Original Research Paper

# Simulating study of atmospheric corrosion of Zn–Ni alloy coating on steels in marine zone: Structure and properties of artificially synthesized Ni(II)-doped zinc hydroxychloride rust particles

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## ABSTRACT

To simulate the atmospheric corrosion of Zn–Ni alloy coating on the steel in marine zone, artificial Ni(II)-doped zinc hydroxychloride ($Zn_5(OH)_8Cl_2 \cdot H_2O$:ZHC) rust particles were prepared by hydrolysis of ZnO particles in a mixture of aqueous $ZnCl_2$ and $NiCl_2$ solutions at 85 °C and were characterized by various means. Then, the Ni(II)/(Zn(II) + Ni(II)) atomic ratio in starting solution ($X_{Ni}$) was 0–0.10. XRD results indicated that crystallization of the layered structure of ZHC was strongly inhibited with an increase of $X_{Ni}$ and no new particles were generated. The Ni(II) was incorporated into ZHC crystal by substitution with Zn(II) and the Ni/(Zn + Ni) molar ratio in the particles was almost consistent with $X_{Ni}$. The ZHC particles formed at $X_{Ni} = 0$ were hexagonal plate with a size of ca. 3.2 μm and a thickness of ca. 0.3 μm. Increasing $X_{Ni}$ reduced the size and thickness of ZHC particles. Besides, addition of Ni(II) suppressed the adsorption of $CO_2$ and $SO_2$ gasses on ZHC, because of layered structure of this material to be disintegrated. The foregoing results suggest that atmospheric corrosion of Zn–Ni alloy coating in marine zone forms dense and compact zinc rust layer composed of fine Ni(II)-doped ZHC particles with a low affinity to corrosive gasses on the steels, leading to the suppression of further corrosion of steel. Also, role of Ni on the atmospheric corrosion of Zn–Ni alloy coating in marine zone can be suggested by studying the structure and properties of artificial Ni(II)-doped ZHC rust particles.

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## 1. Introduction

Galvanized steels are widely used for infrastructure such as bridges and building materials because Zn film sacrificially corrodes and protects the steel from atmospheric corrosion. Also, zinc rusts formed on the steel play an important role for corrosion resistance of the steel. Atmospheric corrosion of galvanized steels produces various kinds of zinc rusts such as ZnO, $Zn(OH)_2$ and basic zinc salt (BZS) [1–11]. Among them, BZS rusts form the dense and stable rust layer on the steel to suppress the access of corrosive gasses such as $H_2O$, $SO_x$ and $NO_x$ in interior of the layer and to protect further corrosion of the steel [8]. It has been established that the structure of BZS rusts is dependent of the exposure environment of galvanized steel [1,5,9–11]. The zinc hydroxychloride ($Zn_5(OH)_8Cl_2 \cdot H_2O$:ZHC) rust is formed on galvanized steel in marine zone including air-born chloride and in zones where $CaCl_2$

and $MgCl_2$ are used as anti-freezing and snow-melting agents [4]. The zinc hydroxysulfate ($Zn_4SO_4(OH)_6 \cdot nH_2O$) and $NaZn_4Cl(OH)_6 SO_4 \cdot 6H_2O$ rusts are generated in industrial district [3]. The initial BZS rust contains the hydrozincite ($Zn_5(CO_3)_2(OH)_6$) which is transformed into ZHC, zinc hydroxysulfate and $NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$ rusts [5]. Besides, the authors revealed by synthesis of BZS rust in aqueous $ZnCl_2$–$Zn(NO_3)_2$–$ZnSO_4$ solutions that the preferential formation of the rust is in order of zinc hydroxysulfate > ZHC ≫ zinc hydroxynitrate [12]. Most recently, Yoo and co-workers suggested that the ZHC generated on the steel inhibits the cathodic oxygen reduction ($2e^- + 1/2O_2 + H_2O \rightarrow 2OH^-$) in 5 wt.% NaCl at pH = 7 and 9 [13].

In order to enhance the corrosion resistance of zinc film, various metals such as Ti, Mn, Fe, Al, Ni and Mg are alloyed with the film [14–28]. Actually, corrosion rate ($g/m^2/h$) of metal alloyed zinc film estimated from salt spraying test is in order of Zn (1.12) > Zn–Mn (0.60) > Zn–Fe (0.59) > Zn–Fe–Mg (0.55) > Zn–Al–Mg (0.23) > Zn–Ni (0.21) > Zn–Al (0.05) [14]. Since the Zn–Ni alloy coating with 5–10 mass% Ni shows a high corrosion resistance, this coating is

mainly used as corrosion protective coating for automobile parts and bodies [14–20,24,27,28]. Although, detail role of the alloyed Ni on the formation of zinc rust has not fully clarified by using the conventional electrochemical measurements. Therefore, some researchers have proposed that the rust formation in thin film water and/or adsorbed water on zinc film by atmospheric corrosion regards as the reaction of metal ions eluted from the film [8,12,23,29–32]. When Zn–Ni alloy coating corrodes in marine zone, the coating is dissolved to generate ZHC rust in the presence of Ni(II). It seems that dissolved Ni(II) markedly affects the formation, structure and properties of ZHC rust as well as Ti(IV) [29,30]. Therefore, study of the influence of Ni(II) on the formation and properties of ZHC rust is important to understand the corrosion process of Zn–Ni alloy coatings in marine atmosphere. However, to our knowledge, no study has been reported except for Mosavat et al., [31] Kawafuku et al. [32], and Ishikawa et al. [8]. Mosavat et al. reported the corrosion performance of electrodeposited nanocrystalline Zn–Ni alloy coating and indicated that stable and protective zinc rust layer is formed on the steel [31]. Kawafuku and co-workers revealed that corrosion rate of Zn–Ni alloy coating is dependent of the ZHC content in the rust layer [32]. Also, Ishikawa et al. suggested that Ni(II) slightly inhibits the formation of ZHC rust [8]. Nevertheless, these studies were not fully discussed the formation, structure and properties of the rust particles.

This study was aimed to clarify the role of Ni in Zn–Ni alloy coatings on the structure, morphology and properties of ZHC rust. We synthesized the Ni(II)-doped ZHC rust particles from a mixture of aqueous $ZnCl_2$ and $NiCl_2$ solutions and the resulting products were characterized by various means. Besides, the interaction between artificial Ni(II)-doped ZHC rust and corrosive gas was explored by adsorption of $CO_2$ and $SO_2$. The results obtained in this study would be available for elucidating the corrosion process of Zn–Ni alloy coating on the steels in marine atmosphere.

## 2. Experimental

### 2.1. Materials and synthesis

The ZnO particles were synthesized by following wet method. 50 mmol of $ZnCl_2$ were dissolved into 1 $dm^3$ of deionized-distilled water and the solution pH was adjusted to 9.0 by adding a concentrated $NH_3$ solution. The resultants were aged at 50 °C for 24 h in a sealed polypropylene vessel. After aging, the resulting precipitates were filtered off, fully washed with deionized-distilled water and then dried in an air oven at 50 °C for a over night.

The Ni(II)-doped ZHC particles were prepared using the same procedure producing ZHC as previously reported by the authors [2,12]. The $ZnCl_2$ and $NiCl_2$ were dissolved into 50 ml of deionized-distilled water. Then, total amount of Zn(II) and Ni(II) was 75 mmol and the Ni(II)/(Zn(II) + Ni(II)) atomic ratios in starting solution (abbreviated as $X_{Ni}$) were 0–0.10. After this, 16 mmol of synthetic ZnO particles were added to the solution and the suspension was aged in a sealed polypropylene bottle at 85 °C for 48 h. The formed precipitates were filtered off, washed with deionized-distilled water and finally dried in an air oven at 50 °C for a over night.

All the chemicals used in this study were reagent grade.

### 2.2. Measurements

The samples thus obtained were characterized as follows. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered Cu Kα radiation (30 kV, 15 mA). IR spectra were recorded by a JASCO Fourier transform infrared spectroscopy (FTIR) using a KBr method with a resolution of

$4 cm^{-1}$. Particle morphology was observed by a TOPCON transmission electron microscope (TEM). Zn and Ni contents, and Cl one were respectively assayed by a Shimadzu atomic absorption spectroscopy (AAS) and ion-chromatograph (IC) after dissolving the samples in a concentrated $HNO_3$ solution. Adsorption isotherms of $N_2$ and $CO_2$ were measured with an automatic volumetric apparatus at the boiling point of liquid nitrogen and 25 °C, respectively. The specific surface area was calculated from the $N_2$ adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation. Adsorption isotherms of $SO_2$ were taken by a gravimetric method at 25 °C. Before the $N_2$, $CO_2$ and $SO_2$ adsorption measurements, the samples were pretreated by outgassing at 100 °C for 2 h.

## 3. Results and discussion

### 3.1. Structure, composition and morphology of artificial Ni(II)-doped ZHC rust particles

Fig. 1 shows the XRD patterns of the products formed at different $X_{Ni}$ and 85 °C for 48 h. At $X_{Ni}$ = 0, the diffraction peaks of ZnO used as a raw material of ZHC disappear and new peaks emerge (pattern **a**). All the peaks can be ascribed to ZHC (The International Centre for Diffraction Data (ICDD) no. 7-195). The peaks at $2\theta = 11.2°$, 22.5°, 28.1° and 46.0° are assignable to the reflection from (003), (006), (110) and (0012) planes of the ZHC crystal, respectively. It has been reported by the authors that the ZnO particles are hydrolyzed in aqueous $ZnCl_2$ solutions to form ZHC as follows [2,12].

$$ZnO + H_2O \rightarrow Zn^{2+} + 2OH^-$$

$$5Zn^{2+} + 8OH^- + 2Cl^- + H_2O \rightarrow Zn_5(OH)_8Cl_2 \cdot H_2O$$
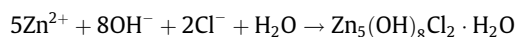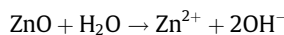
The ZHC peaks dramatically weaken on increasing $X_{Ni}$ and no new peaks are recognized (patterns **b**–**f**). Fig. 2 plots the diffraction intensity of (110) and (003) peaks as a function of atomic ratio $X_{Ni}$. Since the crystal structure of ZHC is rhombohedral as shown in Fig. 3 [11], former and latter peaks respectively correspond to
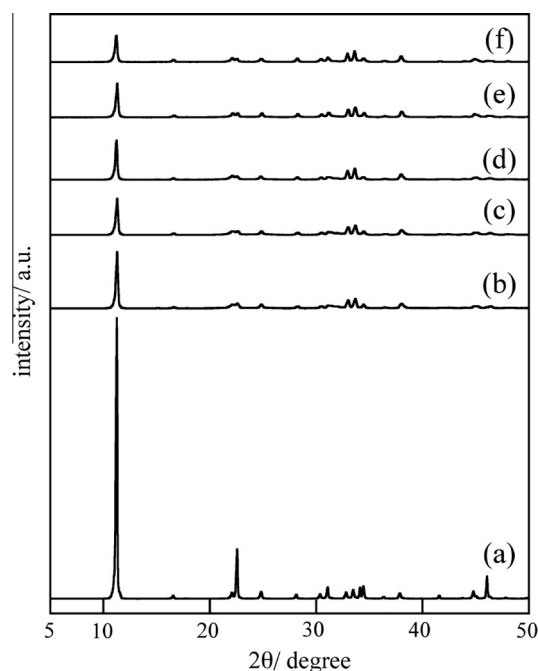


**Fig. 1.** XRD patterns of the products formed at different atomic ratios $X_{Ni}$. Atomic ratio $X_{Ni}$: (a) 0, (b) 0.01, (c) 0.025, (d) 0.05, (e) 0.075 and (f) 0.10.