Corrosion Resisting Steel Eco-view Plus^{TM}, a Repaint Term Extension under High Humid Environment

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Abstract

In transportation infrastructure such as bridges, there is demand for reduction of life-cycle costs from construction through to rebuilding. For steel bridges, a key challenge is addressing corrosion under paint coatings, particularly in areas exposed to harsh environments, such as girder ends and edges. "Eco-view Plus" is a corrosion-resisting steel that contains Ta, Mg, and rare earth metals (REM) which inhibit the underfilm corrosion of steel by enhancing the corrosion resistance of inclusions, and promoting the formation of zinc rust by zinc-rich paint which shields steel surface and the coating-steel interface from corrosive environments. Eco-view Plus can extend the time for the growth of coating blisters to approximately twice than that of conventional steel materials. Its application to girder ends and edges is therefore expected to significantly reduce the life-cycle cost of steel bridges.

Introduction

In the transition toward a sustainable society, it is highly important to account for the life-cycle cost (LCC) of roadway infrastructure such as bridges. The LCC factors in the labor needs and financial aspects of construction, maintenance, repair, and replacement. A primary cause of damage in steel bridges is the corrosion of the steel itself. Therefore, to reduce the LCC of these structures, the steel must have better corrosion resistance, and the coating must inhibit corrosion.[1), 2)] Stormwater and sediment from the surface of the road infiltrate bridges at the girder ends in particular, as shown in **Fig. 1**. Corrosion promoting agents such as moisture and salt stagnate in these poorly ventilated, enclosed areas for extended periods, creating an adverse corrosion environment. This makes the interface between the steel plate and the coating prone to underfilm corrosion.[3)] The corrosion protection afforded by the coating then degrades, and periodic recoating is necessary. The associated maintenance costs have prompted ample research into various countermeasures.[4), 5), 6)] Using steel with superior resistance to underfilm corrosion (i.e., underfilm corrosion-resistant steel) in areas exposed to such adverse corrosion environments could extend the period before repainting is necessary and thus reduce the LCC.[7)]

Kobe Steel has been a trailblazer in developing underfilm corrosion-resistant steel designed to extend the period until repainting is necessary. We helped reduce the LCC of bridges in commercializing Eco-View, a steel with underfilm corrosion suppression functionality.[8), 9)] We also developed Eco-View Plus [Note)] to further improve corrosion resistance particularly at the plate edges of bridges, where the paint tends to become thinner, and at their girder ends, where the corrosion environment is particularly adverse. This underfilm corrosion-resistant steel combines the enhanced corrosion resistance of the steel itself with the corrosion prevention functionality of the paint. This product significantly extends the period until a bridge must be repainted to ensure functionality. Eco-View Plus is expected to reduce the LCC of bridges, particularly in regions with adverse corrosion environments, such as coastal areas with high airborne salinity as well as regions that see high usage of deicing agents due to heavy snowfall.[10)] This steel exhibits good weldability and impact resistance, and yields welding joints with good tensile properties. It also meets the base material

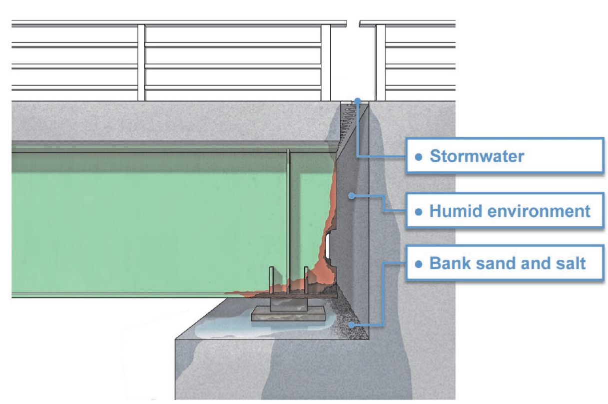


Fig. 1 Image of corrosion environment at girder ends of bridges

[Note)] Registered trademark of Kobe Steel, Ltd. (6769816) standards of JIS SM and SBHS for rolled steel for welded bridge structures, so it can be handled in the same way as conventional steel.[11)] This paper introduces the mechanism behind the characteristic underfilm corrosion resistance function of Eco-View Plus and its effect on extending the period until repainting is necessary.

1. Characteristics of Eco-View Plus

Eco-View Plus shares Eco-View's base composition of Cu-Ni-Ti. However, it exhibits improved corrosion resistance by including certain amounts of Ta, Mg, and REMs (rare earth metals; Ce, La) to protect the surface of the steel against corrosion environments. **Fig. 2** shows the mechanism of underfilm corrosion in typical steels and the mechanism of underfilm corrosion suppression in Eco-View Plus. The coating system is assumed to be a heavy-duty anti-corrosion coating, which has become standard in recent years.[12)] Unevenness and flaws in coatings often occur at the corners and edges of coated steel structures, creating initiation points for corrosion promoting agents such as moisture to penetrate the surface of the steel and cause corrosion. When conventional steel corrodes, the coating blisters and cracks as rust primarily composed of Fe forms and grows under the coating. Conversely, Eco-View Plus contains additives that suppress Fe rust and enhance the capacity of the Zn-rich paint to promote white rust, in turn preserving the surface of the steel. In this way, Eco-View Plus boosts the corrosion prevention functionality of the paint and suppresses underfilm corrosion.

This section covers the mechanism behind improving the underfilm corrosion resistance of steel by adding Ta and Mg and details the validation via testing.

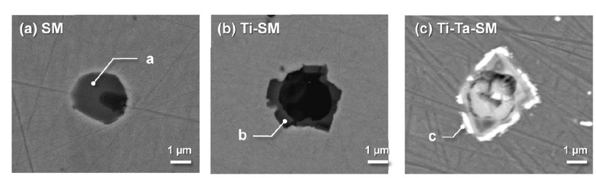
1.1 Enhancing the corrosion resistance of steel by neutralizing the corrosion initiation points

Steel typically contains inclusions made up of trace elements present in the base metal. If these inclusions are more soluble than the steel, they can serve as corrosion initiation points.[13)] Some studies have reported that adding elements to the steel can modify the inclusions by electrochemically stabilizing them, thereby preventing them from becoming corrosion initiation points.[14)-16)] Therefore, using JIS G3106 rolled steel for welded structures as the reference steel (abbreviated "SM" in this paper), we conducted research to identify elements that can render insoluble the inclusions that serve as corrosion initiation points.

As **Table 1** shows, we observed inclusions made up of elements such as S, C, and Mn on the surface of the SM steel. By contrast, in the Ti-SM steel (Ti added to SM), compounds primarily composed of Ti precipitated on the surface of the inclusions. Similarly, we confirmed that in the Ti-Ta-SM steel (Ti and Ta added to SM), compounds primarily

Table 1 SEM image and elemental composition of inclusions on(a) SM, (b) Ti-SM, (c) Ti-Ta-SM

SEM image



Point	Elemental composition (at%)								
	C	N	Al	S	Ca	Ti	Mn	Fe	Ta
a	30	-	-	21	2	-	21	25	-
b	18	20	2	1	1	50	-	8	-
c	35	6	-	-	-	20	-	24	15

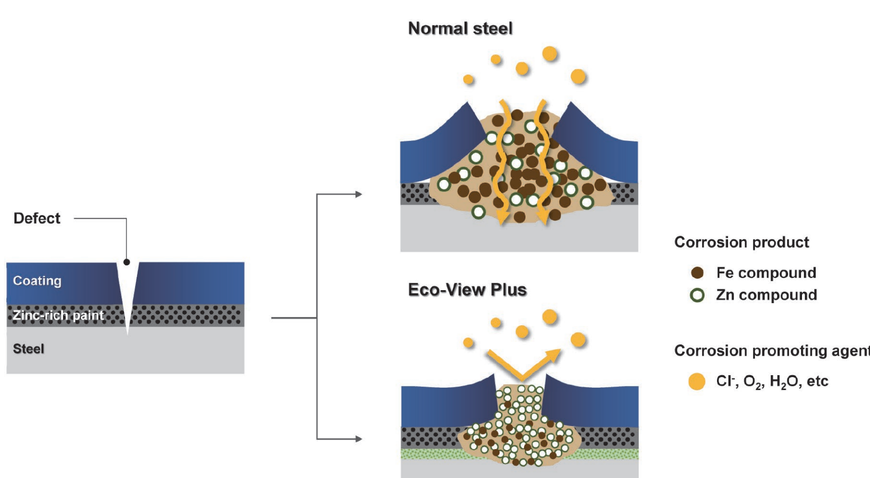


Fig. 2 Inhibition mechanism of under-film corrosion of Eco-View Plus

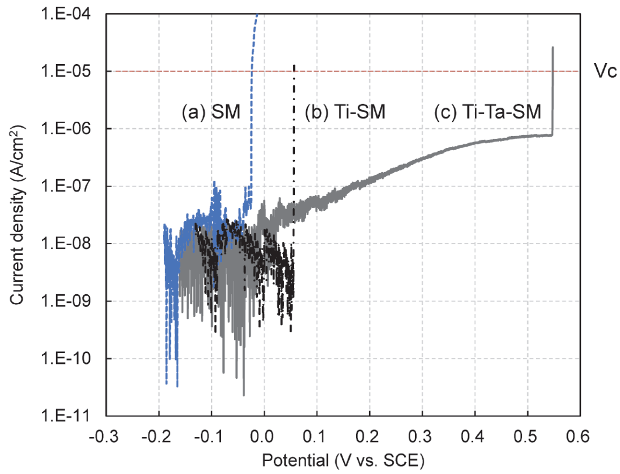


Fig. 3 Anodic polarization curves of (a) SM, (b) Ti-SM, (c) Ti-Ta-SM

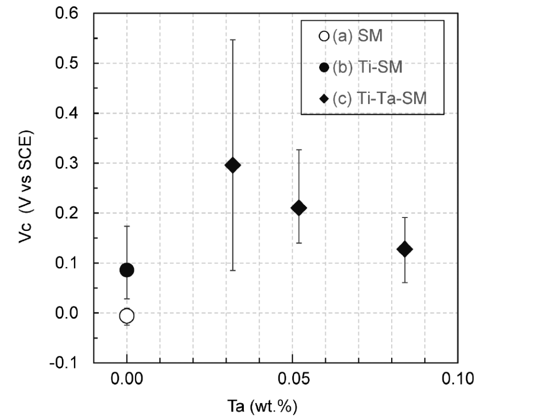


Fig. 4 Relationship between Vc and Ta content of steels (a) SM, (b) Ti-SM, (c) Ti-Ta-SM

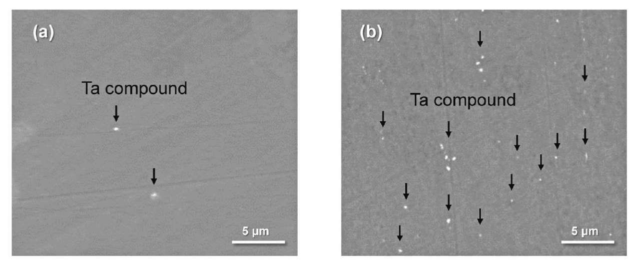


Fig. 5 SEM image of inclusions in Ti-Ta-SM with different Ta content (a) Ta 0.03wt%, (b) Ta 0.08wt%

comprising Ti and Ta precipitated on the surface of the inclusions. These results suggest that added Ti and Ta coat inclusions effectively.

Next, we conducted polarization tests to measure the corrosion initiation potential of each steel, which confirms the degree to which the added Ti or Ta improves the corrosion resistance of inclusions. The test was conducted in an aqueous solution of 0.15M H_3BO_3-0.0375M $Na_2B_4O_7$-0.010M NaCl at 25℃ per JIS G0577, "Methods of pitting potential measurement for stainless steels." The potential at which the current density during anodic polarization exceeded 10^{-5} A/cm^2 was taken to be the corrosion initiation potential (Vc) of the steel. As **Fig. 3** shows, while the Vc of the SM steel was -0.024 V, that of the Ti-SM steel was 0.056 V, indicating an increase in the corrosion initiation potential. Furthermore, the Vc of the Ti-Ta-SM steel was 0.55 V, suggesting a significant improvement in the steel's corrosion resistance. These results indicate that adding Ti or Ta provides electrochemical stabilization by coating the surface of inclusions, and that the combined addition of both elements yields a particularly large effect.

Fig. 4 shows the average Vc from five measurements as a function of the amount of Ta added to the steel. The Ti-Ta-SM steel with an added Ta content of 0.03% had a higher Vc compared with the SM and Ti-SM steels, indicating improved corrosion resistance. However, no further improvement in corrosion resistance was observed with higher levels of added Ta. **Fig. 5** shows images of the inclusions in Ti-Ta-SM steels with different Ta contents. These images show that more Ta compound precipitates with a higher Ta content. These results indicate that there is an upper limit to the effect of coating inclusions by adding Ta. Excessive addition causes the precipitation of Ta compounds that do not coat inclusions, in which case the effect on corrosion resistance has reached saturation.[14]

The results of this study indicate that appropriate amounts of added Ti and Ta can coat inclusions that serve as corrosion initiation sites, thereby improving the corrosion resistance of the steel.

1.2 Providing a barrier against corrosion environments by coordinating with coating composition

Zinc-rich paint, which has recently become standard as a base coating for bridges, has metallic zinc particles that impart steel with sacrificial protection against corrosion. Dissolved zinc forms corrosion products (white rust) that cover the surface of the steel, creating a barrier against the corrosion environment. It has been reported in particular that basic zinc compounds (white rust) formed in the presence of basic compounds containing Mg provides excellent protection because it is chemically stable and has a dense crystalline structure.[17] Therefore, we added Mg to steel sheet and studied how this affected the environmental barrier effect of white rust formed under Zn-rich paint.[18]

The SM and Mg-SM steels were primed with zinc-rich paint (thickness 35 μm) and top-coated with a polyurethane coating (thickness 25 μm). We used a utility knife to make cross-cuts in the dried coating to simulate damage and thin areas that occur during application. We subjected the specimens to a 1.5-year outdoor exposure test at the Japan Weathering Test Center in Miyakojima City, Okinawa Prefecture. The topcoat was clear so it would be possible to visually observe the formation of underfilm corrosion.

Fig. 6 shows the change in the appearance of the SM and Mg-SM steels during exposure testing. The SM steel exhibited reddish-brown Fe rust around the cross-cuts after three months of exposure. The Mg-SM steel exhibited less Fe rust than the SM steel. After nine months, Fe rust had formed in the cross-cut and the intact painted surface of the SM steel. By contrast, the cross-cut of the Mg-SM steel exhibited white rust. After 15 months, Fe rust had spread over almost the entire surface of the SM steel, and there was significant blistering and peeling of the paint. Although the Mg-SM steel also developed rust in the intact painted area, it was primarily basic Zn compounds, meaning that the corrosion products are substantially different.

Fig. 7 shows images of the cross-sections of the specimens' damaged areas after the exposure test alongside the results of the chemical analysis. In the SM steel, thick Fe rust formed between the white rust and the base metal, confirming that Cl penetrated into the Fe rust. By contrast, basic Zn compounds grew to cover the surface of the Mg-SM steel, inhibiting the formation of iron rust. Furthermore, most Cl had concentrated on the surface of the basic Zn compounds rather than penetrating into it.

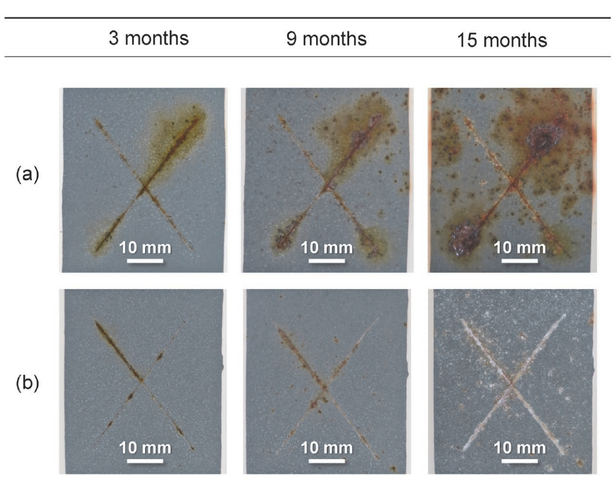


Fig. 6 Appearance of painted steels of (a)SM and (b)Mg-SM during exposure test at Miyakojima

Table 2 shows the crystallite phases and diameters of the corrosion products formed on the surfaces of the specimens as determined by X-ray diffraction. Unlike the SM steel, the Mg-SM steel did not have FeOOH-based compounds, the main component of Fe rust. Instead, it showed a high proportion of basic zinc compounds such as simonkolleite and gordaite. Additionally, the crystallite diameter of the gordaite was smaller in the Mg-SM steel than in the SM steel. These results indicate that adding Mg to steel promotes the formation of basic zinc compounds in corrosion environments, thereby affording high corrosion resistance.

1.3 Protection at the coating/steel interface

REMs react with water to form a dense precipitate of hydroxides, which improves corrosion resistance by serving as a protective coating on the surface of the steel.[19] As such, when moisture penetrates the coating/steel interface of steel with REM additives, it reacts with the REMs in the steel to form a dense coating on the surface of the steel. This coating should afford protection at the steel/coating interface. The increased corrosion potential of steel has been confirmed based on polarization tests in aqueous solutions with REMs. We will detail the effects of REMs on another occasion.

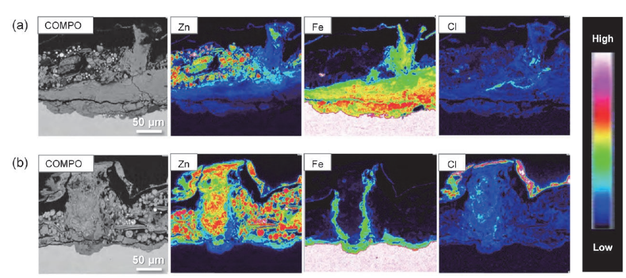


Fig. 7 Cross-sectional images of corrosion product of (a) SM and (b) Mg-SM after exposure test

Table 2 Composition and crystallite size of corrosion products of steels after exposure test

Corrosion products		SM		Mg-SM	
		Fraction (%)	Crystallite diameter (nm)	Fraction (%)	Crystallite diameter (nm)
Fe based compound	α-FeOOH (Goethite)	31.6	20.7	-	-
	β-FeOOH (Akaganeite)	19.3	27.6	-	-
Zn based compound	$Zn_5(OH)_8Cl_2H_2O$ (Simonkolleite)	-	-	20.6	66.6
	$NaZn_4(SO_4)Cl(OH)_6(H_2O)_6$ (Gordaite)	8.9	95.4	26.1	57.1
	ZnO (Zincite)	35	36.7	45.2	35.8
	Metal Zn	5.2	-	8.0	-

2. Developing Eco-View Plus

As explained in Section 1, Ta and Mg improve the corrosion resistance of steel and provide a barrier against corrosion environments through different mechanisms. By incorporating these elements and REMs into Eco-View, Kobe Steel's underfilm corrosion-resistant steel should yield excellent durability in adverse corrosion environments such as the girder ends of bridges. This concept served as a springboard in developing Eco-View Plus, a steel that provides underfilm corrosion resistance in high-humidity environments. This section introduces the results of evaluating Eco-View Plus in terms of underfilm corrosion resistance as well as the expected extension of the period before repainting is necessary.

2.1 Evaluating underfilm corrosion resistance via cyclic corrosion testing (CCT)

We used CCT to evaluate the underfilm corrosion resistance of the SM steel and Eco-View Plus with the compositions shown in **Table 3**. Our coating for the test was based on the C5 corrosion protection rating, which is currently standard for bridges. The three-layer structure of the coating comprised a zinc-rich paint as the anti-corrosion base coat, an epoxy-based intermediate coat, and a fluoropolymer topcoat. To shorten the test period, we applied a thinner coating than usual.[20] Steel specimens were iteratively exposed to cycles of salt spray, humidity, and air drying. We measured the coating blister length and area around the cross-cuts every two weeks. To simulate the environment at the girder ends of bridges, we based the conditions of CCT on JIS K 5600-7-9 Cycle D, making adjustments according to the results of environmental monitoring at the girder ends of bridges as shown in **Table 4**.[21]

Fig. 8 shows the cross-cuts after 16 weeks of CCT. Reddish-brown Fe rust developed near the cross-cut of the SM steel. Additionally, swelling of rust due to underfilm corrosion caused the coating to blister. Conversely, the Eco-View Plus was white near the cross-cut. This result is similar to the exposure test described in Section 1.2 and confirms that white rust formed and iron rust was suppressed. Furthermore, the blister length and area were smaller than those of the SM steel.

2.2 Effect on extending the period until repainting is necessary

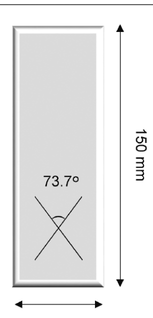
Fig. 9 shows the change over time in the blister length and blister area at the cross-cut of each steel. Eco-View Plus tends to suppress increases in blister length and area compared with the SM steel. For example, the time required to reach a blister length of 5.0 mm was about 1.5 times longer for Eco-View Plus (10.3 weeks for SM steel, 15.5 weeks for Eco-View Plus) (Fig. 9(a)).

In determining the service life of coatings on steel sheets, various approaches have involved predicting the time required to reach a certain deterioration area by using a coating deterioration curve to regress the change in coating blister area over time.[22]

Table 3 Chemical compositions of SM and Eco-View Plus

Steel	Elemental composition (wt%)									
	C	Si	Mn	P	S	Cu	Cr	Ni	Ti	Others
SM (JIS G3106)	0.17	0.36	1.38	0.015	0.003	0.01	0.04	0.01	0.001	-
Eco-View plus	0.05	0.30	1.24	0.010	0.001	0.70	<0.01	0.48	0.05	Ta, REM, Mg

Table 4 Cyclic corrosion test (CCT) conditions

Sample image	Surface preparation	CCT process	Environment	Time
	Sand blast • ISO Sa2 1/2	Salt spray	30°C ± 2°C 5% NaCl	0.5 h
		Condensation humidity	30°C ± 2°C 95 ± 3%RH	2.5 h
	Coating • Inorganic zinc 35 μm • Epoxide (Clear) 20 μm • Fluoride (Clear) 20 μm	Air drying 1	50°C ± 2°C 20 ± 3%RH	1.5 h
		Air drying 2	30°C ± 2°C 20 ± 3%RH	1.5 h

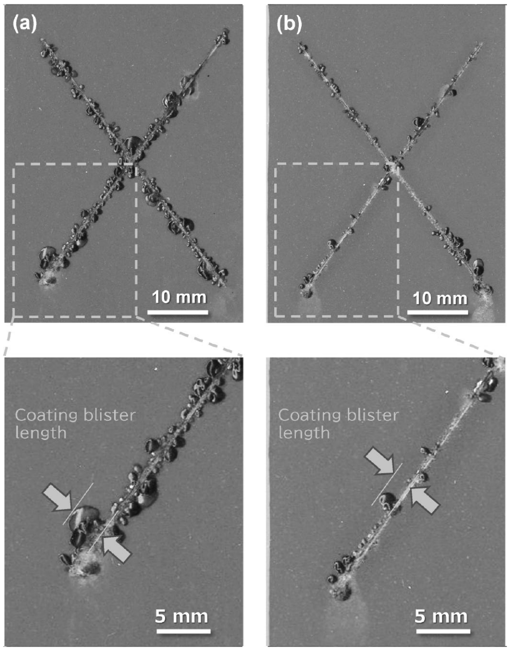


Fig. 8 Appearance of painted steels of (a) SM and (b) Eco-View Plus after 16 weeks of CCT

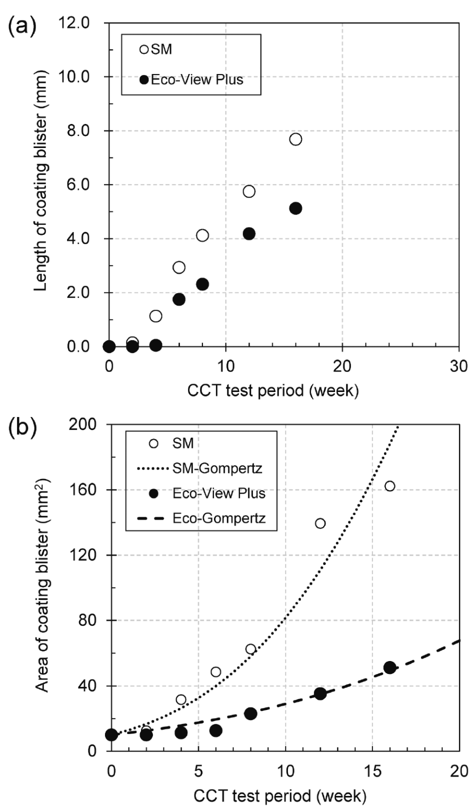


Fig. 9 Changes in (a) maximum length and (b) total area of coating blister on steels during CCT

A Gompertz curve[23] can be used to estimate long-term deterioration behavior based on early-stage coating deterioration results such as those obtained in this study. Therefore, we estimated the period until repainting is necessary using the Gompertz curve resulting from Equation (1).

Table 5 Prediction results of repainting cycles on steels with Gompertz curve

Steel	K (mm^2)	a	b	Correlation coefficient	$t_{6.6}$ (week)
SM	2,000	0.005	0.9982	0.94	14
Eco-View Plus	2,000	0.005	0.9992	0.89	29

$$y(t) = K \cdot a^{b^t} \quad \cdots\cdots (1)$$

Here, y(t) = blistered area of the coating (mm^2)
K = evaluation area (mm^2)
t = test duration (weeks)
a, b = constants ($0 < a, b < 1$)

Note that y(t) represents the deterioration area of the steel and is defined as the area with Fe rust. K is 2,000 mm^2 (50 mm long × 40 mm wide) to encompass the entire cross-cut area as shown in Table 4. The early-stage deterioration area ratio (a at t = 0) was defined as 0.5%. Fig. 9(b) and **Table 5** show the results of regression analysis using a Gompertz curve for the time-dependent change in blister area. The standard period until repainting is necessary is regarded as the period until the blister area reaches 6.6 - 36.8% of the total painted surface.[23] Calculating the time required for each steel to reach the minimum threshold of 6.6% (t6.6), that is, y = 132 mm^2, yields 14 weeks for the SM steel and 29 weeks for Eco-View Plus. This indicates that Eco-View Plus extends the period until repainting is necessary to approximately twice that of the SM steel in an environment simulating the girder end of a bridge.

Conclusions

We developed Eco-View Plus, an underfilm corrosion-resistant steel suitable for high-humidity environments. This steel exhibits high corrosion resistance even in the adverse corrosion environment at the girder ends of bridges. Eco-View Plus incorporates Ta, Mg, and REMs to (1) enhance the corrosion resistance of the steel via Ta, (2) provide a barrier against the corrosion environment via functional matching between Mg and the coating composition, and (3) protect the coating/steel interface via REMs. These benefits suppress underfilm corrosion on steel plates in high-humidity and high-salinity environments. Using this product in areas such as the girder ends of bridges, where coating life is short, extends the period until repainting is necessary. This reduces the management and maintenance costs necessary for maintaining bridge functionality, in turn reducing life cycle costs (LCC).

Acknowledgments

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