

Development of Monitoring System for Hydrogen Absorption into Steel Under an Actual Vehicle Environment

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Abstract:

In this study, a new hydrogen absorption monitoring system based on the electrochemical hydrogen permeation method was developed to measure quantity of absorbed hydrogen under an actual vehicle environment. It was confirmed that this monitoring system was capable of accurate assessments of hydrogen absorption into steel sheet by minimizing the changes in residual currents with external temperature. By applying this monitoring system, it was clarified that hydrogen permeation current in the vehicle environments was related to both driving states of a vehicle and environmental conditions such as temperature and relative humidity and the amount of absorbed hydrogen into the steel had a quite good correlation with the corrosion loss of steel.

1. Introduction

Application of high strength steel sheets in the automotive field has expanded in recent years with the aim of satisfying both auto body weight reduction and crashworthiness¹⁾. One issue accompanying higher strength of steel sheets is increased hydrogen embrittlement susceptibility²⁾ caused by hydrogen absorption from the use environment. In the past, hydrogen embrittlement had become a problem in linepipes³⁾, which are used under a severe corrosion environment and are characterized by large amount of hydrogen absorption, and in PC steel bars⁴⁾, high strength bolts⁵⁾ and other materials in which higher strength steel materials were used from a comparatively early date.

Therefore, study on hydrogen embrittlement characteristics was carried out from the metallurgical viewpoint using materials in which a certain amount of hydrogen absorption was induced by the electrolytic method⁵⁾, acid immersion method⁶⁾, etc. However, since hydrogen absorption by high strength bolts, for example, is caused by hydrogen evolved in the corrosion process in a natural atmospheric environment, in-situ measurement of the hydrogen absorption of the material while corrosion is continuing and elucidation of its behavior are important. From this viewpoint, the hydrogen absorption behavior of steel materials in atmospheric exposure environments was studied by using the electrochemical hydrogen permeation method⁷⁾, as this method enables in-situ and continuous evaluation of hydrogen absorption behavior. Study using this method revealed that the formation of rust influences hydrogen absorption behavior⁸⁾ and clarified hydrogen absorption behavior over the exposure period and during one day⁹⁾, etc.

The corrosion environment of automotive steel sheets is a natural atmospheric environment, but since a vehicle is a moving body, its corrosion environment is thought to change in a complex manner depending on the region where the vehicle is driven, the vehicle travel period and the condition of the road surface. Up to now, Suzuki et al¹⁰⁾ conducted an investigation of the corrosion environments under the actual vehicle use conditions by using an ACM (Atmospheric Corrosion Monitor)-type sensor, and clarified the fact that the corrosion environment differs depending on weather

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conditions and whether the vehicle is moving or not. Accordingly, in order to evaluate hydrogen embrittlement in the use environment of automotive steel sheets, it is necessary to quantitatively evaluate vehicle use conditions such as weather phenomena, road surface conditions, etc., and the hydrogen absorption behavior of the steel sheets.

In this study, a hydrogen absorption monitoring system for vehicles was developed, and its validity for evaluation of the hydrogen absorption behavior of vehicles in the actual driving conditions was studied. In addition, the relationship between the amount of hydrogen absorption and corrosion of steel sheets in the actual vehicle environment was also examined.

2. Hydrogen Absorption Monitoring System for Vehicular Use

Because the actual vehicle environment is considered to change in a complex manner, the Devanathan-type electrochemical hydrogen permeation method⁷⁾, which enables *in-situ* and continuous evaluation of hydrogen absorption behavior, was adopted as the basic principle of this monitoring system. The hydrogen absorbing surface in this method is configured so that it is possible to evaluate the amount of hydrogen absorption due to corrosion by exposing the surface to the atmosphere. However, when this system was mounted on a vehicle, it was necessary to solve two problems, namely, long-term stability and safety as issues of the measurement system, and removal of the temperature-dependent background current for reliability of the data.

2.1 Long-term Stability and Safety

In the electrochemical hydrogen permeation method, the amount of hydrogen is detected as the electrons, i.e., current discharged accompanying the anodic reaction at the hydrogen detection surface when the hydrogen which is formed at the hydrogen absorbing side of an electrochemical cell and absorbed into a steel sheet diffuses to the hydrogen detection side of the cell. Since it is necessary to maintain the potential necessary for the hydrogen to ionize the steel sheet surface on the hydrogen detection side at this time, a reference electrode is necessary in this measurement. Generally, an Ag/AgCl electrode or an HgO/Hg electrode is used, but when the purpose is long-term measurement with the system mounted on a vehicle, measurement error due to chlorides in the solution and environmental pollution due to electrode damage are concerns. Therefore, as a result of a study of metal electrodes, an Ir/IrO₂ electrode was applied. This potential of this electrode is stable over the long term in the alkaline solution of

the hydrogen detection side.

2.2 Removal of Temperature-Dependent Background Current

As mentioned above, in the electrochemical hydrogen permeation method, a certain current (hereinafter, background current) is detected because the potential for hydrogen necessary to ionize the steel sheet surface on the hydrogen detection side is maintained. Although the background current (i_{BG}) is not caused by hydrogen absorption, the measured current value (i_{total}) is measured as the sum of the current (i_H) corresponding to the amount of hydrogen absorbed by the steel sheet, as mentioned previously, and the background current on the hydrogen detection side. In other words, for accurate measurement of the amount of absorbed hydrogen, it is necessary to subtract i_{BG} from i_{total} . However, because i_{BG} changes depending on the temperature, temperature compensation taking these temperature changes into account is necessary in actual vehicle environments, where the temperature changes continuously.

Here, the temperature compensation method for i_{BG} developed in this study will be explained by using the schematic diagram of the monitoring system shown in Fig. 1. This monitoring system consists of the steel sheet and four separate electrolytic cells. A Pt counter electrode and an Ir/IrO₂ reference electrode are installed in each cell. In this system, one of the four cells is used as a reference cell (Ref-cell) for measurement of i_{BG} . The surface of the steel sheet in the Ref-cell is covered with a sealant so that the cell can only

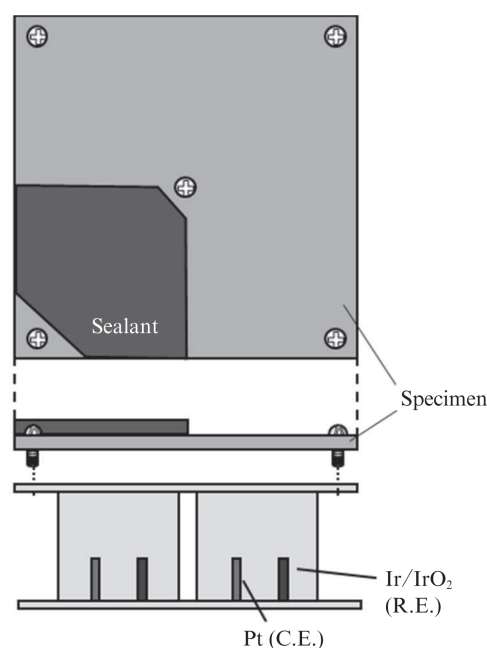


Fig. 1 Schematic image of the hydrogen monitoring system

measure i_{BG} , which is not caused by the corrosion reaction. On the other hand, because the other three cells measure the sum of i_{BG} and i_H , which is caused by the amount of absorbed hydrogen generated by corrosion, the i_{BG} of the Ref-cell is subtracted after simultaneous measurement of these four channels, enabling highly accurate detection of only the current (i_H) caused by the hydrogen absorbed by the steel sheet as a result of the corrosion reaction.

3. Experimental Method

3.1 Test Material

The test material was a 270 MPa class cold-rolled steel sheet (thickness: 0.7 mm) having the chemical composition shown in **Table 1**. After polishing one side of the specimen with emery paper to #2000, the specimen was immersed in a mixed solution of hydrofluoric acid and hydrogen peroxide water (6 ml : 94 ml), and chemical polishing was performed so as to reduce the thickness by 50 μm or more only for polished side, after which a Pd plating was applied. In the schematic diagram of the hydrogen absorption monitoring system shown in Fig. 1, a steel sheet which was prepared in advance was fixed so that the Pd-plated surface was installed in the solution. This Pd-plated surface becomes the hydrogen detection surface. Furthermore, as shown in Fig. 1, part of the steel sheet is isolated from the corrosion environment by completely covering that part with a silicone sealant, and this is used as the reference cell for compensating for changes in the current accompanying temperature changes. The solution injected into each cell is a 0.1 mol/dm³ NaOH solution that was deaerated with nitrogen for at least 40 h. Following injection of the solution, constant potential polarization of the hydrogen detection surface was performed to +0.20 V vs. Ir/IrO₂, and after waiting a sufficient time for the current to reach 10 nA/cm² or less, measurement of the hydrogen permeation current was started.

3.2 On-Vehicle Tests

On-vehicle tests with an actual vehicle were performed two times. The effectiveness of the hydrogen absorption monitoring system was evaluated in Test 1, and the relationship between environmental changes in

the actual vehicle environment and the amount of absorbed hydrogen was investigated in Test 2.

3.2.1 Verification of background current removal system (Test 1)

The hydrogen absorption monitoring system was installed on the underside of the front bumper on the outside of the auto body so that the steel sheet surface in contact with the atmospheric environment faced the road surface. A temperature and humidity sensor was also attached near the monitoring system. The location of the on-vehicle test was the roads in JFE Steel West Japan Works (Fukuyama District), and the vehicle was driven intermittently only during daytime on weekdays. The test period was January 2011. The actual record of movement and the changes over time in the current density in the monitoring cell were compared by comparing the movement start time and movement distance.

3.2.2 Evaluation of relationship between absorbed hydrogen and corrosion in actual vehicle environment (Test 2)

In order to clarify the effect of the amount of corrosion (corrosion mass loss) of the steel sheet on the amount of absorbed hydrogen, hydrogen absorption monitoring systems were installed at the back side of the front wheels on the driver side and passenger side (one unit on each side). The steel sheet surfaces on the driver side and passenger side were sprayed with 36 g/m² of a 0.5% NaCl aqueous solution or pure water, respectively, at a frequency of one time per week, and the amount of absorbed hydrogen when the amount of corrosion in the respective locations was changed was evaluated. In addition, exposure to water by splashing and the wetting condition of the steel sheets during the on-vehicle test were also evaluated by installing a Zn/Ag-type ACM (Atmospheric Corrosion Monitor) near the hydrogen absorption monitoring systems. The location of movement in this test was the same as that in Test 1, as mentioned in section 3.2.1, and the test period was July 2012. Movement was performed intermittently limited to daytime on weekdays, and the record of movement was recorded and correlated with the weather and road surface condition. To determine the corrosion mass loss during the test period, test specimens were installed near the monitoring systems, and the change in weight before and after corrosion was calculated using those steel sheets.

Table 1 Chemical composition of the steel used in this study

C	Si	Mn	P	S	Fe
0.02	0.01	0.15	0.01	≤ 0.01	bal.

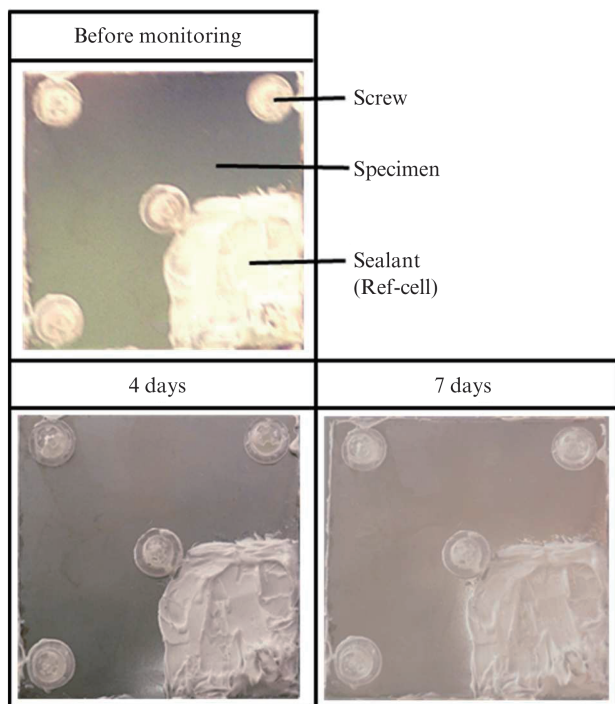


Fig. 2 Appearances of specimen on hydrogen monitoring cell during on-vehicle test for 0, 4 and 7 days of TEST 1

4. Experimental Results and Discussion

4.1 Verification of Background Current Removal System (Test 1)

Figure 2 shows photographs of the appearance of the steel sheet specimens on the monitoring cell before and after the on-vehicle test in Test 1. From this figure, it can be understood that there was no change in appearance that could be detected by visual inspection during the 7-day period from the start of the test, indicating that substantially no corrosion occurred. Here, the validity of the background current removal system was verified from this measurement period.

Figure 3 shows (a) temperature, (b) current density change of the non-sealed part and (c) current density change of the sealed part (Ref-cell). From Fig. 3(b) and (c), it can be understood that the changes in the current densities of both the non-sealed part and the sealed part responded to the temperature changes in Fig. 3(a), and these current density changes showed peaks when the daily temperature is high in the daytime. Next, Fig. 4 shows the change over time in the current density when the current of the non-sealed part is removed from the current of the sealed part as described in section 2.2. Because it is thought that there was no current accompanying hydrogen absorption due to corrosion in this test, it was clear that the identical background current was measured in both the non-sealed part and the sealed part.

Based on these results, the temperature compensa-

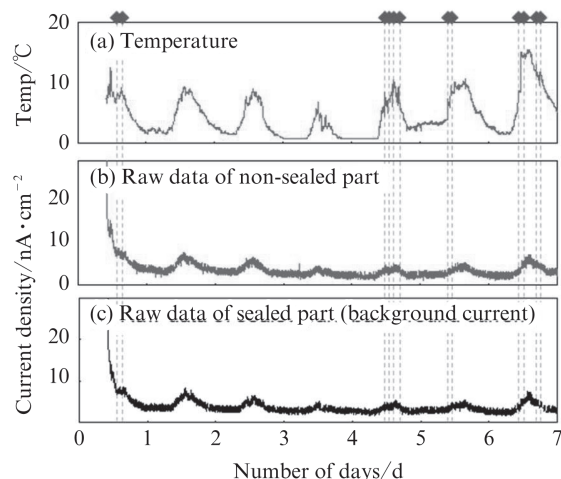


Fig. 3 Changes in the current density and the temperature in initial 7 days of TEST 1

(a) temperature, (b) raw data of non-sealed part, (c) raw data of sealed part

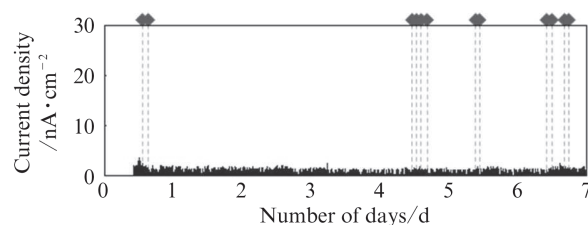


Fig. 4 Changes in the current after background current removal in initial 7 days of TEST 1

tion effect of the hydrogen absorption monitoring system will be discussed. Figure 5 shows the relationship between the current density obtained when the current before and after temperature compensation was averaged in each 0.5 °C temperature range of the ambient temperature, and average temperature. The temperature dependency of the current density can be clearly confirmed from this figure, as the current value before temperature compensation (raw data in the figure) increase linearly as the temperature rises. From the above, it can be said that the current change during the non-corrosion period captured the temperature-dependent changes of the background current of the hydrogen detection surface. On the other hand, based on the fact that temperature dependency of the current density is not observed if temperature compensation is performed by removing the current of the sealed part from the current of the non-sealed part, it is possible to remove the background current, which is temperature-dependent, in this monitoring system. Thus, in cases where a hydrogen permeation current due to corrosion occurs, it was suggested that the hydrogen permeation current can be calculated accurately by performing the temperature compensation operation.

It may be noted that superimposition of noise origi-

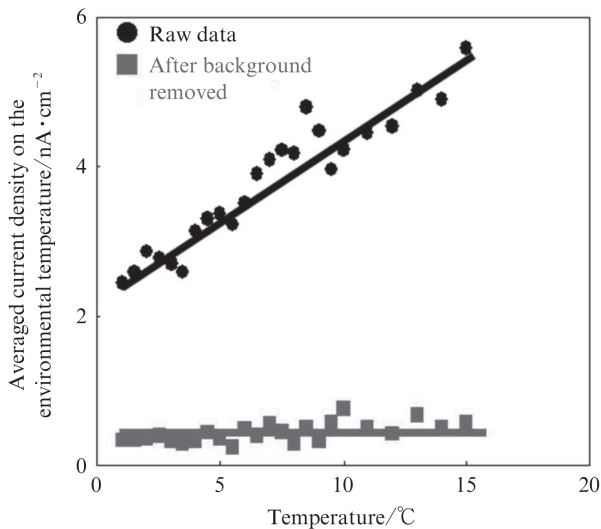


Fig. 5 Temperature dependence of the current density under non corrosive environment

nating from electromagnetic waves, voltage fluctuations and vibration on the electrochemical signals was a concern, as many electronic devices are used in vehicles and vibration occurs while a vehicle is moving. However, as shown in Fig. 4, current vibration due to vehicle movement (times shown by \blacklozenge in the figure) was not observed in the current density after temperature compensation. This showed that the monitoring system can measure the hydrogen permeation current, unaffected by electromagnetic waves, vibration, etc. during vehicle movement, and thus is applicable to actual vehicle environments.

4.2 Relationship of Absorbed Hydrogen and Corrosion Mass Loss in Actual Vehicle Environment (Test 2)

Figure 6 shows photographs of the appearance of the steel sheets before and after the on-vehicle test in Test 2. During the 3-day period after the start of the test, measurements were made in the natural movement condition without applying the salt water or pure water. Although the photographs of the appearance on the 3rd day in this figure were taken immediately before applying salt water or pure water, it can be understood that formation of rust is comparatively slight. Next, in the photographs after 7 days and 13 days, i.e., after applying salt water or pure water, it can be seen that the entire surface is covered with red rust.

Figure 7 shows the change over time in the current on the pure water sprayed side and the salt water sprayed side measured during the first 12 days after the start of Test 2, together with the ACM sensor output and the hydrogen permeation current for the same period. Here, the change in the current density shows the hydrogen permeation current caused by hydrogen

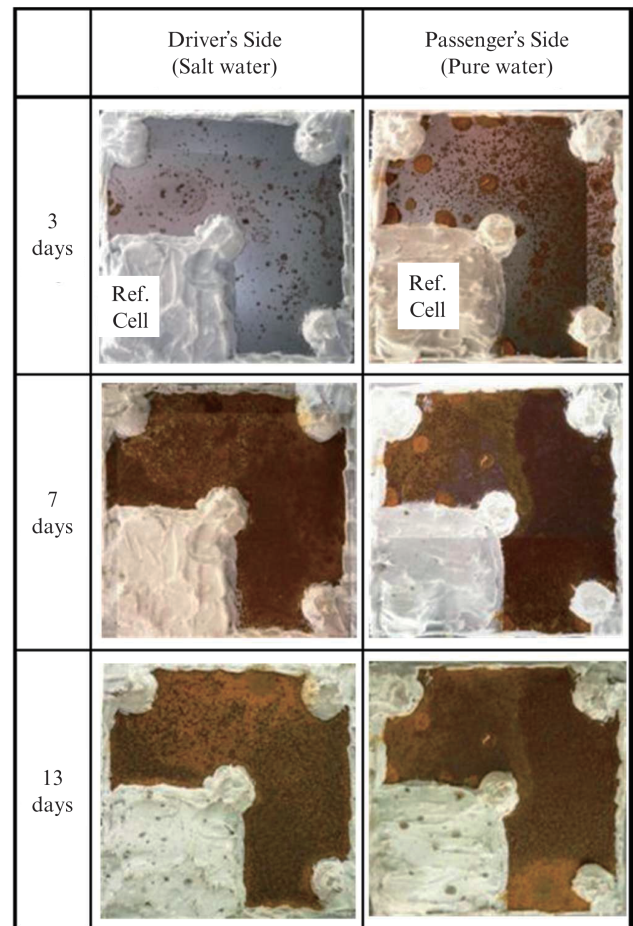


Fig. 6 Appearances of specimens of hydrogen monitoring cell during on-vehicle test for 3,7 and 13 days of TEST 2

absorption, which was obtained by performing the temperature compensation operation to remove the background current. Regarding the symbols A to E in the figure, A and E are the timing of water spraying, and B to D correspond to the timing of movement on a wet road surface on the 4th day, 5th day and 6th after the start of the test, respectively. The periods shown by the color gray in the figure are periods when the road surface was wet.

In the results on the pure water sprayed side, no remarkable changes could be seen in the hydrogen permeation current or the ACM sensor output during the period until A. After A, the output of the ACM sensor increased due to pure water spraying, but then quickly decreased to approximately the same level as before water spraying. In cases of B, C, and D, it also trended to decrease after showing a high output. No large changes were observed in the hydrogen permeation current.

Next, on the salt water side, the ACM sensor output was similar to that on the pure water side until salt water spraying. However, when salt water was sprayed, the sensor output increased and then kept a high value until B. A higher value than that on the pure water

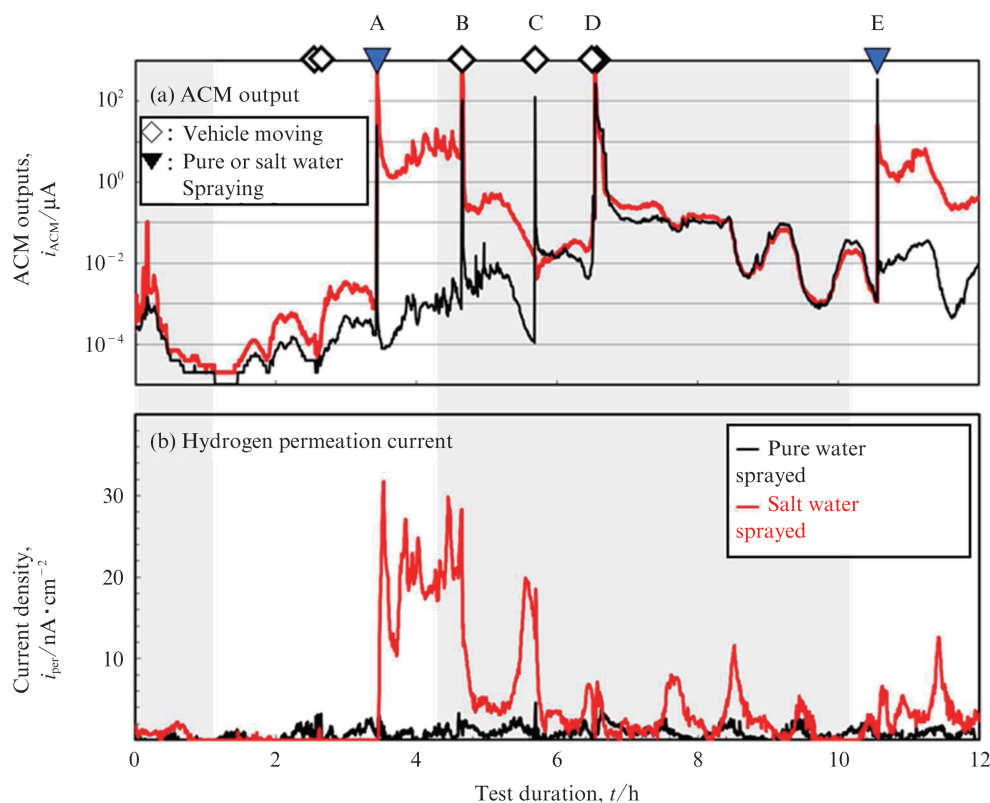


Fig. 7 Time variation of the hydrogen permeation current and the ACM output current
(a) ACM output current, (b) hydrogen permeation current

sprayed side was observed during the period from B to C, but after C the output value trended at about the same value as on the pure water side. Then, when salt water was sprayed at E, the ACM output showed a high value in comparison with the pure water side. The hydrogen permeation current increased due to salt water spraying and then kept a high value from A to B, and then showed a decreasing behavior after B and C, when the vehicle was driven on a wet road surface.

From the results described above, changes in the hydrogen permeation current were observed in the actual vehicle environment when corrosion factors such as road surface water, salt, etc. adhered to the steel sheet. Moreover, since the hydrogen permeation current showed a high value on the salt water sprayed side in comparison with the pure water side, it was suggested that the amount of absorbed hydrogen increases under a severe corrosion environment. Because hydrogen absorption by steel sheets under atmospheric corrosion environments is caused by hydrogen generated by corrosion, the hydrogen permeation behavior under an atmospheric corrosion environment will be discussed based on the relationship between the corrosion mass loss and the hydrogen permeation current in Test 2.

The hydrogen permeation current is caused by the oxidation reaction of hydrogen atoms on the hydrogen detection surface, as expressed by Eq. (1). Accordingly,

the amount of absorbed hydrogen m_H (mol/cm^2) per week can be obtained from the integrated value of the hydrogen permeation current for 1 week.



On the other hand, as the corrosion mass loss of the steel sheet, the mass loss of the steel sheet when the corrosion products after the on-vehicle test were removed was divided by the exposed area and corrosion period, and the result was used as the weekly averaged corrosion mass loss m_{Fe} (mol/cm^2). The relationship between the obtained corrosion mass loss and amount of absorbed hydrogen is shown in Fig. 8. From this result, it can be understood that the amount of absorbed hydrogen increases as corrosion mass loss becomes larger. This clarified the fact that the hydrogen generation reaction is included in part of the cathodic reaction, the total volume of the hydrogen generation reaction increases accompanying acceleration of corrosion, and as a result, the amount of absorbed hydrogen increases, even in a neutral corrosion environment containing chloride ions.

5. Conclusion

In this study, a temperature compensation-type

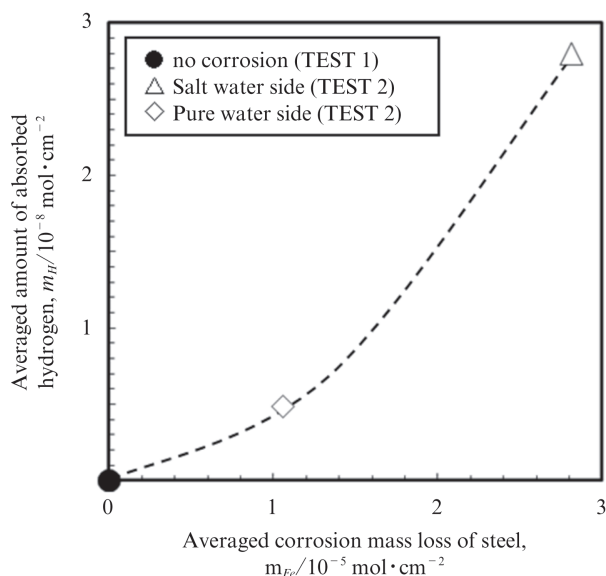


Fig. 8 Relationship between the corrosion mass loss and the absorbed hydrogen

hydrogen absorption monitoring system was developed in order to measure the behavior of hydrogen absorption by steel sheets in actual vehicle environments. The possibility of monitoring hydrogen absorption by steel sheets in actual vehicle environment, was evaluated and the relationship between the corrosion mass loss of the steel sheets and the amount of absorbed hydrogen was investigated. As a result, the following knowledge was obtained.

1) It was found that the hydrogen permeation current in the actual vehicle environment can be measured with good accuracy by performing a temperature compensation operation, in which temperature-dependent changes in the background current are removed. It was also shown that this system is capable of continuously monitoring the amount of absorbed hydrogen, unaffected by noise originating from vehicle movement.

2) In the actual vehicle environment, it was found that corrosion mass loss and the amount of absorbed

hydrogen increase due to spraying salt water on the steel sheet. It was shown that the corrosion environment of the steel sheet surface changes due to pick-up of rain water from the road surface during vehicle movement, and the amount of absorbed hydrogen also changes corresponding to those changes.

3) A correlation between the corrosion mass loss of the steel sheet and the amount of absorbed hydrogen during a 12-day period was recognized, and it was found that the hydrogen generation reaction occurs as part of the cathodic reaction of the corrosion reaction, and hydrogen absorption occurs as a result of that reaction.

It was possible to evaluate the amount of hydrogen absorbed by steel sheets correctly in various vehicle corrosion environments by using the temperature compensation-type hydrogen absorption monitoring system developed in this study. Development to a technology for appropriately evaluating delayed fracture initiation in automotive steel sheets by applying this technology is currently under study.

References

- 1) Krupitzer, R. P.; Urban, D. M.; Witmer D. A. Proc. Galvatech'04, Chicago, USA, 2004, p. 31–50.
- 2) Hirth, J. P.; Johnson, H. H. Corrosion 32, 1976, P. 3–26.
- 3) Shimizu, M.; Iino, M.; Kimura, M.; Nakate H.; Ume, K. Corrosion 87, 1987, Paper No. 45.
- 4) Takai, K.; Seki, J.; Homma, Y. Tetsu-to-Hagane. 1995, vol. 81, no. 10, p. 1025–1030.
- 5) Kushida, T.; Matsumoto, H.; Kuratomi, N.; Tsumura, T.; Nakasato, F.; Kudo, T. Tetsu-to-Hagane. 1996, vol. 82, no. 4, p. 297–302.
- 6) Toji, Y.; Takagi, S.; Yoshino, M.; Hasegawa, K.; Tanaka, Y. Tetsu-to-Hagane. 2009, vol. 95, p. 887.
- 7) Devanathan, M. A. V.; Stachurski, Z. Proc. Roy. Soc. London, Ser. A. 1962, vol. 270, p. 90.
- 8) Omura, T.; Hushida, T.; Kudo, T.; Nakasato, F.; Watanabe, S. Zairyo-to-Kankyo. 2005, vol. 54, p. 61–67.
- 9) Omura, T.; Kudo, T.; Fujimoto, S. Mater. Trans. 2006, vol.47, p. 2956–2926.
- 10) Suzuki, S.; Mizuno, D.; Fujita, S. Galvatech'07, Osaka, Japan. 2007, Paper No. C-7–3.