

Fundamental Research on Factors Affecting the Under-Film Corrosion Behavior of Coated Steel Members

T. Sakamoto, S. Kainuma

Abstract—Firstly, in order to examine the influence of the remaining amount of the rust on the coating film durability, the accelerated deterioration tests were carried out. In order to prepare test specimens, uncoated steel plates were corroded by the Salt Spray Test (SST) prior to the accelerated deterioration tests, and then the prepared test specimens were coated by epoxy resin and phthalic acid resin each of which has different gas-barrier performance. As the result, it was confirmed that the under-film corrosion occurred in the area and the adjacency to great quantities of salt exists in the rust, and did not occurred in the specimen which was applied the epoxy resin paint after the surface preparation by the power tool. Secondly, in order to clarify the influence of the corrosive factors on the coating film durability, outdoor exposure tests were conducted for one year on actual steel bridge located at a coastal area. The tests specimens consist of coated corroded plates and the uncoated steel plates, and they were installed on the different structural members of the bridge for one year. From the test results, the uncoated steel plates which were installed on the underside of the member are easily corrosive and had highly correlation with the amount of salt in the rust. On the other hand, the most corrosive under-film steel was the vertical surface of the web plate. Thus, it was confirmed that under-film corrosion rate was not match with corrosion rate of the uncoated steel. Consequently, it is estimated that the main factors of under-film corrosion are gas-barrier property of coating film and corrosive factors such as water vapor and temperature. The salt which significantly corrodes the uncoated steel plate is not directly related to the under-film corrosion.

Keywords—Accelerated deterioration test, Coating durability, Environmental factor, Under-film corrosion.

I. INTRODUCTION

PAIN T is a common method to prevent corrosion of the steel structures. Generally, the coating film consists of an organic polymer whose durable life is about several decades. Accordingly, a re-painting is desirable to refresh the degraded coating and maintain corrosion protection. Since re-painting costs a lot, long term durability of a coating material is strongly required.

The re-painted coating film degraded easier than the coating film applied at the time of new construction. One of the reasons is that repainting is performed although the rust still remains at the surface preparation. In order to provide a long-time durability, a coating film for steel structure used as a laminated coating film formed by several times painting. However, it is

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impossible to completely protect the environmental factors such as water vapor and oxygen; therefore, the coating film covered on the rust is degraded by the progress the under-film corrosion due to various corrosive factors. Thus, in order to inhibit the under-film corrosion, it is important to understand the relationship among corrosive factors, remaining amounts of the rust and coating durability. Fig. 1 shows under-film corrosion of a steel structure.



Fig. 1 Appearance of Under-film Corrosion

Despite of a number of researches about the relationship between the corrosion rate and environmental factors such as water, oxygen and chloride ions have been reported in the case of uncoated steel, it is not clear about the intensity of environmental factors on the under-film corrosion [1]-[3].

In this paper, in order to investigate the influence of the remaining amount of the rust on the coating film durability, the accelerated deterioration tests were carried out using the coated rusty steel plate. Furthermore, in order to grasp the influence of the corrosive factors on the coating film durability, outdoor exposure tests were conducted for one year on actual steel bridge located at a coastal area.

II. LABORATORY ACCELERATED DETERIORATION TEST

A. Test Method

A test piece with dimensions of 150 x 70 x 3.2 mm was prepared from JIS G 3101 SS400 cold-rolled steel plate which was sand-blasted. One side surface of test piece was coated by epoxy resin. The other bare surface of the test piece was corroded by the procedure of the salt water spraying test (SST). SST was executed using a 0.01 wt % NaCl solution for 168 or 840 hour according to the instructions prescribed in the Manual

of Painting-design and Application for Steel Structure (MPASS) [4].

Three methods of the surface preparation on corroded surface are selected as follows. Fig. 2 shows the corroded surface after each surface preparation.

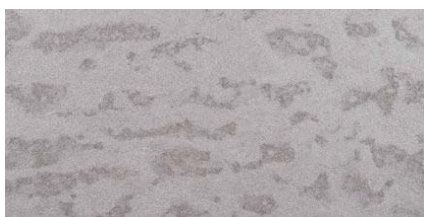
- Wire Brushing was applied to the steel surface to remove rust particles. The rust layer adhering tightly to the steel substrate was not removed by wire brushing.
- Wire Brushing + Cup Wire Treatment: After a) Wire brushing, the rust layer adhering tightly to the steel substrate was removed by cup-wire which was driven by electric motor. Cup-wire treatment was continued until any more rust particles are not removed. The rust layer was slightly remaining on the steel substrate.
- Wire Brushing + Cup Wire Treatment + Blast Treatment: After b) Wire brushing and cup wire treatment, the rust remaining on the steel substrate was almost removed by blast treatment. A preparation grade is Sa 2 according to the instructions prescribed in ISO 8501-1.



(a) Wire Brushing



(b) Cup Wire Treatment



(c) Blast Treatment

Fig. 2 Appearance of Corroded Surface after Each Surface Preparation

Then, in order to grasp the chemical components of the rust layer, the rust which remained on steel substrate after wire brushing was quantitatively analyzed by X-ray diffraction.

The steel surface was painted after the surface preparation. The applied coating system was B-7 type or T-7 type according to MPASS. B-7 type consists of Pb and Cr-free rust inhibiting paint and long oil phthalic resin paint, and T-7 type consists of

epoxy resin paint and polyurethane resin paint. The service life of B-7 type is expected for 15 years in a standard atmospheric environment, and T-7 type has the longer term durability than B-7 type. Table I shows the painting process of respective coating system.

TABLE I
PAINTING PROCESS OF EACH COATING SYSTEM

	B-7 type	T-7 type
1st layer	Pb, Cr-free rust inhibiting paint (35 μ m)	High build type epoxy resin paint (60 μ m)
2nd layer	Pb, Cr-free rust inhibiting paint (35 μ m)	High build type epoxy resin paint (60 μ m)
3rd layer	Long oil phthalic resin paint (25 μ m)	High build type epoxy resin paint (60 μ m)
4th layer	Long oil phthalic resin paint (20 μ m)	High build type polyurethane resin paint (50 μ m)

The combined cyclic test (CCT) defined in the MAPSS was used for the laboratory acceleration deterioration test. A single cycle of this acceleration test consisted of four processes as exhibited in Fig. 3 a) exposure to an ozone atmosphere which aimed for acceleration of coating-layer degradation and promotion of water absorption of the coating layer, b) spraying with synthetic sea water, c) spraying with simulated concentrated rainwater, and d) drying, all of which (b), c), d) aimed at promoting corrosion of the steel substrate.

After each CCT cycle, the state of blistering of the coating was inspected visually using photographic images. The area ratio of blistering was estimated based on digitalization of the obtained photographic image.

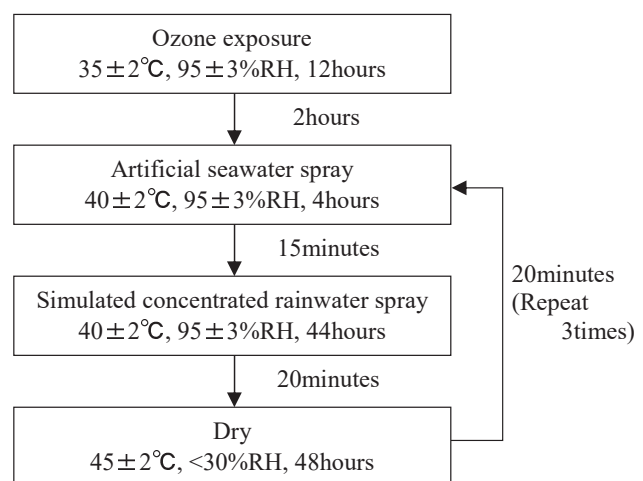
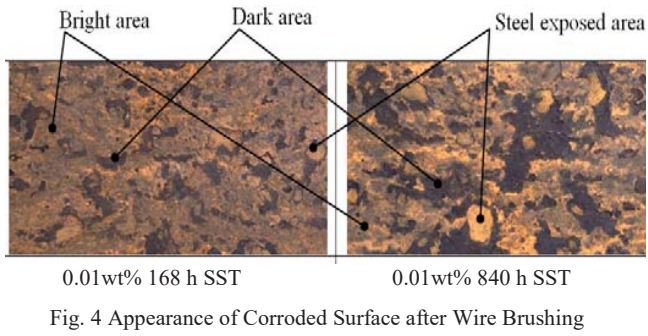


Fig. 3 Test cycle of CCT in MPASS

B. Result and Discussion

The surface appearance after removal by wire blushing was shown in Fig. 4. The rust layer tightly adhering to the steel substrate roughly distinguished two images: a bright area and a dark area. In addition, some surface areas had an exposed steel substrate. In Fig. 4, it is also find that dark areas and the exposed steel substrate tended to increase by prolonging the SST time duration.



had little formed on the specimen painted after blast treatment. Accordingly, it was confirmed that the remaining amount of the rust layer had large influence on the coating film durability.

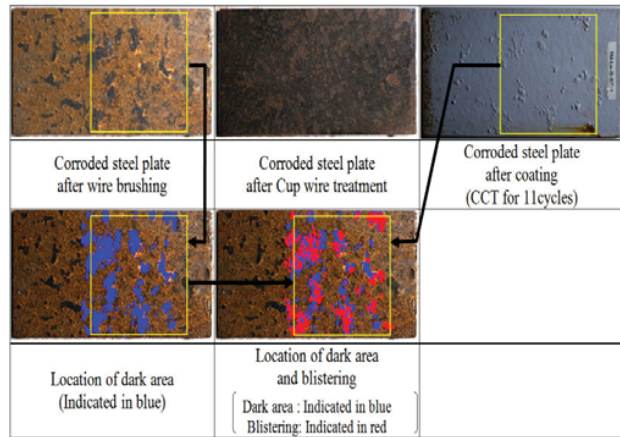


Fig. 5 Relationship of dark area and blistering of coating (Corroded steel plate by SST for 168 h)

Table II shows the X-ray diffraction result of the rust in a dark area or a bright area. The rust in a dark area contained β -FeOOH which was formed by existence of a chloride ion in the rust. Accordingly, it was considered that the rust in a dark area contains more amount of chloride ion than that in a bright area.

TABLE II
X-RAY DIFFRACTION RESULT OF THE RUST

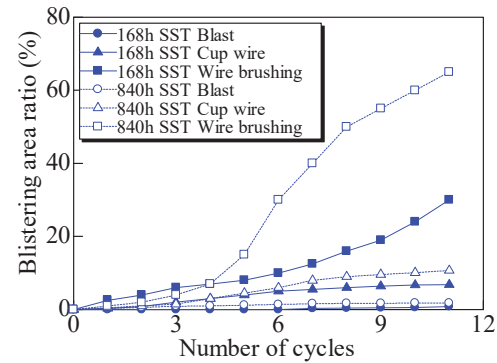
Area	Crystalline component	168h	840h
Dark area	α -FeOOH	1.6 %	1.6 %
	β -FeOOH	1.2 %	0.3 %
	γ -FeOOH	0.6 %	0.8 %
	Fe_3O_4	29.6 %	20.3 %
Bright area	α -FeOOH	3.2 %	2.7 %
	β -FeOOH	0.0 %	0.0 %
	γ -FeOOH	1.3 %	2.6 %
	Fe_3O_4	24.2 %	21.1 %

Fig. 5 shows appearances of 168 h SST and cup wire treatment specimens after 11 CCT cycles. The blistering tended to develop around the dark area detected after preliminary wire brushing. It was reported that the dark area of the surface image corresponded to the area with enriched Fe_3O_4 as a consequence of reduction of β -FeOOH and the amorphous constituent measured by XRD (X-ray diffraction). As well, due to localized enrichment of chloride ion in such area, macro cell corrosion must have been promoted with the steel substrate/rust interface as the anode and the top surface of rust as the cathode [5].

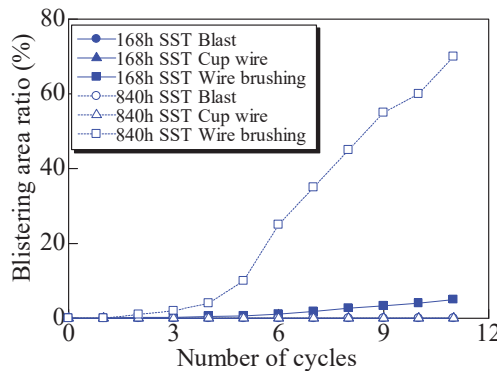
Taking into account this result, the dark area must refer to the anodic zone with enriched chloride ion. The volume of the rust increase based on the conversion of β -FeOOH and the XRD amorphous rust constituent to Fe_3O_4 by the reduction reaction. Thus, the Fe_3O_4 formed by the reductive reaction becomes porous. When the steel surface coated over remaining Fe_3O_4 , moisture penetrates into the rust through the coating film by the osmotic pressure. Therefore, it was estimated that the dark area was highly vulnerable to under-film corrosion.

Fig. 6 and Table III show the relationship between the measured blistering area ratio during the CCT and the number of cycles. For most of the specimens, it is seen that the blistering area ratio tended to increase with increasing number of cycles. On the other hand, the blistering was little formed on the specimens to which T-7 type was applied after cup wire or blast treatment.

In the case of B-7 type applied specimen, the blistering was most formed on the specimens painted after wire brushing, and



(a) B-7 type



(b) T-7 type

Fig. 6 Blistering Area Ratio during the CCT as a Function of the Number of Cycles

TABLE III
BLISTERING AREA RATIO DURING THE CCT FOR 11 CYCLES

	Surface preparation	Blistering area ratio (%)	
		B-7 type	T-7 type
0.01wt% 168 h SST	Wire Brushing	30.0	5.0
	Cup Wire Treatment	6.8	0.0
	Blast Treatment	0.8	0.0
0.01wt% 840 h SST	Wire Brushing	65.0	70.0
	Cup Wire Treatment	10.7	0.0
	Blast Treatment	1.8	0.0

The blistering was more formed on the specimens of B-7 type application than those of T-7 type application. The result was attributed to the durability of each coating system. On the other hand, the same degree of blistering was formed on the 840 h SST specimens painted either coating system after wire brushing, then it was confirmed that the durability of each coating film had drastically degraded. Furthermore, in the case of comparing for the same number of cycles, the blistering degree appeared to be more severe for specimens after 840 h SST than 168 h SST. It is reported that the longer the SST duration, the higher the chloride ion content in the rust [6]. Thus, it is suggested that salt in the rust yielded by undercoat corrosion is harmful to the durability of the coating.

III. OUTDOOR EXPOSURE TESTS

A. Test Method

We prepared coated corroded-steel plates and uncoated steel plates as the test specimens. The reasons uncoated steel plates applied were to estimate the influence of sea salt and the steel corrosion rate at the each position on which specimen set up.

The test pieces with dimensions of 75 x 70 x 3.2 mm were prepared from JIS G 3101 SS400 cold-rolled steel plate which was sand-blasted. As for the coated corroded steel plates, one side surface of test piece was coated by epoxy resin. The other bare surface of the test piece was corroded by the SST. Salt water spraying test was done using a 0.01 wt % NaCl solution for 840 h. After the surface preparation using wire brushing (Fig. 7), the corroded steel surface was painted. The applied coating system was B-7 type or G-7 type according to MPASS. G-7 type consists of epoxy resin paint and has the durability equivalent to that of T-7 type. Table IV shows the Painting process of G-7 coating system.



Fig. 7 Appearance of Corroded Surface before Painting (840 h SST, wire brushing)

TABLE IV
PAINTING PROCESS OF EACH COATING SYSTEM

	B-7 type	G-7 type
	1st layer	Pb, Cr-free rust inhibiting paint (35 μ m)
2nd layer	Pb, Cr-free rust inhibiting paint (35 μ m)	High build type epoxy resin paint (60 μ m)
3rd layer	Long oil phthalic resin paint (25 μ m)	High build type epoxy resin paint (60 μ m)
4th layer	Long oil phthalic resin paint (20 μ m)	High build type epoxy resin paint (60 μ m)

Outdoor exposure tests were conducted for one year on actual steel bridge located at a coastal area. Fig. 8 shows the appearance of the actual steel bridge. The distance between the bridge and the coast is approximately dozen meter; it was reported that there was a highly corrosive environment [7]. Fig. 9 indicates the outline of the set up position of each specimen. Uncoated steel plate had set up on the I girder at the all surface direction except for upper surface of the upper flange (S2~S8, M2~M8). Coated corroded-steel plate had set up at the web plate and lower surface of the lower flange (S3, S5, S7, M3, M5, M7). The exposure period was around one year from November 2013 to October 2014.

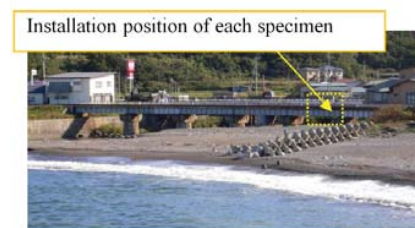


Fig. 8 Appearance of the Steel Bridge

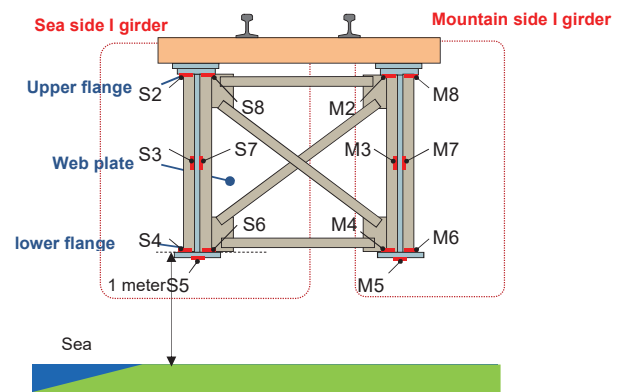


Fig. 9 Outline of the Installation Position of Each Specimen

In order to determine the amount of chloride ion in the rust layer which was formed on the uncoated steel plates, the chloride ion was eluted into KNO₃ solution by the electrolysis using corroded steel plate as anode electrode. The concentration of chloride ion was measured in the eluted solution.

A mean corrosion depth was calculated using the uncoated steel plate weight before and after exposure by an expression

(1). In order to remove the rust layer from the uncoated steel plate after exposure, the specimen was soaked in boiling 10wt% di-Ammonium hydrogen citrate solution for 30~60 minutes and the rust layer was dissolved.

$$D_{mean} = \frac{W_1 - W_2}{d_{Fe} \times S} \quad (1)$$

D_{mean} : Mean corrosion depth of specimen, W_1 : Weight of specimen before exposure, W_2 : Weight of specimen after removing the rust layer formed by exposure, d_{Fe} : The specific gravity of iron (7.85), S : Surface area of specimen

After exposure of coated corroded steel plate, the state of blistering of the coating was inspected visually using photographic images. The area ratio of blistering was estimated based on digitalization of the obtained photographic image.

B. Result and Discussion

Fig. 10 shows the measurement results of the mean corrosion depth and the amount of chloride ion in the rust layer of uncoated steel plates. And Table V compares the mean corrosion depth and the amount of chloride ion in the rust layer of uncoated steel plates and the blistering area ratio of coated corroded-steel plate.

It was confirmed that there was a significant correlation between the mean corrosion depth and the amount of chloride ion in the rust layer, and the respective results were significant on the specimen which had set up on a surface facing to the sea (ex. M3) and on underside of the member on which the adhered salt hardly be washed by a rainfall (ex. S5, M5). Furthermore, the results of the specimen which had set up on the web plate facing to the sea (S3) were relatively small. It was considered that the sea salt adhered in such position was easily washed-off by a rainfall. On the other hand, the blistering was formed on all the coated corroded-steel plates. The blistering area ratio indicated different trends as compared to the mean corrosion depth and the amount of chloride ion of uncoated steel plates. All specimens applied B-7 type indicated similar results of blistering area ratio. In the case of G-7 type, the blistering area ratio tended to increase on the specimens which were installed on the front surfaces facing to the sea (S3, M3).

It is reported that moisture and oxygen passes through the coating film; however, anions such as chloride ion hardly pass through the coating film [8]. Moreover, the gas-barrier performance of coating film is different depending on the coating systems. Therefore, it is estimated that the main factors of under-film corrosion are coating performance such as gas-barrier performance and durability against environment factors such as water vapor and temperature. The salt which significantly influences on the uncoated steel plate is not directly related to the under-film corrosion.

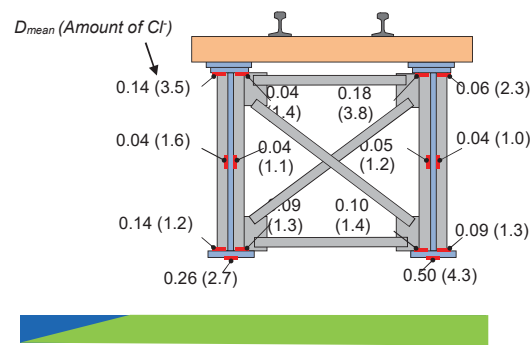


Fig. 10 Mean Corrosion Depth and the Amount of Chloride Ion of Uncoated Steel Plates

TABLE V
RESULT OF EACH SPECIMEN

Position	Uncoated steel plate		Coated corroded-steel plate (Blistering area ratio)	
	Mean corrosion depth (mm)	Amount of chloride ion (g/m ²)	B-7 type	G-7 type
S2	0.14	3.5		
S3	0.04	1.6	10%	30%
S4	0.14	1.2		
S5	0.26	2.7	20%	5%
S6	0.09	1.3		
S7	0.04	1.1	15%	3%
S8	0.04	1.4		
M2	0.18	3.8		
M3	0.05	1.2	25%	20%
M4	0.10	1.4		
M5	0.50	4.3	25%	3%
M6	0.09	1.3		
M7	0.04	1.0	20%	4%
M8	0.06	2.3		

IV. CONCLUSION

In order to examine the influence of the remaining amount of the rust on the coating film durability, the laboratory accelerated deterioration tests carried out with use of the coated rusty steel plate. Furthermore, in order to clarify the influence of the corrosive factors on the coating film durability, outdoor exposure tests were conducted for one year on actual steel bridge located at a coastal area. The main findings of this research are summarized as follows.

1. From the accelerated deterioration tests, blistering of the coating tended to emerge in and around the dark area in the corrosion product, and the degree of blistering damage based on the rust layer growth seemed to vary depending on the SST duration.
2. After surface preparation by the power tool, the blistering of the coating hardly occurred in the specimen which was applied the epoxy resin paint through accelerated deterioration tests.
3. From the exposure test results, the corrosion rates of the uncoated steel plates which were set up on the underside of

the member was relatively high and have close correlation with the amount of salt in the rust.

4. The vertical surface of the web plate indicated the most promoted under-film corrosion. Thus, it was confirmed that under-film corrosion rate was different from corrosion rate of the uncoated steel.

ACKNOWLEDGEMENT

The authors were appreciated to Dr. Mikiya ITO for review and useful suggestion to this paper.

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