powder addition. The impedance spectra were fitted using an equivalent circuit of the model 1 in Fig. 12 except for the coated specimen containing 70 phr Ni, for which the model 2 was used to fit the impedance spectrum with two time constants. The R_s is the solution resistance, CPE_1 is the constant phase element of the coating, R_{ct} is the charge transfer resistance of the defect sites of the coating and CPE_2 is the constant phase element of the defect sites of the coating. The model 2 was used following the previous studies^{4), 6)}. Fig. 13 shows the change in the coating resistance, R_c , with the

Fig. 11 Bode plots of the electro-galvanized steel with epoxy coatings containing (a) Ni and (b) Al powders measured in the corrosive solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 20°C (Online version in color.).

Fig. 12 Two equivalent circuits used to fit the EIS data in this study.

Fig. 13 Change in the coating resistance, R_c , with the content of Al or Ni powders.

amount of metal powders. Regardless of the type of metal powders the coating resistance decreases with the amount of metal powders; less protective coatings are formed by the addition of metal powders. The results obtained by EIS measurements, showing the reduced corrosion protection of the coatings by the addition of metallic powders, are consistent with the corrosion tests and polarization measurements.

4. Discussion

4.1 Influence of Ni powder addition in paint film

In comparison with the coating consisting of only epoxy resin, clear enhanced deterioration of corrosion resistance by the addition of Ni powders was observed in the corrosion tests. From the SEM observations, the Zn layer near the Ni powders was severely corroded (Fig. 5). The amount of Zn dissolved into the corrosive solution during the corrosion tests was much larger for the Ni-containing coatings than that free from metal powders and also those with the same amounts of Al. The potentiodynamic polarization curves revealed that the cathodic current density is highly increased by the addition of Ni powders, because of high cathodic activity of Ni powders in contact with the Zn layer. Galvanic corrosion by the addition of Ni powders promoted the corrosion of the Ni-containing coated steels. The generation of voids around the spike-shaped Ni powders also appears to enhance the penetration of the corrosive solution through the coating and accelerate the corrosion. It is likely that the increased anodic current density by the addition of Ni in the potentiodynamic polarization curves is also associated with the increased penetration of the corrosive solution through the coating because of the presence of voids near the Ni powders. The deterioration of the coating resistance was also evident from the EIS measurements; the coating resistance decreases with an increase in the Ni content.

4.2 Influence of addition of Al powder to paint film

Al powders have been added to organic coatings. Gonzalez et al. examined the corrosion resistance of the carbon steel and galvanized steel coated with alkyd and epoxy resins containing Al powders in 3% NaCl solution by EIS measurements.^{3), 9)} The addition of Al powders into the coatings improved the corrosion resistance of both the carbon steel and galvanized steel and they explained that the Al powders provides a cathodic protection of the substrate and the corrosion products precipitating in the pores improve the barrier nature of the coatings. Similar results were also reported by Xue et al.¹⁰⁾

In contrast, the addition of flaky Al powders in the epoxy coatings in the present study accelerated the corrosion of the electro-galvanized steel in the mixed solution containing formic acid, acetic acid and NaCl. The difference of the present study from the previous investigations is probably related to the corrosive

environment. Seri et al. reported that the corrosion of 1100 Al in NaCl solutions was accelerated by the addition of acetic acid in the solutions.¹¹⁾ Severe pitting corrosion proceeded during immersion of 1100 Al in 10 g L⁻¹ NaCl solution containing 60 g L⁻¹ acetic acid. They reported that Al-acetate complex ion, $\text{Al}(\text{OAc})_2^+$, is stably present in the pH range of 3.1-5.5, reducing the Al_2O_3 stable pH range to 5.5-9.1. In the present corrosive solution of pH 3.2 containing acetate and chloride, the corrosion of Al proceeds probably due to the formation of the Al-acetate complex ions. In fact, more than 30% of the Al added to the coating with 40 phr Al dissolved into the solution during the corrosion tests.

The oxygen gas permeation is clearly reduced by the addition of Al powders. The water vapor permeation does not increase with the addition of Al powder. Thus, in contrast to the addition of Ni powders, the Al-containing coatings do not show the reduced barrier nature. Thus, the increased cathodic current by the addition of Al powders in the potentiodynamic polarization is not due to the reduced barrier nature of the coatings. The cathodic activity of Al is most likely to be higher than that of Zn in this solution.

4.3 Simultaneous additions of Ni and Al powders

Findings in this study indicate that the separate additions of Ni and also Al powders deteriorate the corrosion protection properties of the epoxy coatings on the electro-galvanized steel. In contrast, our previous study revealed that the corrosion protection of the Ni-containing epoxy coatings were highly improved by the simultaneous addition of Al powders. This is contrast to the reduced corrosion protection of the Al-added coatings without Ni in this study. Thus, some synergistic effect plays an important role in improving the corrosion protection by the simultaneous additions of Ni and Al powders.

As discussed in the previous study,⁸⁾ the flaky Al powders were often located at the bottom of the epoxy coatings, which separated the particulate Ni powders from the Zn layer. Severe Zn corrosion by forming a Ni/Zn galvanic couple is effectively suppressed by the addition of Al powders. However, the present study disclosed that the Zn corrosion was also accelerated by the addition of Al and no Zn layer was remained continuously as shown in Fig. 7. This is contrast to the almost un-corroded Zn layer beneath the flaky Al powder, above which a Ni powder was present.⁸⁾ One possible explanation of the suppression of corrosion of Zn and Al by the simultaneous additions of Ni and Al powders is an increase in pH of the corrosive solution incorporated into the coating. Ni is the noblest element among Ni, Zn and Al such that the Ni powders acts as a cathodic site. The cathodic reaction is either hydrogen evolution or oxygen reduction, resulting in an increase in pH. If pH increased to >5.5 where Al_2O_3 is stable, the corrosion of Al is suppressed by forming a passive film. The Zn corrosion is also suppressed with an

increase in pH.

The present study suggests that the corrosion protection properties of the organic coatings are improved by simultaneous addition of Ni and Al powders, even though the separate additions of these powders accelerates the corrosion. Findings in this study open up a new design principle of the composite organic coatings containing metallic powders. Detailed understanding the role of metal powders in the organic coatings in corrosion process is a key to design corrosion resistant coatings with different metal powders, which plays synergistic roles in improving the corrosion resistance.

5. Conclusions

Coatings containing either particulate Ni powders or flaky Al powders were prepared on electro-galvanized steel, and their corrosion resistance in a mixed aqueous solution containing 100 ppm formic acid, 100 ppm acetic acid and 83 ppm NaCl at 40°C for 350 h was investigated by surface observations, SEM observations and solution analysis. In addition, potentiodynamic polarization, EIS and oxygen gas and water vapor permeation studies were conducted. The following conclusions were drawn.

- (1) When Ni powders are added to the epoxy coating, the corrosion resistance deteriorates as the amount of Ni powders increases from 0 to 70 phr. At 70 phr Ni, the entire specimen surface is covered with white rust.
- (2) Corrosion is also accelerated by the addition of Al powders, although the corrosion morphology is different from the coatings with Ni powders. No corrosion products are formed on the epoxy coating.
- (3) Corrosion products are preferentially formed on the coating near the Ni powders because of Ni/Zn galvanic corrosion when Ni is added to the coating. When Al powders are added, more uniform Zn dissolution occurs. The dissolved Zn increases as the content of the metallic powders in the coating increases.
- (4) The addition of both Ni and Al powders in the coating enhances the cathodic activity of the coated specimens. The coating resistance is reduced with an increase in the metallic powders. As a consequence, the corrosion is accelerated by the addition of metallic powders.
- (5) The gas permeability increases with Ni addition because of void formation around Ni powders, while Al addition improves the gas barrier nature.
- (6) Therefore, the improved corrosion resistance by the simultaneous additions of Ni and Al powders in the epoxy coating is not explained from the corrosion behavior of the coatings containing either Al or Ni powders. The enhanced cathodic activity at Ni sites may increase the local pH in the coating and the formation of the Ni/Zn galvanic couple is avoided by the insertion of flaky Al powders, probably contributing to the improved corrosion protection of the coatings with both Al and Ni powders.

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要 旨

最近、筆者らは鱗片状 Al 粉と粒子状 Ni 粉とを混合添加したエポキシ樹脂塗膜を電気亜鉛めっき鋼板上に被覆することにより燃料タンク内面の耐食性が改善されることを報告した。この有機被覆電気亜鉛めっき鋼板の腐食挙動に及ぼす塗膜中の Ni 粉および Al 粉の各々の役割を理解するために、Ni 粉または Al 粉のいずれかを含むエポキシ樹脂被覆電気亜鉛めっき鋼板を作製し、蟻酸、酢酸および NaCl を含む水溶液中での腐食浸漬試験、動電位分極測定、電気化学インピーダンス分光法(EIS)測定、ならびに酸素ガスおよび水蒸気透過測定を実施し腐食挙動を調査した。その結果、塗膜中の Ni および Al 粉は、いずれも腐食を加速した。分極曲線よりアノードおよびカソード電流の増加を、EIS 測定においては、Ni および Al 粉の添加による塗膜抵抗の減少が確認された。Ni および Al 粉の両方を含有するコーティングの改善された耐食性は、Ni または Al 粉のみを含有する被覆鋼の腐食挙動によって単純に説明されないことから、両粉の耐食性改善の相乗効果について議論した。

キーワード 腐食, 有機皮膜, 金属粉, 亜鉛めっき鋼, 耐劣化ガソリン性