Protective Ability Index of Rust Layer Formed on Weathering Steel Bridge

* S. Hara¹, T. Kamimura², H. Miyuki², M. Yamashita³, and H. Uchida³

 ¹Investigation & Research Div., Sumitomo Metal Technology Inc., 1-8 Fusocho Amagasaki, Hyogo 660-0891, Japan
²Corporate Research and Development Laboratories, Sumitomo Metal Industries, Ltd., 1-8 Fusocho Amagasaki, Hyogo 660-0891, Japan
³Graduate School of Engineering, University of Hyogo, 2167 Shosha Himeji, Hyogo 671-2201, Japan

For a quantitative inspection on the performance of weathering steel bridges, we have investigated the relationship between the corrosion rate and the composition of the rust layers formed on weathering steel bridges located in various environments in Japan and applied a protective ability index (PAI) to the bridges. The corrosion rates were clearly classified by the PAI, α/γ^* and sub index of $(\beta+s)/\gamma^*$, where α , γ^* , β and *s* are the mass ratio of crystalline α -FeOOH, the total of γ -FeOOH+ β -FeOOH + the spinel-type iron oxide (mainly Fe₃O₄), β -FeOOH and spinel-type iron oxide, analyzed by powder X-ray diffraction, respectively. In the case of $\alpha/\gamma^*>1$, the rust layer works protective enough to reduce the corrosion rate less than 0.01 mm/y. The sub index $(\beta+s)/\gamma^*<0.5$ or >0.5 classifies the corrosion rate of the non-protective rust layers, therefore the former state of the rust layer terms inactive and the latter terms active. The quantitative inspection of a weathering steel bridge requires a performance-inspection (PI) and periodical deteriorationinspections (DI). The PI can be completed by checking of the PAI, α/γ^* . The DI on the weathering steel bridges where deicing salt is sprinkled can be performed by checking the PAI, $(\beta+s)/\gamma^*$.

Keywords : low alloy steel, weathering steel, atmospheric corrosion, X-ray diffraction, rust, protective ability index, deicing salt, chloride, bridge inspection.

1. Introduction

It is well known that weathering steel which contains a small amount of alloying elements such as Cu, Cr or Ni, has been widely used because of its unique ability to form a protective rust layer which lowers the corrosion rate of the steel. To minimize maintenance and cost by eliminating the need to paint, many bridges made of weathering steel have been built in the US, Europe and East Asia, especially in Japan since the 1960s. Today, this large stock of infrastructure, including other painted steel bridges and pre-stressed concrete bridges, is about to enter the maintenance period. Therefore, emphasis in civil engineering is shifting from construction to maintenance and rehabilitation of existing stock.^{1),2)}

It is well recognized that weathering steel is not maintenance-free but needs appropriate rehabilitation. Because a new design concept of weathering steel bridges requires a lifespan of at least 100 years,^{1),3),4)} periodical inspection is indispensable. During inspections, it is definitely important to quantitatively evaluate the protectiveness of the rust layer for the corrosion assessment of weathering steel bridges. Nevertheless, no useful, practical method has been established. Direct monitoring of the corrosion rate of steel bridges by thickness measurement is very difficult especially in a short time, because the accuracy of on-site thickness measurement is not acceptable for estimating the corrosion rate. Visual inspection is not quantitative, but is essentially a sensory test. Therefore, adequate judgment based on the inspection requires a specialist having sufficient experience.

In the last decade, estimation of the protective ability of the rust layer based on its composition formed on weathering steel, the Protective Ability Index (PAI), has been studied since Yamashita *et al.*^{5),6)} found that the composition of the rust layer changes with the duration of corrosion. The PAI α/γ * was well discussed by Kamimura et al.,^{7),8)} where α and γ are the mass ratio of

^{*} Corresponding author: hara-shu@smt-co.com

crystalline α -FeOOH, and the total of γ -FeOOH, β -FeOOH and spinel-type iron oxide, respectively. The PAI is expected to be useful as a quantitative criterion of the protective rust layer formed on weathering steel bridges. However, very few studies on the PAI of the rust layer formed on bridges in various atmospheres have been reported. Hara et al.⁹⁾ examined the PAI of the rust layer formed on bridges, and found a quantitative correlation between α/γ^* and the corrosion rate relating to the potential¹⁰ of steel covered with a rust layer in mountainous environments. However, less correlation was observed between the corrosion rate and α/γ^* at lower α/γ^* value.To extend these studies on evaluating the protectiveness of the rust layer formed on weathering steel, we investigated the PAI for bridges and the usefulness.¹¹⁾ The quantitative inspection for weathering steel bridges strongly requires both performance-inspection (PI) after a certain period and periodical deterioration-inspection (DI). In this paper we discussed the application of the PAI to some bridges. Then we investigated the relationships between soluble chloride concentration and the PAI of the rust laver formed on the bridge where de-icing salt was sprinkled.¹²⁾⁻¹⁴⁾ Finally we discussed the usefulness of the PAI as the quantitative indices of PI and DI.

2. Protective ability index (PAI) FOR BRIDGE

We have examined 21 bridges located in various atmospheric conditions such as rural, mountainous and coastal environments in Japan, exposed for various lengths of time (1.5-20 years). These bridges are made of JIS G3144 type weathering steel (SMA400W, 490W and 570W). From the relation between the corrosion rates and the composition of the rust layers, the protective ability index (PAI) for bridges was found. Finally we applied and verified the PAI to some bridges.

2.1 Corrosion rate estimation and rust analysis

We observed close-up photographs of the appearance of coupons whose corrosion loss was already known in the previous study¹⁵⁾⁻¹⁷⁾ and classified them into 5 appearance indices using the method which was developed by the Japan Iron and Steel Federation (JISF) and Japan Association of Steel Bridge Construction (JASBC).¹⁸⁾ We derived the correlation in Fig. 1. The corrosion rates of bridges were estimated using this correlation.

Rust analysis by X-ray diffraction (XRD) was carried out with a Rigaku Model-RU200 rotating anode X-ray generator operating at 30 kV and 100 mA with a Co target. On the bridge site, the rust layer on a certain area (approximately 0.01m^2) at the specified position such as web or

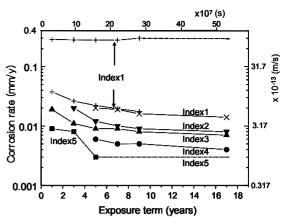


Fig. 1. Relationship between corrosion rates as a function of exposure term for each appearance index of coupons.

lower flange of the girders was scraped off to the steel surface using a sharp cutter-knife. The powdered rust was weighed with an electronic balance and desiccated for several days before testing. The powders (approx. 0.2 g) were analyzed after mixing with ZnO powder (approx. 0.05 g) as an internal standard. Relative mass fractions of α -, β - and γ -FeOOH and spinel-type iron oxides such as magnetite (Fe₃O₄) or maghemite (γ -Fe₂O₃), expressed by the symbols α , β , γ and s respectively, were quantitatively analyzed following the reference procedure.^{8),19}

2.2 Relationship between estimated corrosion rate and α/γ^*

Fig. 2 shows the relationship between the PAI, α/γ^* of the rust layer formed on the bridges and the estimated corrosion rates, where γ^* indicates the total mass ratio of γ , β and s. When α/γ^* was more than 1, the higher corrosion rate of more than 0.01 mm/y was not observed under any atmospheric conditions. When α/γ^* was less than 1, the corrosion rates were scattered and both the higher and lower corrosion rates were observed. Here, we labeled the above provisional domains in Fig. 2 with three Roman letters I, II and III as follows:

 $\alpha/\gamma * < 1$: corrosion rate is scattered higher than 0.01 mm/y (I) and lower than 0.01 mm/y (II). $\alpha/\gamma * > 1$: corrosion rate is not higher than 0.01 mm/y (III).

2.3 Classification of corrosion rate using $(\beta + s)\gamma^*$ in $\alpha/\gamma^* < 1$

The relationship between the corrosion rates and $(\beta + s)/\gamma^*$ of the rust layers of bridges under the condition of α/γ^* less than 1 is shown in Fig. 3 (a). In this case, the corrosion rate depended upon $(\beta + s)/\gamma^*$. If $(\beta + s)/\gamma^*$ was less than approximately 0.5, the corrosion rate never exceeded 0.01 mm/y, otherwise the corrosion rate was

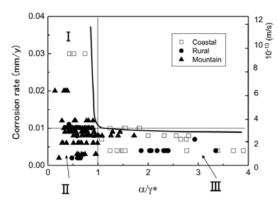


Fig. 2. Relationship between estimated corrosion rate and α/γ^* of the rust layer formed on the bridge. α and β^* are the mass fraction of α -FeOOH, and total mass fraction of γ -FeOOH, β -FeOOH and spinel, respectively.

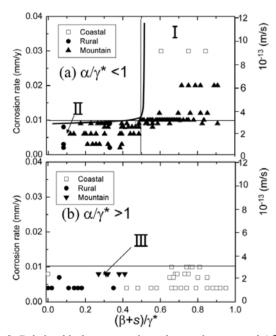


Fig. 3. Relationship between estimated corrosion rate and $(\beta + s)/\gamma^*$ of the rust layer formed on the bridge under the two conditions of which α/γ^* less than 1 and α/γ^* more than 1. The symbol β and s are the mass fraction of α -FeOOH and spinel-type iron oxide, and γ^* is the same as shown in Fig. 2. The designation of I, II and III are the same as shown in

more than approximately 0.01 mm/y. In contrast, under the condition of α/γ^* more than 1 shown in Fig. 3(b), the corrosion rate did not exceed 0.01 mm/y, indicating that the corrosion rate was independent of $(\beta+s)/\gamma^*$. The former fact indicates that $(\beta+s)/\gamma^*$ is an essential factor for classifying the corrosion rates when $\alpha/\gamma^* < 1$. The latter result confirms again that $\alpha/\gamma^* > 1$ shows that the rust layer is sufficiently protective against the corrosion

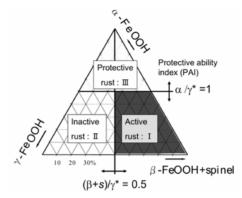


Fig. 4. Ternary diagram of composition of rust layer.

environment.

The protectiveness evaluation by both indices of α/γ^* and $(\beta+s)/\gamma^*$ of the rust composition can be classified using a ternary rust diagram of α , γ and $(\beta+s)$ as shown in Fig. 4. The active, inactive and protective rust layers correspond to categories I, II and III, which are characterized by β -FeOOH + spinel-type iron oxide rich, γ -FeOOH rich and α -FeOOH rich domains, respectively.

In conclusion, the PAI described by both α/γ^* and $(\beta+s)/\gamma^*$ is useful for a quantitative evaluation of the protectiveness of the rust layer. Thus, the PAI is an important item for checking the corrosion performance of weathering steel bridges.

2.4 Application of the PAI

To illustrate the usefulness of the PAI, we investigated the PAI and surface appearance in the weathering steel bridges used for 7 years in the mountainous region of Hyogo prefecture. The results are shown in Table 1. The rust layer classified into level-1 or level-2 by means of surface observation were successfully evaluated active by the PAI. However the rust layer classified into level-4 were evaluated inactive. The rust layer classified into level-5 was evaluated protective. By means of the PAI the rust layers were classified into active, inactive and protective rust layer independently of the surface appearance indices groups, respectively. This indicates that the appearance index classified into level-4 or level-5 is misjudged easily by the surface color of the rust layers.

In contrast, the PAI described by both α/γ^* and $(\beta +s)/\gamma^*$ is not influenced by the surface appearance. Thus the PAI can be supported as a quantitative evaluation index of the rust layer formed on weathering steel bridges.

3. Effect of chloride on DEicing SALT corrosion

We discuss in this section the relation between the PAI of the bridges where deicing salt is sprinkled in winter

Fig. 2.

Appearance Index	α -FeOOH mass%	β-FeOOH mass%	γ-FeOOH mass%	Fe ₃ O ₄ mass%	others mass%	PAI		
						α/γ*	$(\beta + s)\gamma *$	- evaluation
Level-1	8	4	3	8	77	0.5	0.8	Active
Level-2	8	5	3	1	83	0.9	0.7	Active
Level-3	11	2	10	0	77	0.9	0.2	Inactive
Level-4	10	3	8	1	78	0.8	0.3	Inactive
Level-4	11	2	11	0	76	0.8	0.2	Inactive
Level-5	17	1	11	0	71	1.4	0.1	Protective

3

Table 1. Comparison between Appearance index and PAI of rust layer formed on the weathering steel bridges.

and chloride ion concentration in the rust layer.

3.1 Bridges for investigation and characterization

Three bridges (S, U and H-bridge) located in a typical mountainous region (Kochi Expressway) of Japan were selected for this experiment. Their bridges have been in use for more than 10 years since 1992, and many partially thick and flaky rust layers (appearance index; level-2) have been found at lower flange surface position after 5 years. However good rust layers (appearance index; level-3) have been also found at web position.¹²⁾⁻¹⁴⁾

The chloride ion concentration (Cl⁻, *C*) of the rust layers was analyzed by ion chromatography using a DIONEX Model-2010i and the composition of the rust layers was also analyzed by means of X-ray diffraction. The soluble chloride ion of the powdered rust samples, (approximately 0.1g), was extracted into de-ionized water, (20 cm³), at room temperature for 2 h (7.2ks) with an ultrasonic stirrer. The chloride ion obtained by water extraction is defined here as soluble chloride. It can be supported that this parameter, *C* is treated as a better indicator than air borne salt particles by dry gauze method or measurement of salt attached on the rust layer surface.

3.2 Relationship between chloride concentration and PAI

The chloride concentration contained in the rust layer shows a peak value at winter in every year, with the application of deicing salts.¹²⁾⁻¹⁴⁾ Fig. 5 shows that relationship among the soluble CI⁻ concentration, *C* in winter (from Dec. to Mar.) resulting from deicing salt, the PAI (α/γ^*) and PAI ((β +s)/ γ^*) of the rust layer formed on the weathering steel bridges. Only one web position shown in Fig. 5 situated in protective state and all the other flange positions were in non-protective state. It was found that the PAI, α/γ^* decreased less than 1 in the case of *C* > approximately 0.1 mass % and the rust layer changed drastically from protective state to non-protective (inactive or active) state. Moreover it was found that the PAI, (β

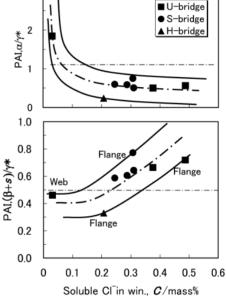


Fig. 5. Relationship among the soluble Cl[°] content; *C* in winter (from Dec. to Mar.) resulting from deicing salt, the PAI, $(\alpha/\gamma)^*$ and the PAI, $(\beta+s)/\gamma^*$ of the rust layer formed on the weathering steel bridges.

 $+s)/\gamma^*$ increased more than 0.5 in the case of *C* >approximately 0.2 mass % and the rust layer changed from inactive state to active state. In conclusion, we confirmed that the PAI of the bridges where deicing salt is sprinkled in winter has deteriorated markedly by the chloride.

4. Performance-inspection (PI) and deterioration-inspection (DI)

Performance-inspection (PI) after a certain period and periodical deterioration-inspection (DI) is absolutely necessary for the maintenance of weathering steel bridges. However their basic theory is not established. According to the results and discussion in the previous section we intended to propose them.

4.1 Performance-inspection (PI)

Performance-inspection (PI) is the process for checking the protective ability performance of the rust layer formed on weathering steel bridges. We propose the PAI described by α/γ *of the rust layer composition by XRD. However it should be noticed that the PI should not to be done within initial stage of rusting, i.e. approximately 5 years as shown in Fig. 1.

4.2 Deterioration-inspection (DI)

Deterioration-inspection (DI) is the process for checking the degree of deterioration of protectiveness of the rust layer influenced by deicing salt or air borne sea salt.

The DI of the rust layer can be performed periodically checking by both threshold concentration of residual water soluble chloride (C > -0.2 mass %) in the rust layer. However the index ($\beta + s$)/ $\gamma * > 0.5$ of the rust layer composition by XRD can show more clearly the DI of the rust layers.

5. Conclusions

(1) In the case of $\alpha/\gamma * > 1$, the rust layer works protective enough to reduce the corrosion rate less than 0.01 mm/y.

(2) The sub index $(\beta + s)/\gamma * < 0.5$ or >0.5 classify the corrosion rate of the non-protective rust layers, therefore the former rust layer is named inactive and the latter is active.

(3) The PAI described by these two indices is useful for a quantitative inspection of weathering steel bridges.

(4) The PAI described by α/γ^* of the rust layer composition by XRD after minimum 5 years is proposed for the performance-inspection (PI).

(5) The index $(\beta + s)/\gamma^* > 0.5$ of the rust layer composition by XRD is proposed for the deterioration-inspection (DI).

(6) The criterion of the index $(\beta + s)/\gamma * > 0.5$ of the rust layer composition by XRD corresponded well to the threshold concentration of soluble chloride (C > -0.2 mass %) of the rust layer in winter.

References

1. K.Nishikawa: Journals of structural mechanics and earthquake engineering, Japan Society of Civil

Engineers, 501/I-29 1-10 (1994).

- 2. U.S. Department of Transportation: Asset management primer (1999).
- 3. T. Tamakoshi, Proc.121th Symposium, JSCE (2004) 7-15.
- The highway agency: Design manual for roads and bridges vol. 2, Sec. 3, BD 7/01, weathering steel for highway structures, The Stationery Office, London (2001).
- M.Yamashita, H. Miyuki, T. Matsuda, H. Nagano, and T. Misawa, *Zairyo-to-Kankyo*, 43, 26 (1994).
- M.Yamashita, H. Miyuki, T.Matsuda, H. Nagano, and T. Misawa, *Corros. Sci.*, 36, 283 (1994).
- 7. T. Kamimura, M. Yamashita, H. Uchida, and H. Miyuki, J. Japan Inst. of Metals, 65, 922 (2001).
- T. Kamimura, S. Hara, H. Miyuki, M. Yamashita, and H. Uchida, *Corros. Sci.*, 48, 2799 (2006).
- S. Hara, K. Kashima, H. Kishikawa, H. Miyuki, and T. Misawa, *Tetsu-to-Hagane*, 87, 43 (2001).
- K. Kashima, S. Hara, H. Kishikawa, and H. Miyuki, Zairyou-to-Kankyou, 49, 15 (2000).
- S. Hara, T. Kamimura, H. Miyuki, and M. Yamashita, *Corros. Sci.*, **49**, 1131 (2007).
- 12. S. Hara, M. Miura, Y. Uchiumi, T. Fujiwara, M. Yamamoto, *Corros. Sci.*, **47**, 2419 (2005).
- 13. S. Hara, M. Miura, Y. Uchiumi, T. Fujiwara, M. Yamamoto, *Zairyo-to-Kankyo*, **54**, 337 (2005).
- 14. S. Hara, M. Miura, Y. Uchiumi, T. Fujiwara, M. Yamamoto, *Zairyo-to-Kankyo*, **54**, 344 (2005).
- 15. K. Shiotani, T. Nakayama, H. Kihira, H. Miyuki, M. Takemura, F. Kawabata, K. Abe, T. Kusunoki, Y. Watanabe and K. Matsui, [SABI [rust] Chemistry on the phase-III toward Realizing Minimum Maintenance Bridge Conception.] *Proceedings of JSCE 132ed Symposium* (2001) 73-82.
- Public Works Research Institute (PWRI), Japan Iron and Steel Federation (JISF) and Japan Association of Steel Bridge Construction (JASBC), Cooperative Research Report on The Application of Weathering Steels to Bridges (X VIII) (1993).
- Public Works Research Institute (PWRI), Japan Iron and Steel Federation (JISF) and Japan Association of Steel Bridge Construction (JASBC), Cooperative Research Report on The Application of Weathering Steels to Bridges (X VII) (1993).
- H. Kihira, K. Shiotani, H. Miyuki, T. Nakayama, M.Takemura, and Y.Watanabe, *Journals of Structural Mechanics and Earthquake Engineering*, Japan Society of Civil Engineers, 745/1-65, 77 (2003).
- T. Iwata, T. Nakayama, H. Tomari, S. Takeuchi, T. Yokoi and K. Mori: *Proceedings of JSCE Materials and Environments* 1995, C-306, (1995) 341.