

Effect of Surface Conditions and Specimen Composition on Hydrogen Permeation Behavior of Coated and Uncoated Steels during Wet and Dry Corrosion at a Constant Dew Point

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A wet and dry corrosion test with a constant dew point was applied to investigate the effects of scratches and specimen composition on the hydrogen permeation behavior of Zn and 55 mass% Al–Zn coated steels as well as of uncoated steel. There was an etched size controlled scratch formed on specimens with a laser machining technique. The hydrogen permeation current was observed to be independent of the specimen composition and the area of the formed scratches, the corrosion products were observed after the tests. The hydrogen permeation current of the steels with the formed scratches decreased with number of cycles of the wet and dry tests. Except in the first cycle there were no significant changes in the current with cycle number on steels without formed scratches. It was suggested that the composition, scratch, and corrosion products play an important role in the hydrogen permeation behavior during wet and dry corrosion.

KEY WORDS: coated steel; hydrogen; constant dew point; wet and dry corrosion; laser machining; scratch; electrochemical hydrogen detection.

1. Introduction

With the recent demands for reducing the consumption of natural resources and energy, high strength steels are widely used. It is, however, well known that increasing the strength of steels leads to increasing susceptibility to hydrogen embrittlement.^{1,2)} To ensure reliability and safety in the practical use of high strength steels, a reduction in the susceptibility to hydrogen embrittlement has become an important issue and hydrogen embrittlement has attracted much attention recently.^{3–13)} Koyama *et al.* investigated the effect of hydrogen embrittlement of a Fe–18Mn–0.6C austenitic steel (wt.%) by tensile tests with hydrogen charging at various current densities. They reported that the work hardening behavior was not affected by the hydrogen charging.⁴⁾ Nagao *et al.* reported the hydrogen embrittlement effects of nano-sized (Ti, Mo)C precipitates on the resistance of high-strength tempered lath martensitic steel.¹⁰⁾

For the practical use of steels including high strength steels, atmospheric corrosion plays an important role in the hydrogen generation. Some studies have focused on the hydrogen generated by atmospheric corrosion inducing the hydrogen embrittlement.^{14–20)} Tsuru *et al.* reported the hydrogen entry process when the steel surface is covered by passive films and reported the hydrogen permeation through steels during wet and dry corrosion cycles.¹⁵⁾

With Zn and Zn alloys coatings are widely used to increase the corrosion resistance of steels^{21–23)} because the atmospheric corrosion rate of Zn is more than twenty times smaller than that of steels.²⁴⁾ To elucidate the hydrogen permeability of the coatings, the hydrogen permeation characteristics of steel with Zn and Zn–Cr coatings have been investigated.²⁵⁾ Protective coatings are liable to be scratched during use, and steel is exposed to the environment resulting in the formation of galvanic couples. Such galvanic corrosion is more serious than the corrosion of the Zn coating or steel substrate alone, and high hydrogen entry efficiency (the ratio of hydrogen permeation current/hydrogen generation current) has been reported at scratched areas of Zn coated steels.²⁶⁾ This makes it important to investigate effects of scratches formed on the steels on the hydrogen permeation behavior during atmospheric corrosion.

The purposes of this study are to investigate the effects of composition and corrosion products on the hydrogen permeation behavior of Zn and Zn alloy coated steels, and uncoated steels during wet and dry corrosion tests. A contamination free and size controlled scratch formation technique is essential to conduct these experiments, and a laser machining technique^{27,28)} was applied to form the scratches on the steels. Muto *et al.* reported that the dew point of outdoor air is approximately constant and that the relative humidity (RH) depends on the air temperature, and introduced a wet and dry corrosion test with constant dew point.²⁹⁾ The wet and dry corrosion test with constant dew point can simulate the atmospheric corrosion behavior of

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steels, and it was applied in this study.

2. Experimental

2.1. Specimens

Zn and 55 mass% Al–Zn coated steel sheets (15 mm wide, 30 mm long, and 0.5 mm thick), and steel sheets (15 mm wide, 30 mm long, and 0.7 mm thick) were used as specimens. Chemical composition of the steel used in the specimens (mass %) is shown in **Table 1**. To remove pre-formed layers for the hydrogen detection, one side of the specimens was mechanically ground under running water by SiC paper up to #1500. Specimens were cleaned for 300 s each, in highly purified water and ethanol ultrasonic baths, and following this the side for the hydrogen detection was plated electrochemically with nickel in a $0.312 \text{ kmol m}^{-3}$ NiSO_4 / $0.781 \text{ kmol m}^{-3}$ H_3BO_3 solution at 4 mA cm^{-2} for 720 s.

Following the treatment detailed directly above, the other side of the specimen, the hydrogen entry side of the specimens was irradiated with a focused Nd-YAG laser beam (wave length 532 nm, frequency 10 s^{-1} , pulse width 8 ns, and power 20 mW at the front of the lens) in the highly purified water to form the scratches. The areas of scratches were

Table 1. Chemical composition of the steel used in the specimens (mass %).

C	Si	Mn	P	S	Fe
0.018	0.01	0.18	0.017	0.007	bal.

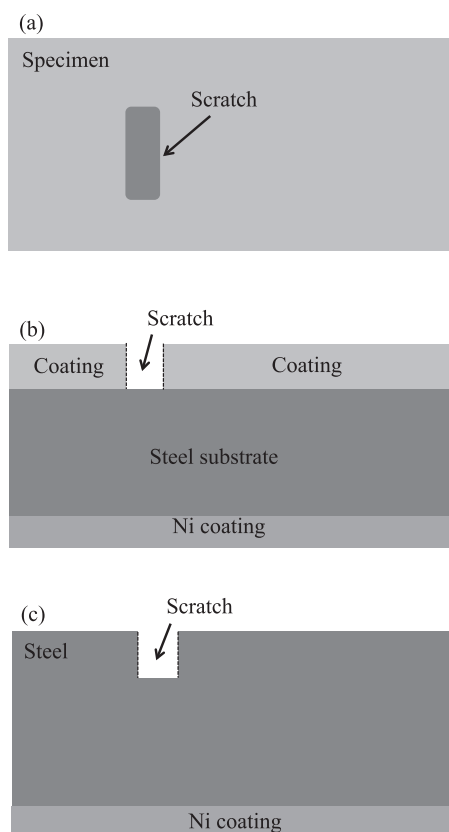


Fig. 1. Schematic representation of specimens with formed scratch, (a) top view, (b) cross section of coated steel, and (c) cross section of uncoated steel.

controlled to be 0.2 mm^2 . **Figure 1** shows a schematic representation of specimens with formed scratch, (a) top view, (b) cross sectional view of the coated steel, and (c) cross sectional view of the uncoated steel. Hereafter, Zn coated steel, 55 mass% Al–Zn coated steel and the uncoated steel with formed scratches are termed S–Zn, S–ZnAl and S–Fe respectively. Uncoated steel specimens without scratches (NS–Fe) were also used in the tests.

2.2. Wet and Dry Corrosion Tests

Figure 2 is a schematic outline of the (a) top and (b) cross section of the corrosion and hydrogen detection cell with a specimen. The hydrogen detection side, the nickel plated side, was placed on (facing) the hydrogen detection cell (bottom in Fig. 2(b)), and then 0.23 cm^3 of 1 kmol m^{-3} NaOH solution was added to the cell. After the hydrogen detection cell was filled in NaOH solution, the cell was placed in a RH and temperature controlled chamber. **Figure 3** shows a schematic outline of the equipment for the wet and dry corrosion tests. Platinum wires were used as the counter, CE, and reference electrodes, RE, for the hydrogen detection cell. To measure the hydrogen generated by the corrosion and permeating through the specimens by electrochemical processes, specimens were polarized at -30 mV vs. Pt during the tests. At this applied potential, the hydrogen atoms reaching the detection side were oxidized to hydrogen ions. After the current of the hydrogen detection cell reached a sufficiently low and steady value (about 86.4 ks after the potential was applied), $10 \mu\text{L}$ of 0.1 kmol m^{-3} NaCl solution was placed on the center of the scratch on

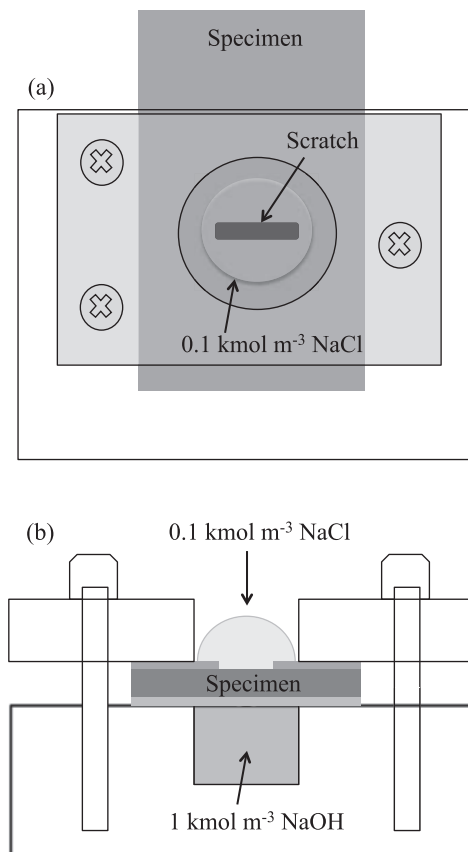
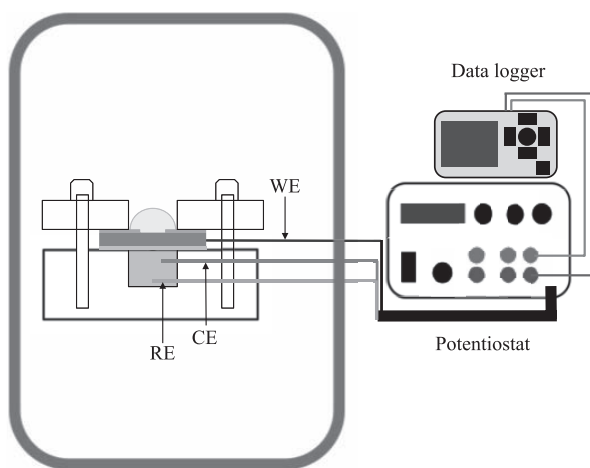
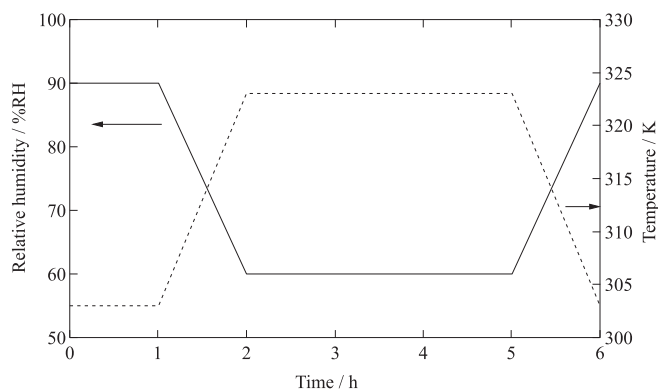


Fig. 2. Schematic outline of the corrosion and hydrogen permeation cell with a specimen, (a) top and (b) cross section views.



RH and temperature controlled chamber

Fig. 3. Schematic outline of the equipment for the wet and dry corrosion tests.

Fig. 4. Schematic representation of the changes in relative humidity, RH, and temperature in the chamber during one cycle of the wet and dry corrosion tests.

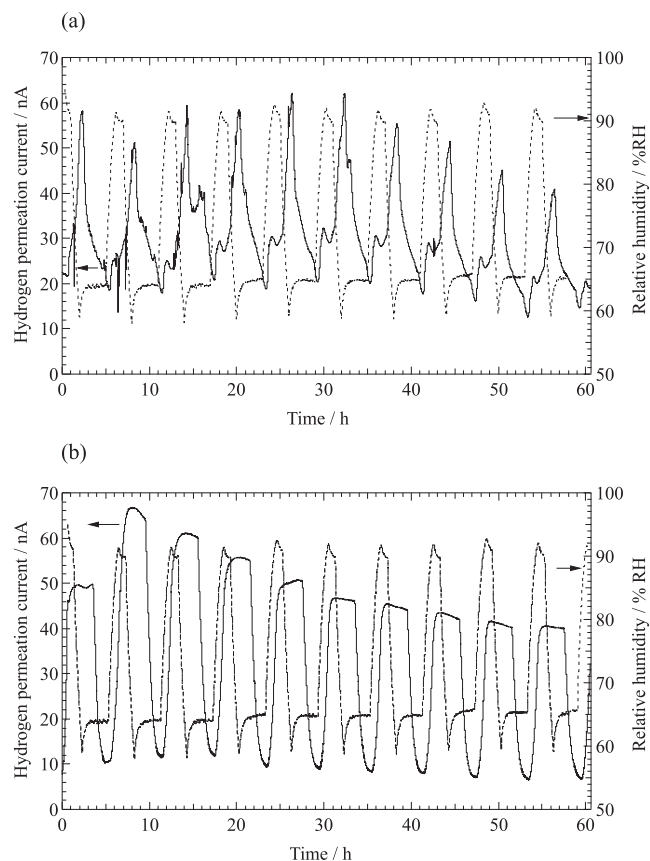
the specimens to initiate the corrosion. After placement of the solution, the hydrogen permeation current, RH, and temperature were recorded. **Figure 4** shows a schematic representation of the changes in RH and temperature in the chamber during a cycle (6 h) of the wet and dry corrosion tests. After the RH and temperature in the chamber reached the initial values (90%RH and 303 K), 10 wet (303 K) and dry (323 K) cycles were carried out. The RH change induced the wet and dry cycles at the area where NaCl solution was initially introduced. Before and after the wet and dry corrosion tests, specimen surfaces were observed by an optical microscope and scanning electron microscope with energy dispersive spectroscopy (SEM-EDS).

3. Results

3.1. Hydrogen Permeation Behavior of Coated Steels

Figure 5 shows the changes in hydrogen permeation current and RH of (a) S-Zn and (b) S-ZnAl specimens during the wet and dry corrosion tests. There are periodic changes of the hydrogen permeation currents following the cyclic changes of RH with both specimens. The shape of the hydrogen permeation currents depends on the composition of the coating.

Figure 6 shows optical microscope images of the speci-


Fig. 5. Changes in hydrogen permeation current and RH of (a) S-Zn and (b) S-ZnAl during the wet and dry corrosion tests.

men surfaces before the corrosion tests (a) for S-Zn and (b) for S-ZnAl, and after the wet and dry corrosion tests (c) for S-Zn and (d) for S-ZnAl. The dark areas in the images before the corrosion tests are the scratch areas formed by laser machining and the surrounding lighter colored parts are coated areas. In Figs. 6(c) and 6(d) after the wet and dry corrosion tests there are white corrosion products around the scratched areas in the two specimens. Ohtsuka reported that zinc corrosion products during atmospheric corrosion were zinc oxide, zinc hydroxide, simonkolleite, hydro-zincite, and zinc hydroxysulfate.³⁰⁾ From EDS analysis of the corrosion products in Figs. 6(c) and 6(d), it was suggested that the white corrosion products were zinc oxide or zinc hydroxide.

Figure 7 shows an enlargement of the current changes in Fig. 5 at the 5th cycle for (a) the S-Zn and (b) the S-ZnAl specimens. Plots of the temperature during the cycle of the tests are added in the figures. The changes of RH are synchronized with those of the temperature, while the changes in the hydrogen permeation current are not synchronized with the changes in temperature and RH. For S-Zn (Fig. 7(a)), the hydrogen permeation current shows about 30 nA at the initial stage (between 24.2 and 25.2 h) of the cycle, then it increases with decreasing RH, and shows a maximum value of about 62 nA at around 26.4 h. After the maximum, the current decreases, first steeply and then more slowly while RH remains at 64%. Then as the RH increases, the current decreases further and reaches a minimum value of about 20 nA at around 29.4 h and the RH value of about 78%, following this it increases to reach a nearly constant value of about 34 nA with further increases in RH.

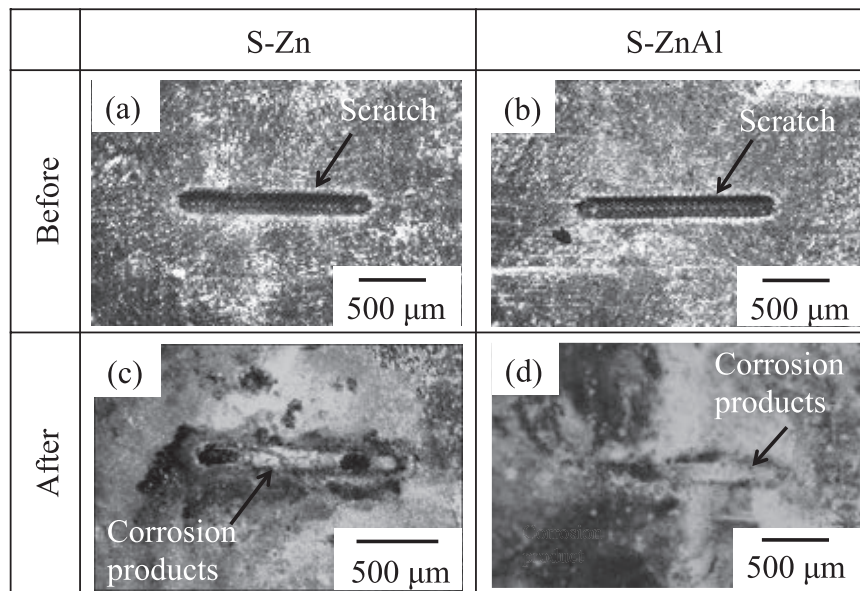


Fig. 6. Optical microscope images of the specimen surfaces before the wet and dry corrosion tests (a) for S-Zn and (b) for S-ZnAl, and after the corrosion tests (c) for S-Zn and (d) for S-ZnAl.

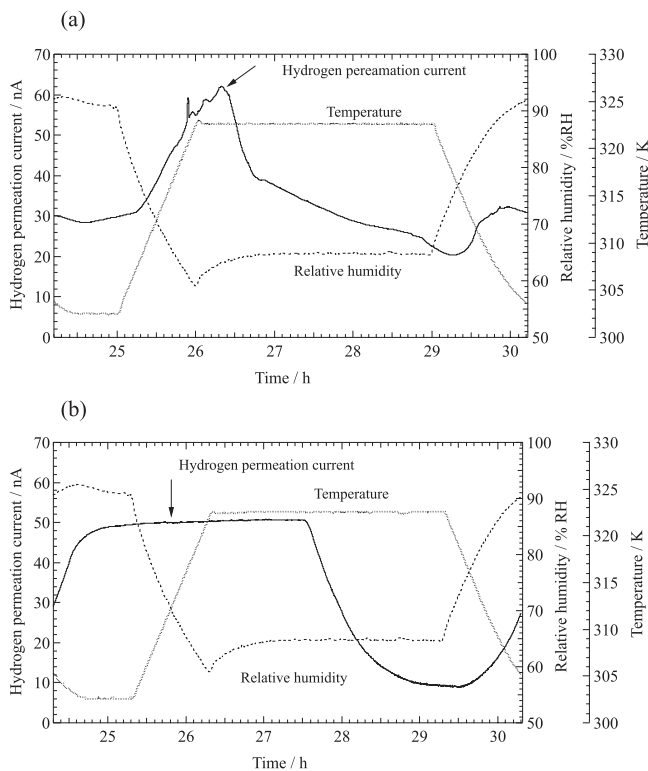


Fig. 7. Enlargement of the current changes in Fig. 5 at the 5th cycle for (a) S-Zn and (b) S-ZnAl. The changes in temperature during the cycle for the tests are plotted in the figures.

For S-ZnAl (Fig. 7(b)), the hydrogen permeation current increases initially (between 24.3 and 24.8 h) and reaches a steady value of about 50 nA at 90%RH, and it remains constant for some time (until around 27.6 h) after the RH has decreased to 64%RH. The current then decreases to about 10 nA around 29.3 h while RH remains at about 64%, then with increasing RH the current increases to about 28 nA. These results suggest that the composition of the coating plays an important role in the hydrogen permeation behavior during wet and dry corrosion.

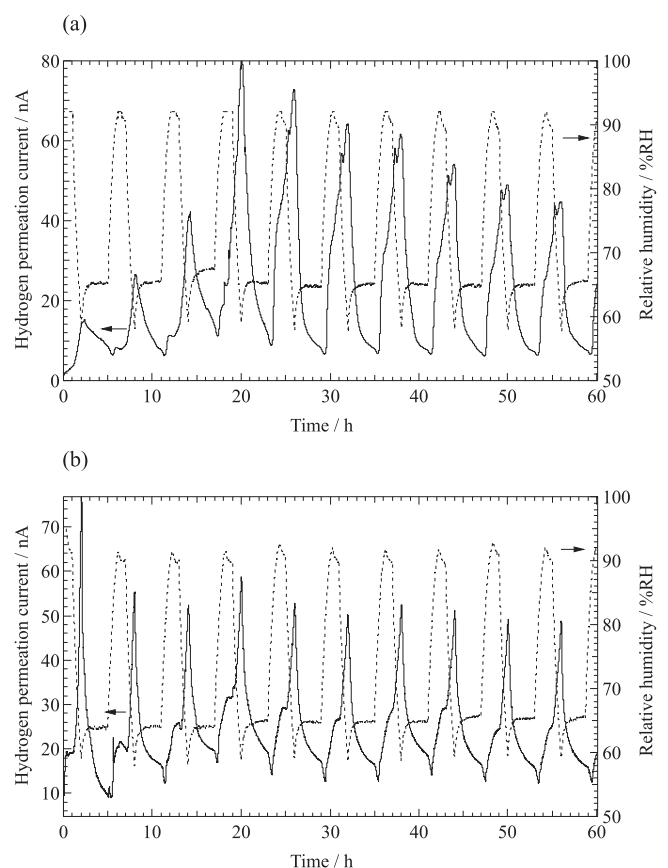


Fig. 8. Changes in the hydrogen permeation currents and RH of (a) S-Fe and (b) NS-Fe during the wet and dry corrosion tests.

3.2. Hydrogen Permeation Behavior of Steels

Figure 8 shows changes in the hydrogen permeation currents and RH of (a) S-Fe and (b) NS-Fe during the wet and dry corrosion tests. As in Fig. 5, there are periodic changes of the hydrogen permeation currents following the cyclic changes of RH with both specimens.

Figure 9 shows optical microscope images of the speci-

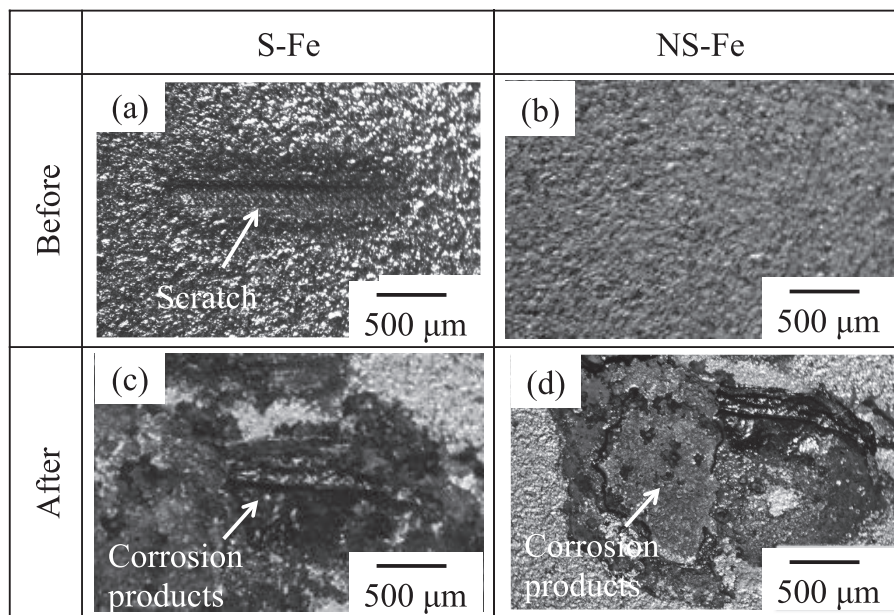


Fig. 9. Optical microscope images of the specimen surfaces before the corrosion tests (a) for S-Fe and (b) for NS-Fe, and after the corrosion tests (c) for S-Fe and (d) for NS-Fe.

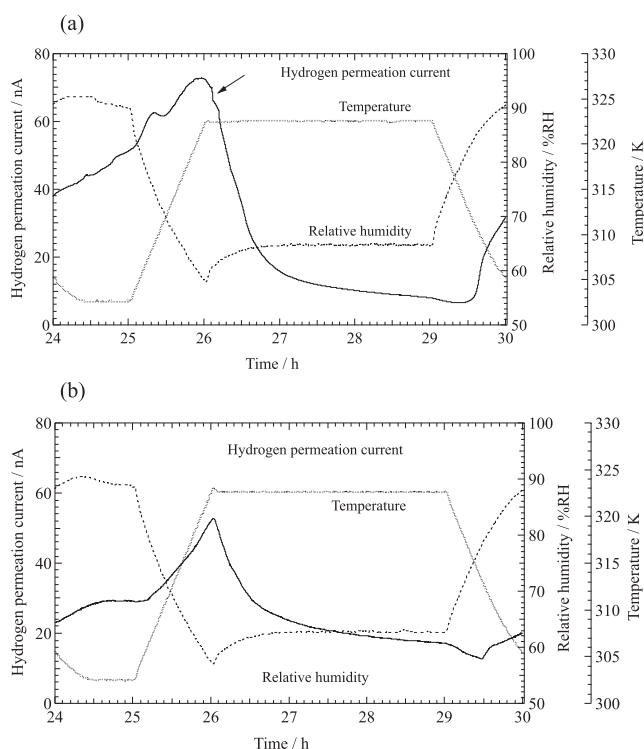


Fig. 10. Enlargement of the current changes in Fig. 8 at the 5th cycle for (a) S-Fe and (b) NS-Fe. The changes in temperature during the cycle for the tests are plotted in the figures.

men surfaces before the corrosion tests (a) for S-Fe and (b) for NS-Fe, and after the corrosion tests (c) for S-Fe and (d) for NS-Fe. After the wet and dry corrosion tests (Fig. 8), there are red corrosion products at where the NaCl solution was placed on both specimens, and no difference of amount of corrosion products on S-Fe and NS-Fe after the tests was observed.

Figure 10 shows an enlargement of the current changes in Fig. 8 at the 5th cycle (a) for S-Fe and (b) for NS-Fe.

The changes in temperature during the cycle are also plotted in the figures. For S-Fe (Fig. 10(a)), the current increases to reach a maximum value of about 72 nA at around 26 h, then it decreases sharply and after around 26.8 h gently while RH remains constant at 64%. Thereafter, the current increases again with increasing RH. For the NS-Fe (Fig. 10(b)), the current increase is initially slow (until around 25.2 h), and it then increases sharply with decreasing RH. It shows a maximum value of about 52 nA at around 26.2 h, then decreases sharply, and after around 26.5 h gently while RH remains constant. The current shows further decreases to reach a minimum value of about 12 nA (around 29.5 h) and then increases with the increasing RH.

3.3. Effect of Wet and Dry Cycles on the Hydrogen Permeation Current

To further elucidate the effects of the composition of the specimens and the scratches on the hydrogen permeation current behavior, the differences between the maximum of the hydrogen permeation current at each cycle and the current value before the tests, ΔI , was determined. **Figure 11** shows the changes in this ΔI value plotted with the cycle number of wet and dry corrosion tests. The ΔI of S-Zn shows almost stable values until the 6th cycle, and then decreases with increasing cycle number. The ΔI of the S-ZnAl shows an initial increase and then decreases to reach a steady value in later cycles. The ΔI of the S-Fe increases until the 4th cycle, and then decreases with further cycles. The ΔI of the NS-Fe shows an initial decrease, and then nearly constant values. These results and the surface observation results after the tests (Figs. 6 and 9) suggest that the hydrogen permeation current of specimens with the formed scratches are reduced by corrosion products.

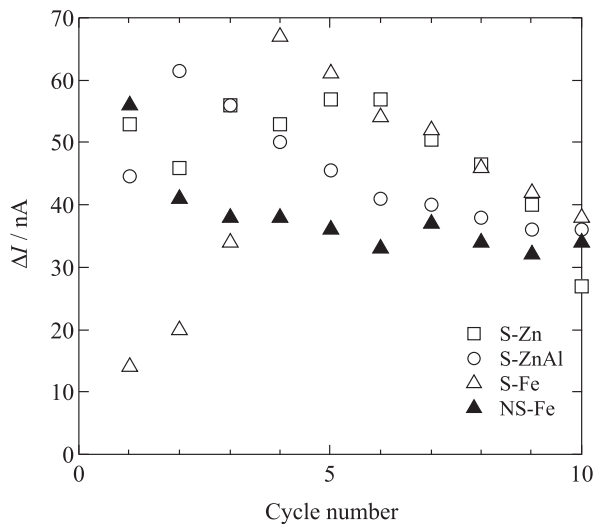


Fig. 11. Changes in difference between the maximum of the hydrogen permeation current at each cycle and the current value before the tests, ΔI , versus the cycle number of the wet and dry corrosion tests.

4. Discussion

4.1. Effects of the Corrosion Products on Hydrogen Permeation of S-Zn and S-ZnAl

The hydrogen entry efficiency, the ratio of hydrogen permeation current / hydrogen generation current (%), of the zinc coated steel without the scratch is about 0.02% and the entry efficiency of the steel with the zinc coating removed by mechanical grinding is about 1%.²⁶⁾ This result indicates that hydrogen permeation site is mainly at the scratches on S-Zn and S-ZnAl. There were white corrosion products around the scratched areas after the corrosion tests (Figs. 6(c) and 6(d)). Figure 12 shows schematic representation of the changes in corrosion products around scratch during the corrosion test. The pH at the scratches of S-Zn and S-ZnAl is about 10,^{31,32)} and a solubility of the corrosion products on the scratch is very small.³³⁾ The corrosion products can be accumulating at the scratch with increase cycle number. This indicated that corrosion products inhibit the hydrogen entry into S-Zn and S-ZnAl. This is the possible reason for the hydrogen permeation current of S-Zn and S-ZnAl were decreased with increase cycle number.

4.2. Effects of Scratch on Hydrogen Permeation

The steel substrate can be rapidly quenched in water after laser irradiation,³⁴⁾ and the rapid quenching changes the coarse grains of the steel to the fine grains. Figure 13 shows schematic representation of hydrogen entry behavior (a) NS-Fe and (b) S-Fe, and (c) schematic representation of gradient of the hydrogen concentration (C_H) from hydrogen entry side to hydrogen detection side in NS-Fe and S-Fe. Adsorbed hydrogen atoms (H_{ad}) enter into the steel as absorbed hydrogen atoms (H_{ab}). There are reports that hydrogen moves immediately along the grain boundary.^{35,36)} The first movement of the hydrogen atoms at the grain boundary can lead to higher concentration of H_{ab} in S-Fe ($C_{Hab-S-Fe}$) than that of NS-Fe ($C_{Hab-NS-Fe}$), and C_H is zero at the hydrogen detection side of both NS-Fe and S-Fe. The higher $C_{Hab-S-Fe}$ means that gradient of the hydrogen con-

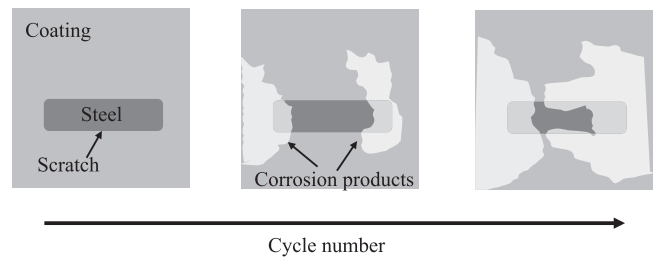


Fig. 12. Schematic representation of changes in corrosion products around scratch during corrosion test.

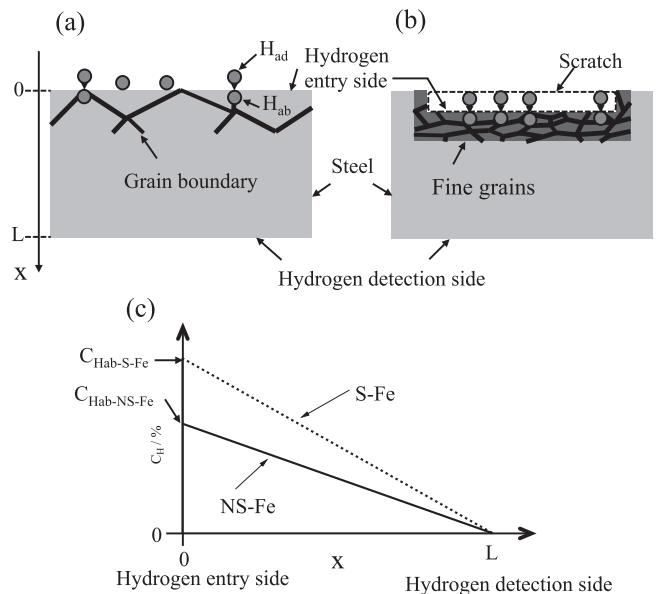


Fig. 13. Schematic representation of hydrogen entry behavior (a) NS-Fe and (b) S-Fe, and (c) schematic representation of the gradient of hydrogen concentration (C_H) from hydrogen entry side to hydrogen detection side in NS-Fe and S-Fe.

centration in S-Fe is larger than that of NS-Fe (Fig. 13(c)). This leads to larger hydrogen permeation current of S-Fe.

The potential during corrosion tests of S-Zn and S-ZnAl is several hundreds mV lower than that of S-Fe and NS-Fe.³¹⁾ This means that the amount of hydrogen permeation at unit area, R_{H-pe} , of S-Zn and S-ZnAl is larger than that of S-Fe and NS-Fe. However, ΔI around 10 cycles shows almost the same value in Fig. 11. As mentioned above, in the case of S-Zn and S-ZnAl, hydrogen permeation site is mainly at the scratch, while the site of S-Fe and NS-Fe is under the droplet. This means that area of the hydrogen permeation site, A_{H-pe} , of S-Zn and S-ZnAl is smaller than that of the steels. The total amount of hydrogen permeation ($R_{H-pe} \cdot A_{H-pe}$) of S-Zn and S-ZnAl might be almost same as that of S-Fe and NS-Fe. This is the possible reason for all specimens show almost same ΔI around 10 cycles in Fig. 11.

5. Conclusions

A wet and dry corrosion test with constant dew point was applied to investigate the effects of scratches and composition on the hydrogen permeation behavior of Zn and 55 mass% Al-Zn coated steels, and uncoated steels. The fol-

lowing conclusions can be drawn.

(1) The shape (changes in) of the hydrogen permeation current at the cycles depends on the composition of the coatings.

(2) For the Zn and 55 mass% Al–Zn coated steels, the hydrogen permeation currents decrease with increasing cycle numbers of the wet and dry corrosion tests.

(3) The hydrogen permeation behavior of steels is affected by the formed scratch.

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