Effect of additives on the properties of phosphate conversion coating on electrogalvanized steel sheet

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ABSTRACT

Ni^{2+} and Mn^{2+} ions have been added separately to the phosphate solution to minimize the porosity of the phosphate conversion coating on electrogalvanized steels. Results showed that the Ni^{2+} or Mn^{2+} in the solution reduced the grain size and porosity of the phosphate coating; thereby, the corrosion resistance was enhanced. However, Ni^{2+} and Mn^{2+} played a different role in the coating formation. Ni^{2+} in the solution was reduced by Zn to form Ni, which enhanced the dissolution of Zn to promote the nucleation of hopeite grains. Mn^{2+} in the solution facilitated the nucleation by increasing the impingement of reacting species.
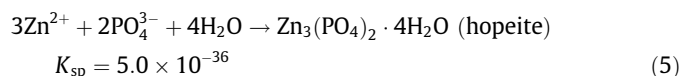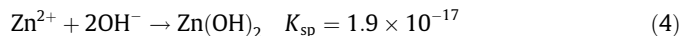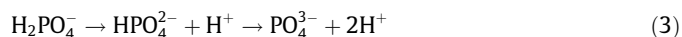
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1. Introduction

Owing to the poor corrosion resistance of iron, zinc coatings are commonly plated via hot-dip galvanizing or electrogalvanizing to enhance the commodity of plain steels through barrier protection and sacrificial protection [1,2]. However, the corrosion product of zinc coating formed in the atmosphere cannot provide sufficient protection over the steel substrate. To further protect the zinc-coated steel against corrosion, surface modification is generally adopted. Conversion coating treatment is known as its simple solution constituents and ease in operation, for instance, the chromate conversion coating treatment has been applied to galvanized steels [3–5] due to its attractive corrosion protection properties and simplicity in operation. However, the use of the hexavalent chromium has been restricted recently due to the high toxicity, signifying an urgent necessity to develop chrome-free treatments such as phosphate [6–10], molybdate [11], and rare earth metal salts conversion coating treatments [12–15].

Phosphate conversion coating treatment has been widely applied treatment on metals to improve the corrosion resistance of the metal substrate and to enhance the adhesion of an organic coating [16–19,21–39]. Phosphate conversion coating treatment is generally carried out in Zn^{2+}-containing $H_2PO_4^-$ aqueous solution with NO_2^- or NO_3^- as accelerators. When the metal substrate is immersed in acidic treating solution, the metal substrate, which is generally covered with an air-form oxide/hydroxide film, is attacked, which, in turn, triggers the formation of the conversion coating. For electrogalvanized steel, the coating is mainly composed of hopeite, which is formed as follows [20,23]:

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

$$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+ \rightarrow PO_4^{3-} + 2H^+ \tag{3}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad K_{sp} = 1.9 \times 10^{-17} \tag{4}$$

$$3Zn^{2+} + 2PO_4^{3-} + 4H_2O \rightarrow Zn_3(PO_4)_2 \cdot 4H_2O \text{ (hopeite)}$$
$$K_{sp} = 5.0 \times 10^{-36} \tag{5}$$

Upon immersion, the zinc substrate and the air-form zinc oxide film will immediately dissolve into the acid solution (Eq. (1)). This dissolution is due to the fact that the most stable species of zinc in aqueous solutions with pH value less than 5.4 is Zn^{2+} when the solution Zn^{2+} concentration is equal to 1 M [20]. Together with the oxidation and dissolution of zinc, the primary cathodic reaction is the reduction of protons, allowing an increase in the pH near the zinc electrode surface (Eq. (2)), which facilitates the dissociation of the $H_2PO_4^-$ ions and HPO_4^{2-} ions (Eq. (3)). Once the near-electrode pH is high enough, Zn^{2+} precipitates as a corrosion protection layer, i.e., the conversion coating (Eqs. (4) and (5)). Crystalline hopeite shows good adhesion on the zinc-coated steel; however, the irregular crystals result in open pores, which are prone to corrosion. The corrosion resistance of the coating is thus closely related to the coating porosity that can be reduced via the increase in the nucleation site of hopeite. For example, the nucleation site of hopeite is

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increased through activation of the zinc-coated steel in a titanium phosphate-containing solution prior to phosphate conversion coating treatment [21–23]. Additives in the treating solution, such as Mg^{2+} [7,8,24,25], Ni^{2+} [26–33], and Mn^{2+} [26,27,29–33], are also found to reduce the porosity of the phosphate conversion coating. Moreover, the corrosion resistance can be enhanced via post-sealing treatments [34–36]. Zimmermann et al. [28] found that the formation of hopeite was facilitated with increasing Ni^{2+} concentration in the treating bath. Tsai et al. showed that increasing the solution Mg^{2+} concentration increased the population density and refined the size of the phosphate crystals [8]. In the automotive industries, the phosphate conversion coating process is usually performed in a trication bath, which is mainly composed of Zn^{2+}, Ni^{2+}, and Mn^{2+} ions [37,38]. Moreover, an activation procedure is generally adapted prior to the phosphate conversion treatment. However, the mechanism of the effect of individual cation on the microstructure and properties of the coating is less studied. This present study thus aims at the clarification of the effect of Ni^{2+} and Mn^{2+} ions in the treating solution on the microstructure and corrosion resistance of phosphated electrogalvanized steels through systematical microstructural characterizations and electrochemical tests. Moreover, the corrosion protection mechanism of the phosphate conversion coatings formed in the presence of Ni^{2+} or Mn^{2+} ions was discussed in detail.

2. Experimental

2.1. Phosphate conversion coating treatment

The material used in this study was electrogalvanized steel ($100 \times 60 \times 0.6$ mm) with a 6-μm-thick zinc layer in the as-received form produced by an industrial batch type production line (Hsieh Shun Plating Co., Ltd., Taoyuan, Taiwan). The electroplating was performed in a commercial cyanide-free alkaline Zn solution (Hyper Zinc 9000 series, JASCO International Co., Ltd., Japan). The electrogalvanized steels were degreased with a pH 13.0 commercial alkaline solvent for 120 s (Model PALKIN-N 365S, Nihon Parkerizing Co., Japan), rinsed with de-ionized water, and cleaned in acetone ultrasonically. Table 1 shows the composition of the phosphating bath, in which Ni^{2+} or Mn^{2+} ions were added in the form of $Ni(NO_3)_2$ and $Mn(NO_3)_2$, respectively. Moreover, the concentration of $NaNO_3$ in each bath was varied in order to maintain the same bath NO_3^- concentration. The pH of the phosphate solution was adjusted to 2.5 via the addition of sodium hydroxide (NaOH). The phosphate conversion coating treatment was performed in the solution at 45 °C for 300 s. After immersion, the plates were rinsed with de-ionized water, dried using a stream of air, and left in atmosphere overnight.

2.2. Phosphate conversion coating characteristics

The surface morphology of the phosphate conversion coating was characterized via scanning electron microscopy (SEM) under back scattered electron scanning mode (BSE). The crystallinity and the phase of the conversion coating were identified using X-ray diffractometer (Rigaku-TTRAX III) with Cu Kα radiation at 15 kW and a scanning speed of 4°/min.

X-ray photoelectron spectroscopy (XPS) was employed to measure the binding energy of the various species in the coating via a VGS Thermo K-Alpha spectrometer with Al Kα radiation. The charging effect was corrected using the C1s peak at 284.6 eV as the reference for all samples. After subtraction of the Shirley's background, the area under each fitting curve was calculated using the XPSPEAK 4.1 software. The area divided by the atomic sensitivity factor was employed to calculate the composition (atomic percentage) of the coating.

The corrosion resistance of the electrogalvanized steels with and without phosphate conversion coatings was examined by potentiodynamic polarization test, electrochemical impedance spectroscopy (EIS), and salt spray test. Electrochemical measurements were accomplished by a model 263A potentiostat/galvanostat and a FRD100 frequency response detector (EG&G Instruments), and each test was performed after 1 h of immersion in 5 wt% NaCl solution. The tested area was 1.77 cm^2. A platinum plate and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The polarization measurements were scanned from −200 mV (relative to the OCP) to +600 mV (relative to the OCP) at a scan rate of 0.5 mV/s. The polarization resistance was calculated via the Stern-Geary equation. The anodic and cathodic Tafel slopes used in the Stern-Geary equation were measured from $E_{corr} \pm 70$ mV, respectively. The EIS data were recorded at the OCP with a sinusoidal perturbation of 10 mV amplitude over the frequency range from 10^5 Hz to 10^{-2} Hz. The ZSimpWin Version 3.21 software was used to simulate the electric elements of the EIS results.

The salt spray test was performed in a chamber containing 5.0 wt% NaCl fog according to the ASTM B117-03 standard [40]. The percentage of the corroded area was recorded at intervals of 24 h and the result was based on the average of three samples. The results were reported in the ASTM D610 standard form [41].

2.3. Coating porosity evaluation

Because the phosphate conversion coating is mainly composed of insulating hopeite, the pore in the coating is generally regarded as the exposed area of the substrate, which can be measured by electrochemical methods such as the linear polarization method and EIS [32,39].

There are some limitations in the linear polarization method. Notter and Gabe [42] reported that the linear polarization method is not applicable if the polarization current is insignificant compared to the metal substrate or no passivation occurs on the metal substrate during the measurement. Owing to the insulation property, the hopeite coating does not participate in the electrochemical reaction. The linear polarization method is thus applicable for measuring the porosity of the phosphate conversion coating. The

Table 1
The chemical composition of the phosphating bath.

Label	Composition (mmol/L)				
	H$_3$PO$_4$	ZnO	NaNO$_3$	Ni(NO$_3$)$_2$	Mn(NO$_3$)$_2$
Phosphated without Ni^{2+} and Mn^{2+}	220.0	18.4	235.3	–	–
Phosphated with 8.5 mmol/L Ni^{2+}	220.0	18.4	218.3	8.5	–
Phosphated with 17.0 mmol/L Ni^{2+}	220.0	18.4	201.3	17.0	–
Phosphated with 34.0 mmol/L Ni^{2+}	220.0	18.4	167.3	34.0	–
Phosphated with 8.5 mmol/L Mn^{2+}	220.0	18.4	218.3	–	8.5
Phosphated with 17.0 mmol/L Mn^{2+}	220.0	18.4	201.3	–	17.0
Phosphated with 34.0 mmol/L Mn^{2+}	220.0	18.4	167.3	–	34.0