Hydrogen Permeation Behavior of Scratch on Zn Coated Steel during 1 000 Hours Wet and Dry Corrosion Test

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In this study, hydrogen permeation current from scratch formed on Zn coated steel during 1 000 h wet and dry cyclic corrosion test was investigated. The scratch was fabricated by focused pulsed Nd: YAG laser irradiation. The obtained hydrogen permeation current has peaks during wetting, and the peak currents decrease with time. Formation of Zn corrosion products prevent hydrogen entry. After the test, there are Zn oxide (ZnO) on the substrate steel, hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) around the scratch boundary and simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2$) on Zn coated region. It is suggested that pH change with distance from the formed scratch is the reason for the composition of Zn corrosion products change with location.

KEY WORDS: electrochemical permeated hydrogen detection; Zn coated steel; scratch; laser fabrication; simulated atmospheric corrosion environment.

1. Introduction

Strength of steels has been increasing and using high strength steels enable us to reduce thickness. However, it is important issue that increasing strength of steels usually leads to high susceptibility of hydrogen embrittlement.^{1–5)} Hydrogen embrittlement is a phenomenon in which the ductility of steel decreases due to hydrogen absorbed in steel. In order to use high-strength steels safely, hydrogen embrittlement has been widely studied. Hydrogen entry occurs during welding, pickling, electroplating and corroding. Corrosion in atmospheric environments plays an important role in hydrogen embrittlement in actual environments.

In order to prevent corrosion, Zn coated steels are widely used. Shinohara reported that the average corrosion rate of Zn was about 1/26 that of Fe.⁶⁾ Zn coated steels are inexpensive and have excellent protective film function and sacrificial protection properties, therefore, it is widely used in automotive and building materials.

The protective film function of Zn coating is achieved by formation of stable Zn oxide films formed on the materials. Zn dissolved zinc ions ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$), which cause a hydrolysis reaction to form zinc hydroxide ($\text{Zn}^{2+} + \text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + 2\text{H}^+$). Zinc hydroxide ($\text{Zn}(\text{OH})_2$) dehydrates to Zinc oxide (ZnO) when humidity is low. These oxides form the protective layers. The protective layers are dense and have good adhesiveness and high corrosion resistance.

It is known that Zn compounds containing environmental anions such as SO_4^{2-} and Cl^- are formed by long-term exposure in an atmospheric corrosive environment.^{7–10)}

Figure 1 is a schematic diagram showing the change of the corrosion products with time during exposing to the atmosphere. Under atmospheric conditions, hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) is formed. Simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2$) is formed in the marine atmosphere and $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ is formed in the rural atmosphere after long exposure periods. It is known that Zn corrosion products in atmospheric corrosion consist of Zinc hydroxide, Zinc oxide, hydrozinc-

Fig. 1. Changes of Zn corrosion product with time.^{7–10)}

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ite, Simonkolleite and so on.

The sacrificial protection properties is an action in which Zn dissolves preferentially over steel. When a scratch forms on Zn coated steel, the sacrificial protection reaction occur. Zn around the scratch is dissolved preferentially over the substrate steel (anodic reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$). Hydrogen generation reaction (cathodic reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) increases at exposed substrate steel surface due to the cathodic polarization. Therefore, hydrogen entry also increases, which also increases the risk of hydrogen embrittlement. Tada *et al.* reported hydrogen permeation current during 150 h wet and dry cycle test.¹¹⁾ Hydrogen permeation behavior of Zn coated steel during long term wet and dry corrosion test is still not fully elucidated. In this paper, the micro-electrochemical hydrogen detection cell was introduced to investigate hydrogen permeation behavior of scratch formed on Zn coated steel during 1 000 h wet and dry cycle corrosion.

2. Experimental

2.1. Specimen

Zn coated steel sheet ($15 \times 30 \times 0.5$ mm) was used as specimen. One side of the specimen (hydrogen detection side) was ground with SiC abrasive paper up to #1500 grit size in order to remove precoated Zn layer, and the surface was plated electrochemically with Ni in $0.312 \text{ kmol m}^{-3}$ $\text{NiSO}_4/0.781 \text{ kmol m}^{-3}$ H_3BO_3 solution at 4 mA cm^{-2} for 720 s. The thickness of Ni plated layer was $1 \mu\text{m}$. The other side of the specimen (the hydrogen entry side of the specimen) was irradiated by pulsed Nd: YAG laser (wavelength 532 nm, pulse duration 8 ns, pulse frequency 10 s^{-1} , and power 20 mW at the front of the lens) in the highly purified water to form the scratches. The shape of scratch was $1\,440 \times 1\,440 \mu\text{m}^2$. Finally, the specimen were cleaned, in highly purified water and ethanol using ultrasonic baths for 300 s.

2.2. Wet and Dry Corrosion Test

The schematic representations of (a) top view and (b) cross-section of micro-electrochemical hydrogen detection cell were shown in Fig. 2. Pt wires were used as the counter electrode (C.E.) and the reference electrode (R.E.) in the hydrogen detection cell (bottom in Fig. 2 (b)).

Solution of 1 kmol m^{-3} NaOH was filled in the hydrogen detection cell and the specimen of the hydrogen detection

(the nickel plated) side was placed on the cell. It was ensured that there were no bubbles in the cell. After the specimen was set the cell, the cell was placed in humidity and temperature control chamber. To measure the hydrogen which was generated by the corrosion and permeating through the specimen, hydrogen detection side of the specimen was polarized at -30 mV vs. Pt during the wet and dry corrosion tests. This applied anodic potential was sufficient to ionize any hydrogen reaching at the surface after permeating through the specimen. After the current of the hydrogen detection cell reached a sufficiently low and steady value under 10 nA (about 86.4 ks after the potential was applied), $10 \mu\text{L}$ of 0.1 kmol m^{-3} NaCl solution was dropped on the center of the scratch. After dropping, wet and dry cyclic corrosion test and the measurement of hydrogen permeation current was started. In wet and dry cyclic corrosion test, one cycle was divided into four processes, 1 h wetting process (maintained at 90%RH), 1 h transition process, 3 h drying process (33%RH) and 1 h transition process. The temperature was controlled at 298 K. The total wet and dry corrosion period was 1 000 h.

2.3. Surface Observation and Analysis

The surface of the specimen after the test was observed with an optical microscope and a scanning electron microscope (SEM). An energy dispersive X-ray spectroscopy (EDS), a Raman spectroscopy, a X-ray photoelectron spectroscopy (XPS) and an Auger electron spectroscopy (AES) were used to analyze the surface of specimen.

3. Results and Discussion

3.1. Hydrogen Permeation Current during 1 000 h Wet and Dry Corrosion Test

Figure 3 shows the hydrogen permeation current during 1 000 h wet and dry corrosion test. The largest peak value of 55 nA is observed at first cycle. The peak currents decrease with time. From Fig. 4, current peaks are observed at wetting period. The peak during (c) 282–354 h is 10–20 nA, which are less than half of the initial peak at the first cycle in (b). Almost no peaks are observed during (d) 924–996 h. Igarash *et al.* reported that during about 60 h wet and dry cycle, hydrogen permeation current of Zn and Zn–Al coated steels were decrease with cycle number. They proposed that corrosion products inhibited hydrogen entry.¹²⁾

Fig. 2. Schematic representation of the electrochemical cell and specimen for hydrogen permeation test. (a) top view and (b) cross section.

Fig. 3. Changes in hydrogen permeation current during 1 000 h wet and dry corrosion test.

Fig. 4. Changes in (a) humidity and temperature and changes in hydrogen permeation current during 1 000 h during (b) 0–72 h, (c) 282–354 h and (d) 924–996 h.

3.2. Surface Observation and Analysis after Wet and Dry Corrosion Test

In order to clarify effect of corrosion products, surface observation and analysis were carried out. **Figure 5** shows optical microscope images of the specimen surface (a)

before wet and dry corrosion test and (b) after the test, and (c) the tested specimen after ultrasonic cleaning. The dark square in the center (Fig. 5(a)) is the formed scratch. After the wet and dry corrosion test (Fig. 5(b)), there are white corrosion products around the scratch. After ultrasonic

cleaning of the specimen (Fig. 5(c)), some of the corrosion products still remain on the scratch. From this result, formed corrosion products have good adhesiveness to the substrate.

Figure 6 shows (a) SEM image and (b)–(f) elemental

mapping at the scratch after ultrasonic cleaning of the specimen. From Fig. 6(b), Fe which is considered to be substrate steel is detected. From Figs. 6(c), 6(d) and 6(e), Zn, Cl and O are detected around the scratch. It is suggested that the

Fig. 5. Optical microscope images of the specimen surface (a) before and (b) after the wet and dry corrosion test, and (c) the tested specimen after ultrasonic cleaning.

Fig. 6. (a) SEM image at scratch on specimen after wet and dry corrosion test. Elemental mapping by EDS, (b) Fe, (c) Zn, (d) Cl and (e) O. (f) Superposition of four elemental mappings. (Online version in color.)

Fig. 7. (a) Superposition of elemental mapping same as Fig. 6(f) and (b) Raman spectra of the specimen surface. (Online version in color.)

corrosion products are made of Zn, Cl and O. Figure 6(f) is the superposition of these four elemental mappings. From Fig. 6(f), there are high Fe intensity regions (blue) in the center at scratch, and there are high O intensity regions (red) around it. High Cl intensity regions (green) are observed around the high O intensity regions (red). From EDS analysis, Zn corrosion products may change with distance from the formed scratch.

To investigate the difference of Zn corrosion products at high O and Cl intensity region, Raman spectroscopy was carried out. **Figure 7** shows (a) the superposition of elemental mapping shown in Fig. 6(f), and (b) Raman spectra of the specimen surface. In Fig. 7(b), there are peaks at $1\,060\text{ cm}^{-1}$ and 390 cm^{-1} . The peak of $1\,060\text{ cm}^{-1}$ is corresponding to hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) and the peak at 390 cm^{-1} is corresponding to simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$).^{7-9,13} In the high O intensity regions (red) ①, ②, ③, ⑥, ⑦, ⑪, ⑫ and ⑬ in Fig. 7(a), the hydrozincite peak at $1\,060\text{ cm}^{-1}$ is observed. In the high Cl intensity regions (green) ④, ⑤, ⑧, ⑨ and ⑩ in Fig. 7(a), there is the simonkolleite peak at 390 cm^{-1} . In addition, the hydrozincite peak at $1\,060\text{ cm}^{-1}$ is hardly observed. These results indicate that hydrozincite and simonkolleite exist in the high O intensity regions, while only simonkolleite exists in the high Cl intensity regions.

For better understanding chemical composition of these Zn corrosion products, the specimen after the wet and dry corrosion test was investigated by XPS. **Figure 8** shows the XPS wide spectrum of the specimen after the test. The peaks are assigned to Zn, O, Fe, C and Cl.¹⁴ These elements may be derived from the Zn corrosion products, substrate steel or contaminated carbon. **Figure 9** shows the XPS narrow spectra of (a) O 1s, (b) Zn 2p_{3/2} and (c) C 1s at the scratch center and Zn coating region. In Figs. 9(a) and 9(b), the obtained spectra may be simonkolleite or hydrozincite.¹⁵ C 1s (Fig. 9(c)) spectra has two peaks; one is carbonates (CO_3) and the other is contamination carbon (C-C).¹⁵ From C 1s spectra, existence of hydorzincite in the corrosion products is confirmed.

Islam *et al.* reported that Zn^{2+} in the solution easily forms

thin Zn protective layer on the steel surface after immersion test.^{16,17} It is seemed that a thin Zn protective layer existed on the scratch. AES surface analysis which can measure the thin surface layer was carried out. **Figure 10** shows (a) SEM image and (b) AES spectra. The peaks are assigned to O (503 eV), Fe (599, 652, 704 eV) and Zn (990 eV).¹⁸ The O and Zn peaks are observed at each position. The Fe peaks are only observed at ④, the scratch center. The Zn peak at ④ is analyzed in detail. **Figure 11** shows the standard spectra of (a) ZnO and (b) Zn. Figure 11(c) shows the obtained spectrum with the convolution of the ZnO and Zn standard spectrum by least-squares method and the residual spectrum. The ZnO and Zn standard spectrum are magnified using magnification percentage in **Table 1**. Tsutsumi *et al.* reported that since the Auger transition involves outer shell electrons, the shape of the Auger peak reflects the chemical state of the specimen.¹⁹⁻²² It is possible to analyze and quantify the chemical state by comparing the obtained spectrum with the standard spectrum. The calculated existence ratio

Fig. 8. XPS wide spectrum at scratch center of the specimen after wet and dry corrosion test.

Fig. 9. XPS narrow spectra of (a) O 1s, (b) Zn 2p_{3/2}, (c) C 1s at scratch center and Zn coating region.

Fig. 10. (a) SEM image with analysis points and (b) AES spectra of the specimen surface. (Online version in color.)

Fig. 11. AES spectra of Zn from 960 to 1040 eV. The standard spectra of reference materials, (a) ZnO and (b) Zn. (c) Obtained spectrum with (d) Convolution curve and Residual curve.

from the magnification is 98.6% for ZnO and 1.4% for Zn. This result suggests that ZnO existing on the steel substrate inhibits hydrogen entry.

3.3. Changes in Zn Corrosion Products with Deposition Position

From surface analysis results, Zn corrosion products change with distance from the formed scratch. Manhabosco *et al.* reported the difference of Zn corrosion products deposited on low-angle cross section of Zn coated steel.²³⁾ Hydrozincite are deposited on the coating/steel interface and simonkolleite are deposited on the outer Zn coating region. Okada *et al.* reported pH change with Fe/Zn interface by numerical analysis.²⁴⁾ In this section, the condition for forming simonkolleite and hydrozincite with pH are calculated.

In the beginning, CO₂ dissolves in water and dissociate. At 298 K, the equilibrium constant is²⁵⁾

Table 1. Magnification factor of standard materials spectra and existence ratio of Zn and Zn²⁺.

Material	Magnification	Existence ratio
Zn	0.002	1.4% (Zn)
ZnO	0.284	98.6% (Zn ²⁺)

$$K_1 = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}} = 3.39 \times 10^{-2} \quad \dots\dots\dots (1)$$

$$\log K_1 = -1.47$$

$$K_2 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} = 4.45 \times 10^{-7} \quad \dots\dots\dots (2)$$

$$\log K_2 = -6.35$$

$$K_3 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11} \quad \dots\dots\dots (3)$$

$$\log K_3 = -10.3$$

From Eqs. (1) to (3), total K_1 , K_2 and K_3 is

$$K = \frac{[\text{CO}_3^{2-}][\text{H}^+]^2}{P_{\text{CO}_2}} \quad \dots\dots\dots (4)$$

$$\log K = \log K_1 + \log K_2 + \log K_3 = -18.2$$

[CO₃²⁻] is

$$\log[\text{CO}_3^{2-}] = \log K + \log P_{\text{CO}_2} - 2 \log[\text{H}^+]$$

Using $P_{\text{CO}_2} = 10^{-3.5}$ ²⁵⁾ and from (4)

$$\begin{aligned} \log[\text{CO}_3^{2-}] &= -18.2 - 3.5 + 2\text{pH} \\ &= -21.7 + 2\text{pH} \quad \dots\dots\dots (5) \end{aligned}$$

From the ionic product of water

$$\begin{aligned} \text{H}_2\text{O} &= \text{H}^+ + \text{OH}^- \\ \log K_w &= \log[\text{H}^+][\text{OH}^-] = -14.0 \quad \dots\dots\dots (6) \\ \log[\text{OH}^-] &= \text{pH} - 14.0 \end{aligned}$$

Hydrozincite is represented as $\text{Zn}(\text{OH})_{1.2}(\text{CO}_3)_{0.4}$. Hydrozincite precipitation is ^{26,27)}

$$\begin{aligned} \text{Zn}(\text{OH})_{1.2}(\text{CO}_3)_{0.4}(\text{s}) &\rightleftharpoons \text{Zn}^{2+} + 1.2\text{OH}^- + 0.4\text{CO}_3^{2-} \\ K_{\text{s,Zn}(\text{OH})_{1.2}(\text{CO}_3)_{0.4}} &= [\text{Zn}^{2+}][\text{OH}^-]^{1.2}[\text{CO}_3^{2-}]^{0.4} \quad \dots (7) \\ &= 6.31 \times 10^{-15} \\ \log K_{\text{s,Zn}(\text{OH})_{1.2}(\text{CO}_3)_{0.4}} &= -14.2 \end{aligned}$$

From (5), (6) and (7), $[\text{Zn}^{2+}]$ is

$$\begin{aligned} \log[\text{Zn}^{2+}] &= \log K_{\text{s,Zn}(\text{OH})_{1.2}(\text{CO}_3)_{0.4}} - \log[\text{OH}^-]^{1.2} - \log[\text{CO}_3^{2-}]^{0.4} \\ &= -14.2 - 1.2(\text{pH} - 14) - 0.4(-21.7 + 2\text{pH}) \\ &= -2\text{pH} + 11.3 \quad \dots\dots\dots (8) \end{aligned}$$

Consider simonkolleite: At 25° C in air and 90% relative humidity, water vapor equilibrates with water containing $[\text{Cl}^-] = 3.5$ (mol/g).²⁸⁾ Assume that the density $\rho = 1.16$ (g/cm³) of the aqueous NaCl solution is²⁹⁾

$$\begin{aligned} [\text{Cl}^-] &= 3.5(\text{mol/g}) \\ &= \frac{3.5}{(1000 + 3.5 \times 58.5) \div 1.16} (\text{mol/cm}^3) \quad \dots\dots (9) \\ &= 10^{0.528} (\text{mol/dm}^3) \end{aligned}$$

The solubility product of simonkolleite is^{24,30)}

$$\begin{aligned} \text{Zn}(\text{OH})_{1.6}\text{Cl}_{0.4}(\text{s}) &\rightleftharpoons \text{Zn}^{2+} + 0.4\text{Cl}^- + 1.6\text{OH}^- \\ K_{\text{s,Zn}(\text{OH})_{1.6}\text{Cl}_{0.4}} &= [\text{Zn}^{2+}][\text{OH}^-]^{1.6}[\text{Cl}^-]^{0.4} \quad \dots (10) \\ \log K_{\text{s,Zn}(\text{OH})_{1.6}\text{Cl}_{0.4}} &= -14.95 \end{aligned}$$

From (9) and (10), $[\text{Zn}^{2+}]$ is:

$$\begin{aligned} \log[\text{Zn}^{2+}] &= \log K_{\text{s,Zn}(\text{OH})_{1.6}\text{Cl}_{0.4}} - \log[\text{Cl}^-]^{0.4} - \log[\text{OH}^-]^{1.6} \\ &= -14.95 - 0.4 \times 0.528 - 1.6(\text{pH} - 14) \\ &= -1.6\text{pH} + 7.24 \quad \dots\dots\dots (11) \end{aligned}$$

From Eqs. (8) and (11), pH dependence of simonkolleite and hydrozincite is different. **Figure 12** shows pH dependence of Zn^{2+} concentration with simonkolleite and hydrozincite. The pH at the intersection of simonkolleite and hydrozincite is $\text{pH} = 10.15$. Hydrozincite precipitates preferentially when $\text{pH} > 10.15$, and simonkolleite precipitates preferentially when $\text{pH} < 10.15$. Ogle *et al.* suggest that the pH going from steel to Zn falls from 11.5 to nearly 8.0 in simulated cut edge corrosion tests.³¹⁾ The calculation results shown in Fig. 12 and the results of this experiment agree with the results of Ogle *et al.*

According to the calculations, the deposition mechanism of Zn corrosion products changed with distance from formed scratch is shown in **Fig. 13**. An anodic reaction (dissolution of Zn) occurs on Zn coating. At the substrate steel exposed

Fig. 12. pH dependence of Zn^{2+} concentration with simonkolleite and hydrozincite. The concentration of NaCl was assumed from the equilibrium with water vapor in RH 90%.

Fig. 13. Schematic drawing of precipitation of simonkolleite and hydrozincite around the scratch on Zn coated steel.

to the solution, a cathode reaction (oxygen reduction reaction) occurs. The region have a high pH due to the oxygen reduction reaction. In the high pH region, CO_3^{2-} is absorbed into the droplet and carbonate ions diffuse from the center of the scratch. As a result, hydrozincite deposits around the scratch, and simonkolleite deposits on the Zn coated region.

In this study, hydrozincite was observed on the surface of the specimen after the test (Fig. 7). This means that there were pH > 10.15 region in the solution layer. Since the amount of hydrogen generation decreases at high pH, the amount of hydrogen permeation could be also decreased. It is also considered that the corrosion product covering the substrate steel reduced the hydrogen generation reaction (cathode reaction) region and also reduced the amount of hydrogen permeation.

4. Conclusions

A hydrogen permeation behavior of scratch on Zn coated steel during 1 000 h wet and dry cycle corrosion was clarified. After 400 h, hydrogen permeation peaks became several nA. Protective layer of Zn corrosion products prevent hydrogen permeation. There are Zn oxide (ZnO) on the substrate steel (at the formed scratch), hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) around the scratch boundary and simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2$) on Zn coated region. The pH dependence of Zn^{2+} concentration with hydrozincite and simonkolleite was calculated. The calculated results suggested that hydrozincite deposit at high pH region (Steel/Zn interface) and simonkolleite deposit at low pH region (Zn coating). The presence of hydrozincite means that some parts of solution layer formed during each cycle was pH > 10.15. This high pH in the solution layer may reduce both the amount of hydrogen generation and permeation.

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