Effect of Solution pH on Layered Double Hydroxide Formation on Electrogalvanized Steel Sheets

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(Submitted September 18, 2018; in revised form February 22, 2019; published online March 7, 2019)

The effect of solution pH on layered double hydroxide (LDH) formation on electrogalvanized steel sheets (EG steel) was investigated in this study. EG steel with a Zn coating weight of 64 g/m² was used as a substrate and was immersed in a 0.25 M Na₂Al₂O₄-based solution having several pH values to form a Zn-Al-based LDH conversion coating. After rinsing and drying, corrosion resistance was evaluated by EIS. It was found that corrosion resistance increased with increasing pH up to pH 12.6. However, above this pH, corrosion resistance tended to display a sharp decrease. To understand this trend, the conversion coating was characterized by FT-IR, XRD and GDOES. The conversion coating was found to consist mainly of Zn₂Al(OH)₆(CO₃)_{0.5}·xH₂O crystals (an LDH). The thickness of the conversion coating layer increased with increasing pH up to pH 12.4, but above this pH, its thickness tended to decrease due to the formation of ZnO. The reason for the dependence of corrosion resistance on solution pH is discussed from the viewpoints of the thickness and changes in the microstructure of the conversion coating layer, including its crystal size, density and uniformity, which could vary during the initial formation of ZnO at pH values above 12.6.

Keywords conversion coating, corrosion resistance, galvanized steel, layered double hydroxide

1. Introduction

Layered double hydroxides (LDHs) are chemical compounds with the general formula $M_{(1-x)}^{2+}M_x^{3+}(\text{OH})_2(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation and A^{n-} is an anion. LDH compounds have layered crystal structures consisting of a mixed M^{2+}/M^{3+} hydroxide layer separated by a layer containing hydrated anions, A^{n-} . Among other cations, Zn^{2+} and Mg^{2+} are common for M^{2+} and Al^{3+} is common for M^{3+} . It is well known that the interlayer anions are exchangeable with anions present in a surrounding solution or corrosion environment.

This anion exchange is the basis for the storage-and-release inhibitor concept that underlies LDH-based corrosion-inhibiting pigments. The effects of addition of LDH-based pigments to organic coatings on corrosion resistance have been widely investigated. R. G. Buchheit and S. P. V. Mahajanam et al. reported that $[\text{V}_{10}\text{O}_{28}]^{6-}$ -intercalated Zn-Al-based LDHs added to an organic coating layer improve the corrosion resistance of an Al alloy substrate (Ref 1-4). They also demonstrated that the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anions were released from the LDHs during

exchange with Cl^- anions found in the surrounding Cl^- -rich corrosion environment (Ref 1-4). G. Williams and H.N. McMurry showed that the addition of CO_3^{2-} , NO_3^- or CrO_4^{2-} -containing Mg-Al-based LDHs to organic coatings improves filiform corrosion resistance on Al alloy substrates (Ref 5-10). These coatings have also been applied to other materials such as galvanized steel sheets and cold-rolled mild steel sheets with promising results (Ref 11-14).

Because the LDH compounds can be produced easily by hydrothermal synthesis, LDH-based conversion coatings produced by simple immersion processes are also possible. These easily produced coatings have been applied on Al alloys and galvanized steel. For example, it was previously shown that a corrosion-resistant Li-Al-CO₃ LDH coating will form on Al alloy substrates by simple immersion of the substrate in a lithium carbonate solution (Ref 15-18). It has also been shown that a corrosion-resistant Zn-Al-based LDH coating forms on hot-dip galvanized steel sheets by immersion of the sheets in a high alkaline sodium aluminate solution (Ref 19). However, the mechanisms of LDH formation and corrosion protection by a LDH conversion coating layer on galvanized steel have not been thoroughly investigated, and the formed LDH conversion coating layers have not yet been fully characterized.

This study seeks to understand the LDH formation mechanism and corrosion protection provided by a conversion-coated Zn-Al-based LDH layer on galvanized steel, the effect of solution pH on LDH formation on electrogalvanized steel (EG steel) and the associated corrosion resistance.

2. Experimental Procedure

2.1 Test Specimens and Treatment Procedures

The test samples were 0.75-mm-thick electrogalvanized mild steel sheets. The coating weight of Zn on the evaluated side of the test specimens was 64 g/m². All the specimens were

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provided by JFE Steel Corporation. The specimens were cut to 50 mm × 70 mm and degreased with ethanol before treatment.

In order to form the LDH conversion coating layer, $\text{Na}_2\text{Al}_2\text{O}_4$ solutions containing 0.1 M KNO_3 , 0.01 M NH_4NO_3 and 0.01 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were prepared. The concentration of $\text{Na}_2\text{Al}_2\text{O}_4$ was varied from 0.050 to 0.250 M. Stirred solutions were aged for various time periods (120 to 480 min), after which the test specimens were immersed in each solution for 16 h at room temperature without stirring. The pH of the treatment solutions varied in the range of 11.5 to 13.3 depending on the concentration of $\text{Na}_2\text{Al}_2\text{O}_4$ and aging time. The parameters for each of the solutions are summarized in Table 1. It is known that the precipitation of aluminum hydroxide can occur in $\text{Na}_2\text{Al}_2\text{O}_4$ solution which contains CO_2 (Ref 20). This could cause the change of the solution pH depending on the aging time in this study, because CO_2 can dissolve in it from air. The pH of the treatment solution No. 9 condition was controlled with addition of 1.0 M NaOH solution to investigate the influence of solution pH without changing the concentration of $\text{Na}_2\text{Al}_2\text{O}_4$ and aging time. After rinsing with deionized water and air drying, the corrosion resistance of each specimen was evaluated and the coating layers were characterized.

2.2 Evaluation of Corrosion Resistance

The corrosion resistance of the coated specimens was evaluated by electrochemical impedance spectroscopy (EIS). Measurements were carried out in a 0.1 M NaCl solution after immersion for 1 h at room temperature. A sinusoidal 10 mV voltage signal was used as the perturbation with frequencies ranging from 10,000 to 0.01 Hz. To evaluate corrosion resistance, impedance at 0.01 Hz was compared, which was demonstrated at the lowest measured frequencies.

2.3 Analyses of Coating Layer

The following surface observations and analyses were carried out in order to determine the interlayer anions, crystal structure, microstructure, appearance and chemical compositions of the resulting LDH conversion coating layers.

Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained with a FT-IR spectrometer (WINSPEC-100, JEOL). The measurements were carried out by reflection absorption spectroscopy with a 75° incident angle and 100 accumulations.

X-ray diffraction (XRD) patterns of the coating layer were determined with an x-ray diffractometer (SmartLab, Rigaku). The incident angle was 3°. The radiation source was a Cu K α target. A scan range of 5° to 45° was employed with a scan speed and step of 10°/min and 0.01°, respectively. The tube voltage and tube current were 45 kV and 44 mA, respectively.

The depth profile of the coating layer was determined by glow discharge optical emission spectrometry (GDOES) (GD-Profilier 2, HORIBA). Ar plasma was used for sputtering with an Ar pressure of 600 Pa. Power of 35 W, a sampling time of 10 ms and an Ar flushing time of 30 s were employed. The measured area was circular with a 4 mm diameter. The sputtering rate under these conditions was determined as approximately 60 nm/sec for mild steel sheets by a measured actual depth of the sputtered area with a 3D microscope and sputtering time.

The surface of the coating layer was observed with a scanning electron microscope (SEM) (JSM-6060, JEOL) equipped with a secondary electron (SE) detector. The acceleration voltage during observation was 5 kV.

Cross sections of the coating layer were observed with an SEM (ULTRA PLUS, Carl Zeiss) and analyzed by energy-dispersive x-ray spectrometry (EDX), which was incorporated in the SEM. The instrument was equipped with a backscattered electron (BSE) detector. The acceleration voltages employed during observation and analysis were 1 and 5 kV, respectively. 45° cross-sectional specimens were prepared with a focused ion beam (FIB) instrument (Quanta 200 3D, FEI) for SEM observations.

3. Results

3.1 Corrosion Resistance

The Nyquist plots from the EIS analysis of the LDH-treated specimens subjected to the solutions of various pH values are shown in Fig. 1. Because the spectra were complex, Fig. 2 shows the impedance at 0.01 Hz as a function of solution pH. The impedance clearly increased with increasing pH of the treatment solution up to a maximum value at pH 12.6. Above this pH, impedance decreased dramatically. These results suggest that corrosion resistance is dependent on the pH of the treatment solution, with optimal results obtained from a treatment solution with a pH of 12.6. The measurement of

Table 1 Conditions of treatment solutions used

No.	Concentration (M)				Aging time, m	pH
	$\text{Na}_2\text{Al}_2\text{O}_4$	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	NH_4NO_3	KNO_3		
1	0.05	0.01	0.01	0.10	120	11.5
2	0.13	0.01	0.01	0.10	120	12.0
3	0.15	0.01	0.01	0.10	120	12.3
4	0.20	0.01	0.01	0.10	120	12.4
5	0.25	0.01	0.01	0.10	120	12.6
6	0.25	0.01	0.01	0.10	180	12.7
7	0.25	0.01	0.01	0.10	240	12.9
8	0.25	0.01	0.01	0.10	480	13.2
9	0.25	0.01	0.01	0.10	120	13.3

Fig. 1 Evolution of EIS spectra for LDH-treated specimens during exposure to 0.1 M NaCl solution. pH refers to the treatment solution conditions

Fig. 2 Relationship between impedance at 0.01 Hz and solution pH. Designated numbers in the figure correspond to the treatment solution number (Table 1)

impedance of the specimens treated with the treatment solution No. 5 condition (Table 1) was repeated three times. The average value and standard deviation were 2071 and 262 $\Omega \cdot \text{cm}^2$, respectively.

3.2 Analysis of Coating Layer

The FT-IR spectrum of an LDH-treated specimen produced under the treatment solution No. 5 condition (Table 1) is shown in Fig. 3. Peaks were observed at 461, 573, 874, 1365, 3296 and 3861 cm^{-1} . These peaks display reasonable agreement with the FT-IR spectra of solid $\text{Zn}_x\text{Al}_{1-x}(\text{CO}_3)_{2/x}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (Ref 21). Analysis of all the test specimens resulted in similar spectra, suggesting that $\text{Zn}_x\text{Al}_{1-x}(\text{CO}_3)_{2/x}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ was

Fig. 3 FT-IR spectrum of LDH-treated specimens produced under No. 5 treatment solution condition

Fig. 4 XRD patterns of LDH-treated specimens. pH refers to the treatment solution conditions

successfully formed on the EG steel samples. $\text{Zn}_x\text{Al}_{1-x}(\text{CO}_3)_{2/x}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, an LDH, is comprised of the basic layers of a mixed Zn^{2+} and Al^{3+} hydroxide and a CO_3^{2-} and H_2O interlayer.

Fig. 5 Depth profile of LDH-treated specimens produced under No. 5 treatment solution condition analyzed by GDOES

The XRD spectra acquired from the specimens after LDH conversion coating are shown in Fig. 4. The spectrum of each specimen displays clear evidence of the presence of a Zn substrate [PDF Card No.: 01-078-9363] and of $\text{Zn}_2\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5} \cdot x\text{H}_2\text{O}$ (Zn-Al- CO_3 LDH) [PDF Card No.: 00-048-1023]. These results also support the above-mentioned results that the LDH conversion coating was successfully applied to the EG steel samples and the conversion coating layer consisted mainly of Zn-Al- CO_3 LDH. Based on the XRD results, although the layer consists of only Zn-Al- CO_3 LDH below pH 12.6, diffraction patterns of ZnO [PDF Card No.: 01-070-8072] were also observed above pH 12.6. This indicates that the composition of the layer changes near pH 12.6. This accords well with the decrease in corrosion resistance observed at pH 12.6 in the EIS experiments (Fig. 2).

A representative GDOES depth profile of an LDH-treated specimen produced under the No. 5 treatment solution condition is shown in Fig. 5. Zn, Al, O, C and H were all detected on the surface of the specimens. This result also supports the conclusion that the Zn-Al- CO_3 LDH conversion coating was successfully formed. It can be said that the thickness of the Zn-Al- CO_3 LDH correlates with the amount of Al because Al is one of the composition of the LDH layer and other layers do not contain Al. The amount of Al can be estimated from integration of Al intensity of GDOES profiles. Integrated Al intensity was obtained by integration of net Al intensity of GDOES profiles, when bulk Al intensity was defined as background, with sputtering time. Figure 6 shows the integrated Al intensity as a function of the pH of the treatment solution. The integrated Al intensity increased as the solution pH increased up to pH 12.4, and above this pH, the integrated Al intensity tended to decrease. This suggests that the thickness of the coating layer increased as the solution pH increased up to pH 12.4, and above this pH, the thickness of the coating layer tended to decrease.

In the conversion coating reaction, Zn could be provided by the dissolution reaction of the Zn substrate in addition to the aqueous $\text{Zn}(\text{NO}_3)_2$ in the treatment solution. Therefore, the increase in the conversion coating layer thickness observed

Fig. 6 Relationship between integrated Al intensity obtained with GDOES and pH of treatment solution. Designated numbers in the figure correspond to the treatment solution number (Table 1)

Fig. 7 Relationship between impedance at 0.01 Hz and integrated Al intensity obtained with GDOES. Designated numbers in the figure correspond to the treatment solution number (Table 1)

with increasing pH could be attributed to the dissolution rate of the Zn substrate, which would be accelerated with increasing pH. However, the solubility of Zn and Al also increases with increasing pH, which would explain why the conversion coating layer thickness decreased with increasing pH above this pH value.

4. Discussion

4.1 Effect of Conversion Coating Layer Thickness on Corrosion Resistance

The similarity between the trends of impedance (Fig. 2) and the integrated Al intensity (Fig. 6) as a function of solution pH

Fig. 8 SEM images of LDH-coated specimens. pH refers to the treatment solution conditions

Fig. 9 Cross-sectional SEM images of LDH-coated specimens. The white boxes in (a-c) were observed at high magnification and (d-f) show the results, respectively

suggest that the conversion coating layer thickness might affect corrosion. The data provided in Fig. 7 further support this relationship. Essentially, impedance tended to increase as the integrated Al intensity increased. This suggests an increase in corrosion resistance with increasing conversion coating layer thickness. However, at pH 12.6, higher impedance was observed even with a thinner coating layer. This suggests that corrosion resistance cannot be explained solely by the coating layer thickness.

4.2 Effect of Solution pH on Microstructure of Coating Layer

In order to understand how the conversion coating layer affects corrosion resistance, SEM images of the surface of the treated

specimens are shown in Fig. 8. Platelike crystals, typical of the shape of LDH crystals, cover the surface after treatment at all pH values. The crystal size, however, tended to increase slightly as the pH was increased from pH 12.0 to pH 12.4, but above pH 12.6, the crystals showed a marked decrease to finer sizes.

The 45° cross sections of three test specimens prepared in solutions at pH 12.4, 12.6 and 12.9 were obtained using FIB. The BSE images of these specimens are shown in Fig. 9. In this pH region, as with the GDOES data, an increase in pH tended to lead to a thinner conversion coating layer. Although a thicker conversion coating layer was observed at pH 12.4, some cracks and crevices were also observed. At the pH values of 12.6 and 12.9, the conversion coating layer appeared denser and more

Table 2 Analytical results of EDX of areas in white boxes (1-10) in Fig. 9 (d)-(f)

Analyzed area	Composition at. %			
	Al	Zn	O	C
1	15	35	46	3
2	11	41	43	5
3	0	95	2	2
4	13	37	48	4
5	1	59	39	2
6	0	96	2	2
7	13	34	47	6
8	1	51	55	2
9	0	54	44	2
10	0	95	3	3

Fig. 10 Schematic images of interface between Zn substrate and treatment. (a) Lower solution pH and (b) higher solution pH

Fig. 11 Cross-sectional schematic images of microstructure of LDH layer depending on solution pH. (a) pH < 12.6, (b) pH = 12.6 and (c) pH > 12.6

uniform than that of the specimens prepared at pH 12.4, and there was also an absence of cracks and crevices. As mentioned above, the crystal size changed drastically around pH 12.6. This could affect whether cracks and crevices were observed or not because larger crystals induce strain and distortion which cause cracks and crevices in coating layer. In addition to the difference, an area of medium brightness was observed in the lower conversion coating layer on the Zn substrate of the specimens prepared at pH 12.6 and 12.9. Because the contrast of the BSE

images is dependent on the layer composition, this indicates that the microstructure of the conversion coating layer is divided into two layers with different compositions when treatment is performed at or above pH 12.6. The areas indicated by the white boxes (1-10) on the cross sections in Fig. 9 (d) and (f) were analyzed by EDX, and the results are shown in Table 2. At pH 12.4, Zn, Al, C and O were detected in both areas 1 and 2, indicating that the conversion coating layer consists of only Zn-Al-CO₃ LDH. At pH 12.6 and 12.9, the area of medium brightness appears to consist of ZnO; only Zn and O were detected in areas 5, 8 and 9. The Zn-Al-CO₃ LDH layer exists on the ZnO layer. These results are in agreement with the results obtained by XRD and, again, indicate that the conversion coating layer consists of ZnO as well as Zn-Al-CO₃ LDH with treatment at a pH at or above 12.6 (Fig. 4). As pH increases in this limited pH region, the ZnO layer tends to thicken and the Zn-Al-CO₃ LDH layer tends to become thinner. In addition to the layer thickness, as mentioned before, differences in the microstructure of the conversion coating layer, such as the density and uniformity of the LDH, along with the fraction of ZnO to LDH, could also affect corrosion resistance.

4.3 Effect of Initial Formation of ZnO on LDH Crystal Growth

The stability diagram of Zn indicates that aqueous Zn(OH)₃⁻ is stable in the pH range from 11.5 to 13.3 and, in addition, solid ZnO can precipitate if the concentration of Zn(OH)₃⁻ is above saturation, indicating a dependence on the concentration of Zn(OH)₃⁻ (Ref 22). From the stability diagram of Al, aqueous Al(OH)₄⁻ is stable in this pH range (Ref 22). As mentioned above, Zn²⁺ could be provided by the dissolution reaction of the Zn substrate and CO₃²⁻ can be provided by the dissolution of CO₂ from air. Therefore, it is reasonable to assume that the following chemical reactions could occur at the lower end of this pH range, resulting in the formation of Zn-Al-CO₃ LDH:

However, at the high end of this pH range, the concentration of Zn(OH)₃⁻ would be expected to be much higher than that at the lower end of the pH range. This should occur because the rate of the dissolution reaction of Zn, Reaction (1), will be accelerated in the solution at the interface with the EG steel surface (Fig. 10). At the high end of the pH range, the dissolution reaction of Zn can be divided into the following two reactions:

The formation of Zn-Al-CO₃ LDH at the interface of ZnO and the solution (rather than on the bare Zn surface) in the higher pH region could affect the microstructure of the LDH layer. The initial formation of ZnO could work as a surface conditioner and could make the LDH crystals finer, denser and more uniform.

4.4 Effect of Microstructure of Conversion Coating Layer on Corrosion Resistance

The changes in the microstructure of the conversion coating layer are summarized in Fig. 11 as schematic images. When the solution pH is below 12.6, cracks and crevices are introduced into the LDH crystals because the LDH crystals form directly on the EG steel surface. This could cause lower corrosion resistance because electrolytes can reach the Zn substrate through cracks and crevices, although corrosion resistance did increase as the layer thickness increased. When the solution pH is around 12.6, higher corrosion resistance is observed in spite of the thinner layer. This is attributed to the presence of the layer of initially formed ZnO, which appears to result in the formation of finer LDH crystals that are denser and more uniform. Additionally, when the solution pH exceeds 12.6, the ratio of ZnO to LDH in the coating increases and this, in turn, could result in lower corrosion resistance because ZnO is not protective due to its high solubility in the NaCl solution.

5. Conclusions

The effect of solution pH on LDH formation on EG steel sheets was investigated, and the following conclusions were reached:

- (1) Carbonate was determined to be the interlayer anion formed in LDH crystals created by the procedure discussed in this paper. $\text{Zn}_2\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5}\cdot x\text{H}_2\text{O}$ (an LDH) readily forms on EG steel surfaces when the surfaces are immersed in the $\text{Na}_2\text{Al}_2\text{O}_4$ -based solution.
- (2) The corrosion resistance observed in association with the above-discussed LDH coating increases with increasing solution pH up to pH 12.6. Above pH 12.6, however, a sharp decrease in corrosion resistance was observed. This trend of corrosion resistance can be explained in some respects by the conversion coating layer thickness.
- (3) However, for samples treated at pH 12.6, the initial formation of ZnO results in the formation of a more uniform and protective LDH layer, resulting in higher corrosion resistance in spite of a thinner layer.

Acknowledgments

The authors wish to thank Prof. Belinda Hurley and Prof. Gerald S. Frankel (The Ohio State University, USA) for their discussions of this paper and help with grammatical editing. They also wish to acknowledge the financial support of JFE Steel Corporation, Japan.

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