論文 / 著書情報
Article / Book Information

論題	
Title	Hydrogen Absorption Behavior into Zn and Zn–Al Coated Steels during Corrosion in Aqueous Solutions
著者	多田 英司
Author	E. Tada, Y. Miura
掲載誌/書名	, Vol. 56, No. 3, pp. 444-451
Journal/Book name	ISIJ International, Vol. 56, No. 3, pp. 444-451
発行日 / Issue date	2016, 3
権利情報 / Copyright	本著作物の著作権は日本鉄鋼協会に帰属します。 Copyright (c) 2016 (THE IRON AND STEEL INSTITUTE OF JAPAN.

ISIJ International, Vol. 56 (2016), No. 3, pp. 444–451

Hydrogen Absorption Behavior into Zn and Zn–Al Coated Steels during Corrosion in Aqueous Solutions

Eiji TADA[1)]* and Yusuke MIURA[2)]

1) Formerly Department of Materials Science and Engineering, Graduate School of Engineering and Resource Science, Akita University. Now at Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8552 Japan.
2) Formerly Department of Materials Science and Engineering, Graduate School of Engineering and Resource Science, Akita University. Now at Ahresty Corp., 1-2 Nakahara, Mitsuya-cho, Toyohashi-shi, Aichi, 441-3114 Japan.

(*Received on July 7, 2015; accepted on August 18, 2015; J-STAGE Advance published date: February 25, 2016*)

In this study, hydrogen absorption behavior into Zn and Zn-55mass%Al coated steels was investigated both in an immersion test and a wet and dry cyclic corrosion test with NaCl and Na_2SO_4 solutions by Devanathan-Stachurski permeation technique. In the immersion test, the hydrogen absorption into Zn coated steels was observed after the surface of the steel substrate under Zn coating was exposed to corrosion environments. On the other hand, hydrogen absorption into Zn–Al coated steels was not observed for the duration of the tests because of slower dissolution kinetics of Zn–Al coating than Zn coating in the corrosion environments. In the case of a wet and dry cyclic corrosion test, hydrogen permeation current for Zn coated steel was observed during the test duration only under the condition with NaCl solution. This may be because dissolution of Zn coating takes place more locally in NaCl solution than in Na_2SO_4 solution. These results were discussed based on corrosion rate of the coating of Zn and Zn–Al alloy and on corrosion morphology of Zn and Zn–Al alloy coatings in NaCl and Na_2SO_4 solutions.

KEY WORDS: electrochemical hydrogen permeation test; Devanathan-Stachurski permeation technique; immersion test; wet and dry cyclic corrosion test; galvanized steel.

1. Introduction

Recently, automobiles have been extremely required to be with quite high efficiency of fuel consumption. In addition, saving of fuel consumption is also needed, since burning of fossil fuels generates CO_2 gas which is believed to be one of the substances for greenhouse warming. Saving of the body weights of automobiles[1,2)] can play an effective role to accomplish these demands. In order to decrease the weights of automobile bodies on the whole, it should be quite effective to replace the parts of steel to those with high strength. Therefore high strength steels have been extensively invented and employed to some of the steel parts for automobile bodies. At present, 1 200 MPa-class high-strength steels are being ready to be used for the assembly of automobiles.[3)]

However, with increasing the strength of steels, a concern about hydrogen embrittlement can be raised.[4,5)] When steels are exposed to atmospheric environments during the service, the steels can suffer from aqueous corrosion to some extent. During the corrosion of steels in atmospheric environments, hydrogen atoms can be generated on a steel surface due to one of the cathodic reactions. Some of the hydrogen atoms formed on the steel surface can be absorbed into the steel[6,7)] and can interact with defects and traps such as vacancies, dislocations and so on, leading to hydrogen embrittlement. Especially, it is well-known that probability of the occurrence of hydrogen embrittlement can be related to the strength of steels and that the critical concentration of hydrogen embrittlement can become lower with increasing the strength. Therefore, it is very important to investigate hydrogen absorption of steels during aqueous corrosion.

Furthermore, some of the steel parts for automobile application are being coated with Zn or Zn alloys. This is because Zn and Zn-alloy coated steels have good corrosion resistance in mild atmospheric corrosion environments.[8–11)] This is due to the following mechanisms: (1) slow corrosion rate of Zn in atmospheric corrosion environments, (2) galvanic action of Zn can prevent steel surfaces exposed to the atmosphere from corrosion, and (3) corrosion products of Zn can retard occurrence of fatal corrosion and degradation of the steel substrate. However, sacrificial dissolution properties of Zn and Zn alloy coatings to prevent steel corrosion may become a drawback because surface potential of the steels with Zn and Zn alloy coatings can become less noble than that without the coatings, resulting that hydrogen evolution reaction can be enhanced more on the steels with the coatings. Therefore, hydrogen absorption behavior of Zn and Zn alloy coated steels during aqueous corrosion should

---

* Corresponding author: E-mail: tada.e.aa@m.titech.ac.jp
DOI: http://dx.doi.org/10.2355/isijinternational.ISIJINT-2015-405

be clarified with corrosion degradation of their coatings.

Hydrogen absorption into metals have been analyzed by using various techniques such as permeation current measurements,[12–14] thermally desorption spectroscopy and so on. Especially, to investigate hydrogen absorption into metals in-situ during corrosion of them, the permeation current measurement is considered to be suitable. In this paper, hydrogen absorption behavior for Zn and Zn–Al coated steels have been investigated by using a Devanathan-Stachurski permeation technique.

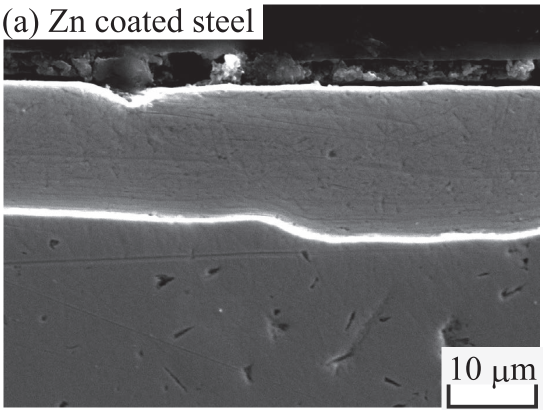
2. Experimental

2.1. Sample

Materials used in this study were 0.5-mm-thick sheets of Zn and Zn-55mass%Al coated steels. These were cut into square-shaped coupons of 7 cm × 7 cm or 4.5 cm × 4.5 cm depending on types of electrochemical cells used in this study. **Figure 1** shows cross-sectional micrographs of the materials. As shown in Fig. 1, both of the coatings are intact without any defects or scratches and the thicknesses of the coatings are ca. 20 um for both coated steels.

The one side of the coatings of a coupon was removed completely by grounding with SiC papers successively down to #2000 grit to have a steel substrate exposed. In addition, steel sheet without any coatings was prepared by grounding both sides of a coupon of Zn coated steel, which was used as a comparison.

On the steel surface of a coupon, 400 nm-thick Ni was electroplated in a mixture of 0.94 kmol/m^3 $NiSO_4$, 0.19 kmol/m^3 $NiCl_2$ and 0.65 kmol/m^3 H_3BO_4 at a constant current density of -3 mA/cm^2 and 40°C. Then silicone sealant was applied on a part of the coating of Zn and Zn–Al coated steels to restrict a surface area exposed to a test solution, as shown in **Fig. 2**. The sample prepared by the above procedure was cleaned ultrasonically in an ethanol bath before the corrosion tests described later.



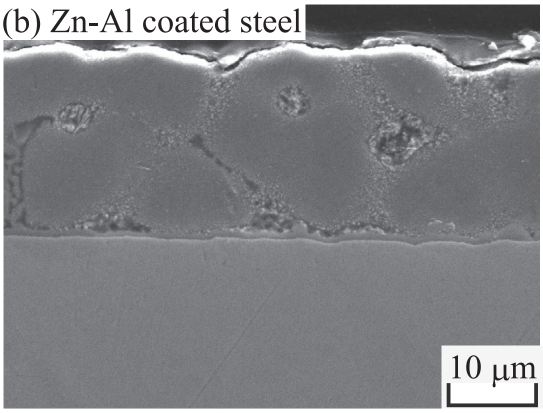


Fig. 1. SEM micrographs of the cross-sections of Zn coated steel and Zn-55Al coated steel used in this study.

2.2. Hydrogen Permeation Measurements

In this study, hydrogen permeation into Zn and Zn–Al coated steels was measured by a Devanathan-Stachurski permeation technique.[12–14] **Figure 3** shows a schematic drawing of the electrochemical cells used for hydrogen permeation measurements. Two types of the electrochemical cells, Cell A and Cell B, were prepared as follows.

Cells A and B were used for an immersion test and for a wet and dry cyclic corrosion test, respectively. As shown in Fig. 3, Cell A has two identical acrylic vessels and a sample is sandwiched with the vessels. Each of the vessels has a counter electrode of a Pt plate and a Luggin capillary which is connected to a reference electrode of an Ag/AgCl electrode in saturated KCl (SSE).

On the other hand, as shown in Fig. 3(b), Cell B is used vertically and the vessel for a hydrogen-withdrawal side is almost the same as that of Cell A except for the volume. However, in Cell B, there is no vessel of a hydrogen-entry side. When a sample is set in Cell B, only a droplet or a thin electrolyte layer is put on the sample surface. The detailed procedure of a wet and dry cyclic corrosion test will be explained later.

Test solution filled in the hydrogen-entry-side vessel was either 0.5 kmol/m^3 NaCl solution or 0.5 kmol/m^3 Na_2SO_4 solution. In the hydrogen-withdrawal-side vessel for Cells A and B, 0.1 kmol/m^3 NaOH solution was poured and the Ni-coated surface of a sample was set in the cells and the surface faced the NaOH solution. All the electrolyte solutions used in this study were prepared with reagent grade chemicals and Milli-Q water (18 MΩcm).

Prior to the exposure of a sample surface to a corrosion environment, the Ni-coated surface of the sample was started to be polarized at 0 V vs. SSE before at least 24 hours, leaving permeation current before a corrosion test very low and constant. From here on, all the potential values shown in this paper are referred to the reference electrode of SSE.

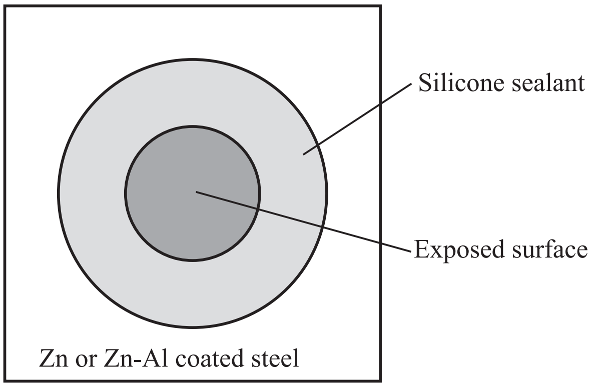
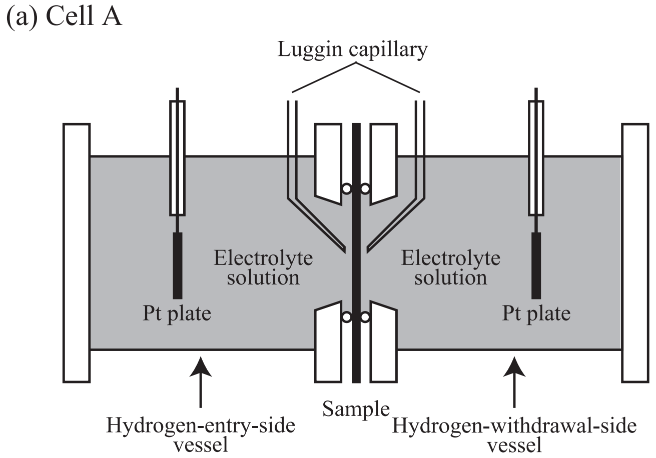


Fig. 2. Schematic drawing of a sample used for the electrochemical hydrogen-permeation tests in this study.



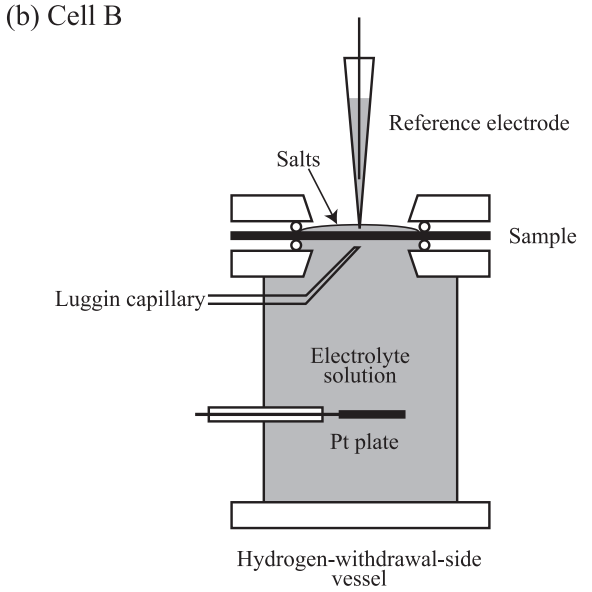


Fig. 3. Schematic drawings of the electrochemical cells for the different electrochemical hydrogen-permeation tests: (a) Cell A for immersion tests, and (b) Cell B for wet-dry tests.

A home-made and battery-powered potentiostat was used to control potential of the hydrogen-withdrawal-side surface and to measure permeation current. The permeation current during the following tests was recorded in a personal computer through a Model 2000 digital multimeter (Keithley Co. Ltd., US).

2.3. Immersion Test

In order to investigate hydrogen absorption behavior into Zn and Zn–Al alloy coated steels during the immersion in NaCl and Na_2SO_4 solutions, hydrogen permeation current was measured by using Cell A. A sample for the immersion test was prepared by the procedure described in 2.1. The coated-side surface of Zn or Zn-55Al coated steel was exposed to a test solution and the exposed surface area was a constant of 4.9 cm^2. All the immersion tests were performed for 7 days at about 25°C.

2.4. Wet and Dry Cyclic Corrosion Test

A wet and dry cyclic corrosion test was done with Cell B. A coupon of 4.5 cm × 4.5 cm for Zn and Zn–Al coated steels was prepared by the procedure described in 2.1. An exposed surface area subjected to a wet and dry cyclic corrosion test was a constant of 1.8 cm^2. As shown in Fig. 3(b), a tiny capillary tip with an Ag/AgCl wire immersed in a mixture of saturated KCl and agar, which is used as a reference electrode, was set just above the surface of a sample to measure corrosion potential during the wet and dry corrosion cyclic test.

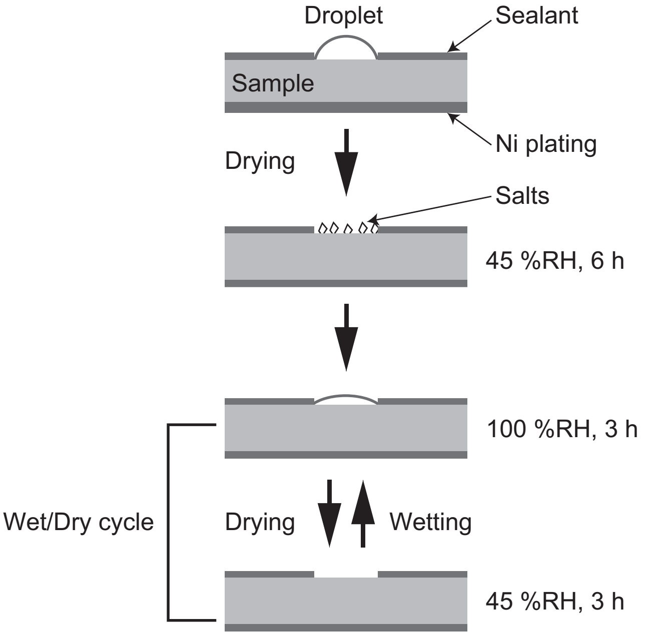


Fig. 4. Schematic drawing of the procedure of a wet and dry cyclic corrosion test.

The wet and dry cyclic corrosion test was performed by the procedure shown in **Fig. 4**. First, a 0.3-mL droplet of 0.5 kmol/m^3 NaCl solution or 0.5 kmol/m^3 Na_2SO_4 solution was put on a surface and dried completely at 25°C and 45%RH for 6 hours. Then the sample was subjected to wet and dry cycles at a constant temperature of 25°C by changing relative humidity cyclically in an SH-221 bench-top type temperature and humidity chamber (Espec Corp., Japan). The wetting cycle was at 100%RH for 3 hours and the drying cycle was at 45%RH for 3 hours. The wet and dry cycle was repeated for 25 cycles (totally 150 hours).

3. Results and Discussion

3.1. Hydrogen Permeation Behavior during Immersion Tests

Figure 5 shows transients of corrosion potential, E_{corr} and permeation current, i_{per} for Zn coated steel during immersion tests in 0.5 kmol/m^3 NaCl and 0.5 kmol/m^3 Na_2SO_4 solutions. Just after the immersion in the test solutions, E_{corr} decreases to a very negative potential less noble than −1.0 V and then does not change very much during the immersion tests. At this time, E_{corr} for NaCl is kept by ca. 30 mV more noble than that for Na_2SO_4. On the other hand, i_{per} for NaCl starts to increase at around 100 ks after immersion and then increases steadily. In the case of Na_2SO_4, i_{per} starts to increase at around 300 ks after immersion, which indicates that the time when i_{per} starts to increase is later than that in the case of NaCl. However, since the increasing rate of i_{per} for Na_2SO_4 is larger than that for NaCl depending

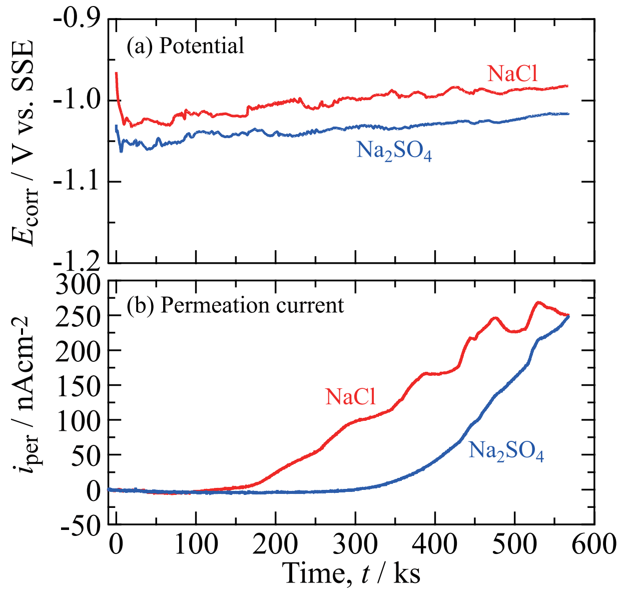


Fig. 5. Changes in (a) corrosion potentials and (b) hydrogen permeation currents for Zn coated steels during the immersion in NaCl and Na_2SO_4 solutions. (Online version in color.)

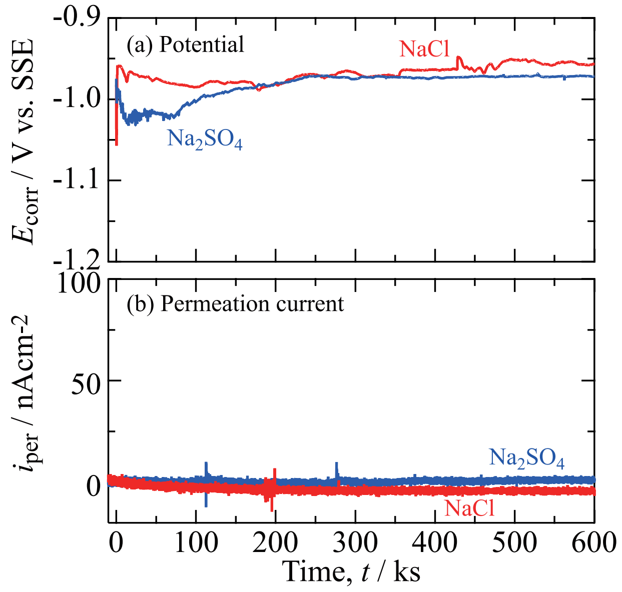


Fig. 6. Changes in (a) corrosion potentials and (b) hydrogen permeation currents for Zn–Al coated steels during the immersion in NaCl and Na_2SO_4 solutions. (Online version in color.)

on E_{corr}, the values of i_{per} after 550 ks immersion in both test solutions become finally almost the same as each other. These results indicate that hydrogen absorption into Zn coated steels can be observed after a certain time immersion in the test solutions.

Figure 6 shows transients of E_{corr} and i_{per} for Zn-55Al coated steels. As shown in Fig. 6, the values of E_{corr} for NaCl and Na_2SO_4 are almost the same although the values of E_{corr} just after immersion in both test solutions are a little bit different from each other. On the other hand, almost no i_{per} is observed during the test duration (7 days) in both test solutions. These results indicate that hydrogen absorption into Zn-55Al coated steel was not taking place during immersion in the test solutions for 7 days, although the values of E_{corr} were kept less noble enough to cause hydrogen evolution reaction.

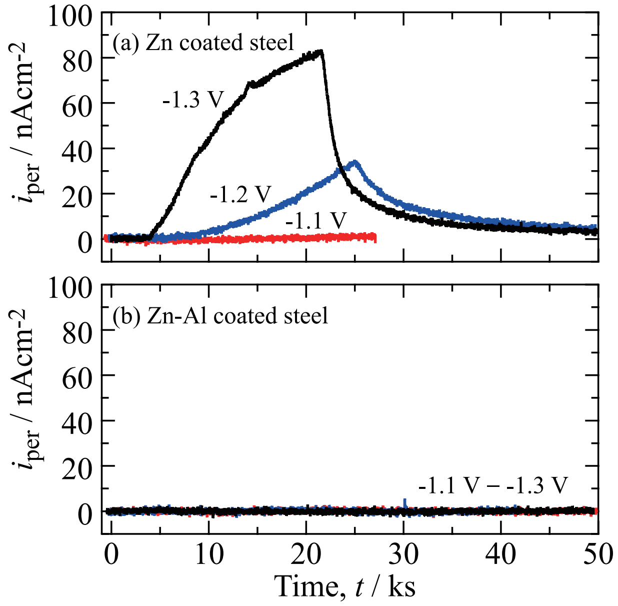


Fig. 7. Changes in hydrogen permeation currents for Zn coated steels and Zn–Al coated steels in NaCl solution at various polarization potentials. (Online version in color.)

From the results shown in Figs. 5 and 6, hydrogen absorption is observed only for Zn coated steels and detected at a certain time after immersion in a test solution. The time for Zn coated steel when i_{per} starts to increase is at several hundred of ks after immersion, which is much longer than that for bare steel even in the same test solutions.[15] In order to investigate hydrogen absorption behavior into Zn and Zn–Al coated steels, hydrogen evolution reaction on Zn and Zn–Al alloy coated steels was forced to be accelerated by applying large cathodic polarization. **Figure 7** shows changes in i_{per} for Zn and Zn–Al coated steels measured in 0.5 kmol/m^3 NaCl solution. As shown in Fig. 7(a), it is found that by applying various cathodic potentials from −1.1 V to −1.3 V, i_{per} at −1.1 V does not change with time and i_{per} at less noble potentials than −1.2 V increases gradually with time. Again, as shown in Fig. 5, in the case of the immersion tests of Zn coated steel, since E_{corr} shows a more noble potential than −1.1 V, it can be considered that i_{per} is not observed during the early stage of the immersion tests. On the other hand, in the case of Zn–Al alloy coated steel, i_{per} measured at the potentials from −1.1 V to −1.3 V does not change at all during the polarization, indicating that no i_{per} due to hydrogen absorption can be observed at least for the duration of the immersion test shown in Fig. 6.

In order to investigate magnitude of hydrogen evolution reaction on Zn and Zn–Al coated steels as a function of potential, cathodic polarization curves for the coated steels were measured in 0.5 kmol/m^3 NaCl solution. The results are shown in **Fig. 8**. As shown in Fig. 8, in the potential region from −1.1 V to −1.3 V, cathodic current densities for Zn and Zn–Al coated steels are much lower than that for bare steel. In addition, in the potential region, oxygen reduction reaction is under a limiting condition for Zn and Zn–Al coated steels and the limiting current for Zn–Al coated steel is ten times smaller than that for Zn coated steel. These results suggest that hydrogen evolution reaction itself is quite small on Zn and Zn–Al coated steels and that i_{per} is not observed at −1.1 V for Zn and Zn–Al coated steels. These results are also in good agreement with the researches done by other researchers.[15–18)]

In addition, even if hydrogen atoms can be absorbed into Zn and Zn–Al coating layers, hydrogen diffusion in the coatings is considered to be slow because diffusion coefficient of hydrogen atom in Zn or Zn alloy coatings is much lower by comparison with that for steels without the coatings.[19–21)] Therefore, it is considered that i_{per} cannot be observed for Zn and Zn alloy coated steels during the immersion test due to slow kinetics of hydrogen evolution reaction and slow diffusion rate of hydrogen in Zn and Zn alloys while the coatings are intact.

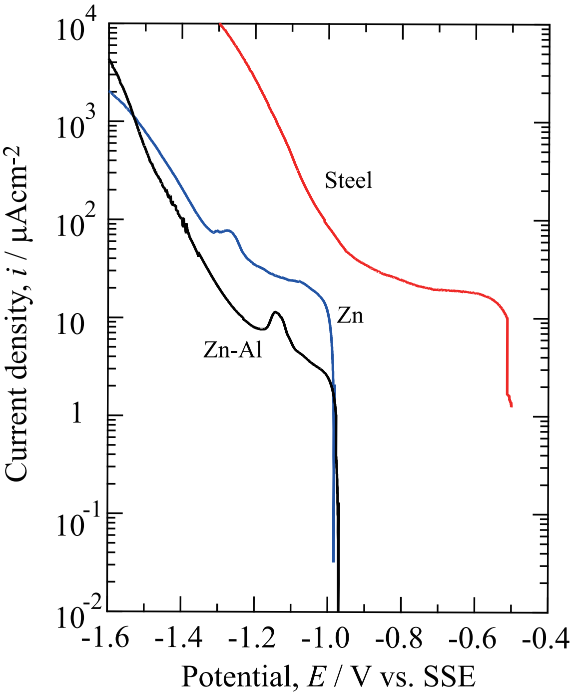


Fig. 8. Cathodic polarization curves for Zn coated steel, Zn–Al coated, and steel measured in NaCl solution. (Online version in color.)

However, when large cathodic polarization is applied to Zn and Zn–Al coated steels, i_{per} can be observed in the case of Zn coated steels. This may be because hydrogen evolution reaction is enhanced to some extent and hydrogen absorption can take place in the coating and because high alkaline condition is formed just above Zn coating by the evolution of OH^-, under which the Zn coating can dissolve out chemically and finally a bare surface of steel substrate can be exposed to an electrolyte, resulting in the enhancement of evolution of hydrogen atoms on the exposed bare steel surface.

By the way, as shown in Fig. 5, in the case of the immersion test for Zn coated steel, i_{per} is observed after a certain time immersion in both NaCl and Na_2SO_4 solutions, even at the potential of around −1 V. In order to investigate the reason why i_{per} was evolved, surface observation was done by a JXA-8230 EPMA (JEOL Ltd., Japan). **Figure 9** shows SEM micrographs of Zn coated steel after the immersion tests in (a) NaCl and (b) Na_2SO_4 solutions. As shown in Figs. 9(a) and 9(b), local dissolution of Zn coating can be observed in the cases of both solutions, although the corrosion morphology is different depending on the test solutions. In both cases, EPMA results show that Fe is detected, which means that during the immersion tests steel substrate is exposed due to dissolution of Zn coating and that hydrogen evolution reaction can be enhanced on the exposed steel substrate. This can also cause hydrogen absorption into steel substrate, resulting in evolution of i_{per}. Conversely, as mentioned above, in the case of Zn and Zn–Al coated steels, hydrogen absorption through the coatings can be ignored while the coatings are intact in the immersion test because of slow kinetics of hydrogen evolution reaction on the coatings and slow diffusion of hydrogen in the coatings.

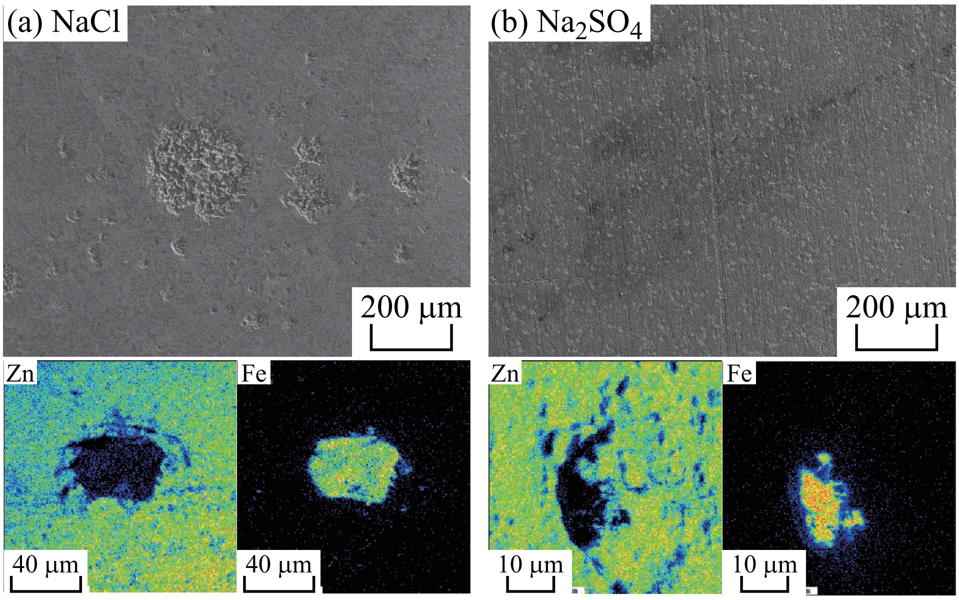


Fig. 9. SEM micrographs and EPMA maps of Zn and Fe for Zn coated steel and Zn–Al coated steel after the immersion test in (a) NaCl and (b) Na_2SO_4 solutions. (Online version in color.)

3.2. Hydrogen Permeation Behavior during Wet/dry Cyclic Corrosion Tests

Figure 10 shows changes in E_{corr} and i_{per} for Zn coated steel during a wet and dry cyclic corrosion test. Figures 10(a) and 10(b) are the data measured with a droplet of NaCl solution and Na_2SO_4 solution, respectively. As shown in Fig. 10(a), in the case of NaCl, E_{corr} and i_{per} change correspondingly with relative humidity at each wet and dry cycle and both values change in a complex manner during the test. On the other hand, in the case of Na_2SO_4, the behavior of E_{corr} and i_{per} is different from that of the case of NaCl, in which E_{corr} and i_{per} do not change very much during the test. These results may be related to corrosion behavior of Zn coatings in NaCl and Na_2SO_4 solutions under a wet and dry condition and will be discussed later.

Figure 11 shows the results of a wet and dry cyclic corrosion test for Zn–Al coated steel. The results indicate that i_{per} keeps a very low level during the tests in both cases of NaCl and Na_2SO_4. This finding is similar to that obtained from the immersion tests in Fig. 6. Therefore, according to the results in Fig. 6, Zn–Al coating is considered to be still intact during the wet and dry cyclic corrosion tests for 25 cycles (150 hours).

From the results of Figs. 10 and 11, evolution of i_{per} was observed only in the case of Zn coated steel during the wet and dry cyclic corrosion tests. Therefore, in order to investigate the changes in E_{corr} and i_{per} for Zn coated steel during the wet and dry cyclic corrosion tests, the data shown in Fig. 10 was rearranged. **Figure 12** shows changes in the averaged values of E_{corr} and i_{per} for one wet and dry cycle as a function of number of the cycles. As shown in Fig. 12, in the early stage of the wet and dry cyclic corrosion test in NaCl solution, the averaged E_{corr} is kept about −1 V and i_{per} is in a quite low level. These results suggest that Zn coating is still intact and steel substrate under the coating is not exposed to the corrosion environment. In this case, since oxygen reduction reaction should be dominant as cathodic reaction taking place on the coating, hydrogen evolution reaction is not considered to be activated very much, leading

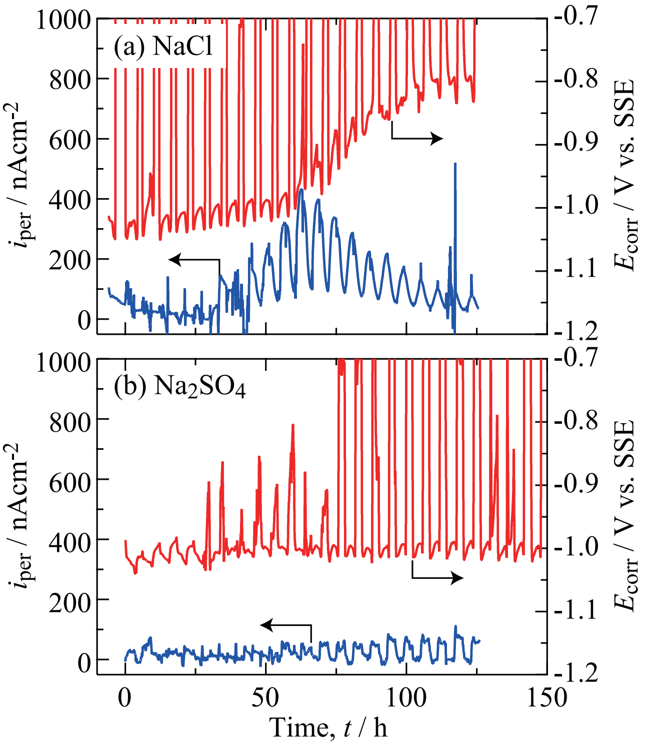


Fig. 10. Changes in corrosion potential and permeation current with the change of relative humidity for Zn coated steel during the wet-dry cyclic corrosion test with a droplet of NaCl solution. (Online version in color.)

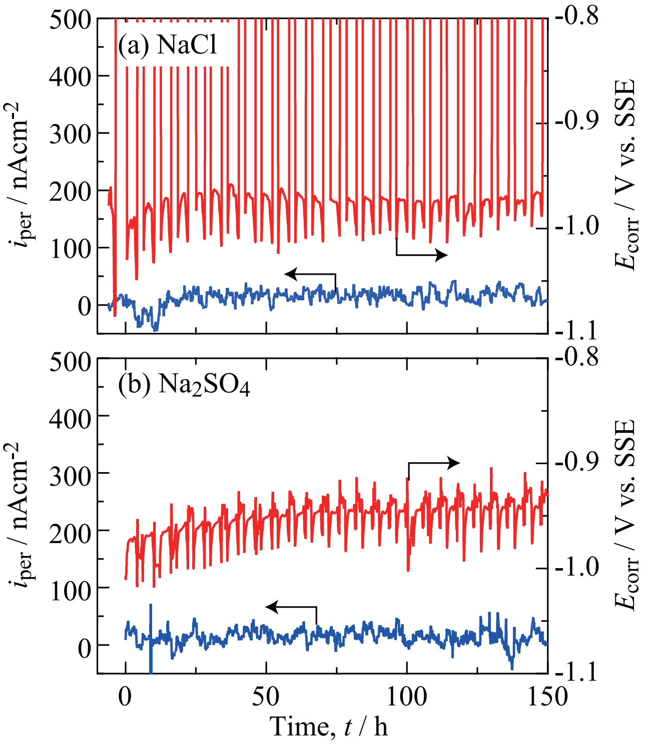


Fig. 11. Changes in corrosion potential and permeation current with the change of relative humidity for Zn–Al coated steel during the wet-dry cyclic corrosion test with a droplet of Na_2SO_4 solution. (Online version in color.)

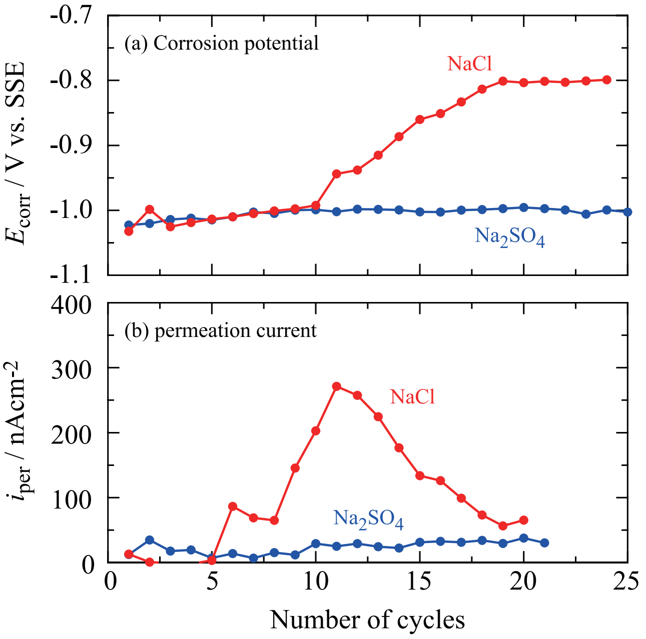


Fig. 12. Plots of averaged values of corrosion potential and hydrogen permeation current for Zn coated steel as a function of number of cycles during a wet and dry cyclic corrosion test. (Online version in color.)

to negligible i_{per} in the stage.

However, in the middle stage of the wet and dry cyclic corrosion test, i_{per} starts to increase although the averaged E_{corr} is still kept at −1 V same as that observed in the early stage of the test. This suggests that on the surface of a sample, a part of the steel substrate may be exposed to the test solution due to the dissolution of Zn coating. This can also mean in parallel that the formation of galvanic couple between the exposed steel substrate and the Zn coating. In this case, since the exposed steel substrate can be polarized cathodically to a less noble potential such as −1 V, near E_{corr} for the Zn coating, hydrogen evolution reaction can be enhanced on the exposed steel substrate. Therefore, hydrogen absorption into the steels can take place from the surface of the exposed steel substrate during a wetting cycle. In addition, the surface area of the exposed steel substrate is considered to increase with increasing the number of the wet and dry cycles, resulting in the increase of the average value of i_{per} for NaCl as shown in Fig. 12.

Furthermore, as shown also in Fig. 12, after the averaged value of i_{per} reaches the peak, the averaged E_{corr} starts to shift to the more noble direction from about −1 V and reaches gradually almost a constant of −0.8 V. At this time, the averaged i_{per} decreases gradually with increasing the averaged E_{corr} in the noble direction. The decreasing in i_{per} is considered to be mainly caused by the decrease of hydrogen evolution rate due to the shift of E_{corr} to a more noble potential. One of the reasons why E_{corr} shifts to a noble potential in the later stage may be due to the increase of the exposed surface area of substrate steel under a thin solution layer during a wet and dry cyclic corrosion test. Another reason may be due to the precipitation of corrosion products of Zn on Zn coated steel. The precipitation of Zn corrosion products can inhibit anodic reaction on Zn coating or steel, resulting in the shift of E_{corr} to more noble one. However, judging from E_{corr} observed in the later stage of the wet and dry cyclic corrosion test, the former reason may be considered to be dominant, although the reason is under investigation.

Here, the relationship between E_{corr} and i_{per} for Zn coated steel observed in the later stage of the wet and dry cyclic corrosion test is investigated in detail. **Figure 13** shows detailed responses of E_{corr} and i_{per} measured for Zn coated steel during the wet and dry test with an NaCl droplet. As shown in Fig. 13, i_{per} increases when a wetting cycle starts after the end of the drying cycle and reaches the almost the maximum at the end of the wetting cycle. Then, in the next drying cycle, i_{per} decays but it indicates still a relatively large value. These results suggest that during the drying cycle for 3 hours the surface of the exposed steel area is considered to be kept wet. To investigate the reasons why this phenomena was observed, i_{per} was measured simultaneously with E_{corr} for a bare steel without Zn coating as a comparison. The result is shown in **Fig. 14**. As shown in Fig. 14, i_{per} is detected on the corroding steel during a wetting cycle but during the next drying cycle the current decreases quickly and then keeps a negligible level until the next wetting cycle starts, although corrosion products of iron were present on the steel during the wet and dry cycles. These results suggest that corrosion product of Zn formed on the surface of the exposed steel substrate may keep moisture longer compared to the iron rusts formed on the bare steel and that hydrogen absorption may continue longer in the drying cycles when the corrosion products of Zn precipitates on the surface of the exposed areas, although i_{per} may decrease with the number of cycles.

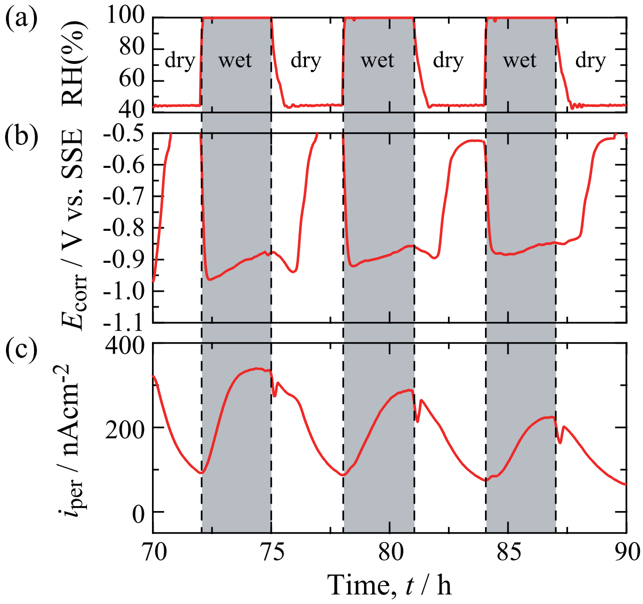


Fig. 13. Cyclic changes of corrosion potential and hydrogen permeation current for Zn coated steel with relative humidity during the wet and dry cyclic corrosion test. (Online version in color.)

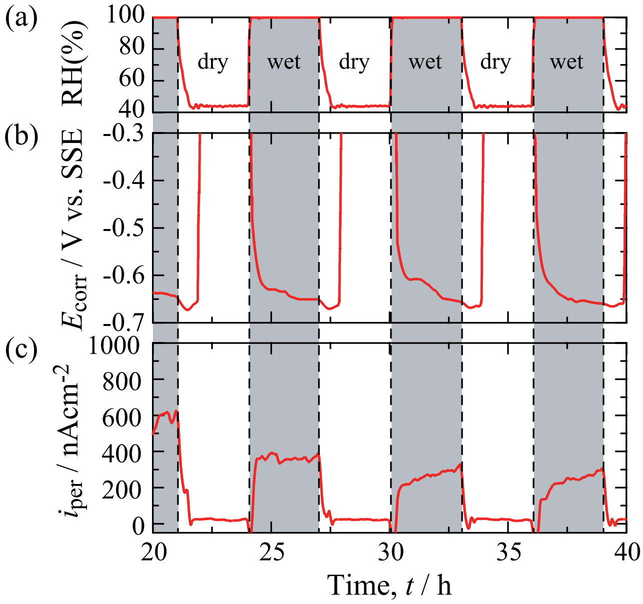


Fig. 14. Cyclic changes of corrosion potential and hydrogen permeation current for steel with relative humidity during a wet and dry cyclic corrosion test. (Online version in color.)

Again, as shown in Fig. 12, from the results for Na_2SO_4, E_{corr} is kept at around −1 V and the evolution of i_{per} is not observed clearly. These results suggest that Zn coating is still present and intact during the wet and dry cyclic corrosion test and that hydrogen evolution reaction on the Zn coating is relatively slow even at the very negative potential of −1 V. At the same time, this means that the time for the exposure of steel substrate is shorter in the case of NaCl than that of Na_2SO_4 because hydrogen absorption into Zn coated steel was retarded in the case of Na_2SO_4 compared to that of NaCl. However, judging from E_{corr} in the test solutions, dissolution rate for both cases should be the same because oxygen reduction reaction is considered to be the rate-determining step for corrosion of Zn coating. According to the results shown in Fig. 9, corrosion morphology of Zn coating in both solutions seems to be different from each other, and especially in the case of NaCl, local dissolution of Zn coating seems to be enhanced. Therefore, the authors are considering that the corrosion morphology in both solutions can be associated with the difference in the behavior of i_{per}. In other word, in the case of NaCl, Zn corrosion takes place locally on the coating, and conversely in the case of Na_2SO_4 homogeneous dissolution rather than local dissolution takes place. If the dissolution of Zn coating is enhanced at a local site, the time for the exposure of the steel substrate to the solution should be shorter, suggesting that hydrogen absorption reaction can be observed in the earlier cycle in wet and dry cyclic corrosion test.

In the case of the Zn–Al coated steels, hydrogen absorption in the sample is not detected. This is because the steel substrate is not exposed during both the immersion test and the wet and dry test. In other word, Zn–Al coating has better corrosion resistance than Zn coating in the neutral environments such as NaCl and Na_2SO_4 solutions. This is because good corrosion resistance of Zn–Al coating is related to the slow kinetics of oxygen reduction reaction on Zn–Al coating.10) Therefore, it will take longer time until the steel substrate under Zn–Al coating is exposed to the solution even in the very severe test of the wet and dry cyclic corrosion.

4. Conclusion

In this study, hydrogen absorption behavior of Zn and Zn-55Al coated steels was investigated under immersion and wet and dry conditions by Devanathan-Stachurski permeation technique. It was found that hydrogen permeation into Zn and Zn–Al coated steels did not take place while the coatings were intact. However, after formation of galvanic couple between the coating and the steel substrate, hydrogen evolution reaction can be enhanced at the surface of the exposed area, resulting in hydrogen absorption into the steels. From the results of a wet and dry cyclic corrosion tests, it was found that hydrogen absorption was observed after steel substrate was exposed to the corrosion environment and that hydrogen absorption may be inhibited due to the shift of corrosion potential in the noble direction with increasing the number of the wet and dry cycles.

REFERENCES

1) K. Sato, T. Inazumi, A. Yoshitake and S. D. Liu: *Int. J. Impact Eng.*, **54** (2013), 1.
2) Y. Li, Z. Lin, A. Jiang and G. Chen: *Mater. Design*, **24** (2003), 177.
3) T. Kushida, H. Matsumoto, N. Kuratomi, T. Tsumura, F. Nakasato and T. Kudo: *Tetsu-to-Hagané*, **82** (1996), 297.
4) Y. Hagihara, C. Ito, N. Hisamori, H. Suzuki, K. Takai and E. Akiyama: *Tetsu-to-Hagané*, **94** (2008), 215.
5) S. Ootsuka, S. Fujita, E. Tada, A. Nishikata and T. Tsuru: *Corros. Sci.*, **98** (2015), 430.
6) E. Akiyama, K. Matsukado, M. Wang and K. Tsuzaki: *Corros. Sci.*, **52** (2010), 2758.
7) T. Tsuru, Y. Huang, M. R. Ali and A. Nishikata: *Corros. Sci.*, **47** (2005), 2431.
8) X. G. Zhang: Corrosion and Electrochemistry of Zinc, Plenum Press, New York, (1996), 261.
9) X. G. Zhang: *J. Electrochem. Soc.*, **143** (1996), 1472.
10) M. Matsumoto: *J. Surf. Finish. Soc. Jpn.*, **57** (2006), 25.
11) E. Tada and H. Kaneko: *ISIJ Int.*, **51** (2011), 1882.
12) M. A. V. Devanathan and Z. Stachurski: *Proc. Roy. Soc. Lond. A*, **270** (1962), 90.
13) M. A. V. Devanathan and Z. Stachurski: *J. Electrochem. Soc.*, **110** (1963), 886.
14) M. A. V. Devanathan and Z. Stachurski: *J. Electrochem. Soc.*, **111** (1964), 619.
15) E. Tada and T. Tsuru: *Bull. Iron Steel Inst. Jpn.*, **17** (2012), 699.
16) D. H. Coleman, G. Zheng, B. N. Popov and R. E. White: *J. Electrochem. Soc.*, **143** (1963), 1871.
17) A. Durairajan, A. Krishniyer, B. S. Haran, R. E. White and B. N. Popov: *Corrosion*, **56** (2000), 283.
18) B. N. Popov, G. Zheng and R. E. White: *Corros. Sci.*, **36** (1994), 2139.
19) D. Figueroa and M. J. Robinson: *Corros. Sci.*, **50** (2008), 1066.
20) C. N. Panagopoulos, E. P. Georgiou and D. Chaliampalias: *Corros. Sci.*, **79** (2014), 16.
21) A. El hajjami, M. P. Gigandet, M. De Petris-Wery, J. C. Catonne, J. J. Duprat, L. Thiery, F. Raulin, B. Starck and P. Remy: *Appl. Surf. Sci.*, **255** (2008), 1654.