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Mössbauer and XRD analysis of corrosion products on weathering steel treated by wet-dry cycles using various solutions

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Abstract Weathering steels (COR-TEN) were corroded by wet-dry cycles using a splay of various solutions in a laboratory. Corrosion products on weathering steel were characterized by X-ray diffractometry and Mössbauer spectrometry at room and low temperatures. Fine α-FeOOH, γ-FeOOH and γ-Fe$_2$O$_3$ are fundamentally formed in various atmospheric conditions. β-FeOOH is additionally formed under the existence of chloride ions, but not formed when sulfate ions are coexisting. Spraying a NaF solution prevents the progress of corrosion.

Keywords Weathering steel · Goethite · Maghemite · Akaganeite · X-ray diffraction · Mössbauer spectra

1 Introduction

Weathering steel occupies nowadays about 30 % of steel materials used for bridge construction in Japan [1]. Weathering steel is designed so as to form protective layers on the surface.

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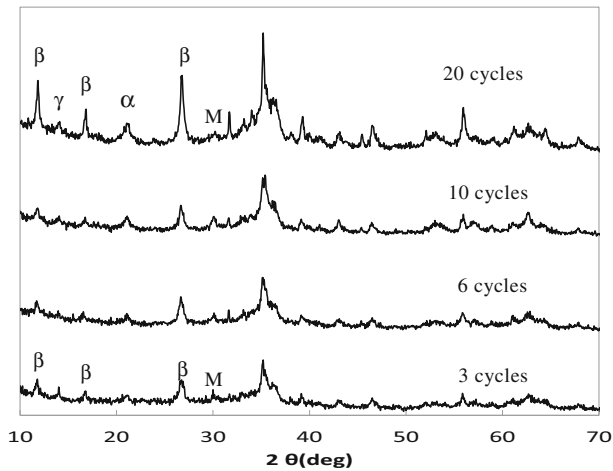4   School of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Meguro-ku, Tokyo, 153-8902, Japan

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Fig. 1 X-ray diffraction patterns of corrosion products by spraying 5 % NaCl solution. Specific peaks: α; α-FeOOH, β; β-FeOOH, γ; γ-FeOOH, M; γ-Fe$_2$O$_3$ (or Fe$_3$O$_4$)

The maintenance cost can be reduced because painting on the steel surface is not needed. The lifetime of weathering steel may be estimated to be over 100 years under a good atmospheric condition [2]. However, the lifetime depends on the environmental atmospheres largely. Weathering steel is hardly used especially in coastal areas because stable oxide layers are not always formed. It is reported that the stable oxide layers might be composed of fine α-FeOOH, γ-FeOOH and Fe$_2$O$_3$xH$_2$O in urban area [3]. Akaganeite, β-FeOOH, is often observed on mild steel under the influence of chloride ions [4]. It is not always confirmed how β-FeOOH influences the oxide layers of weathering steel. In this study, in order to clarify the initial corrosion products, weathering steel was corroded by wet-dry cycles under various atmospheric conditions and the corrosion products were analyzed by Mössbauer spectrometry and X-ray diffractometry.

2 Experiment

Corrosion test: weathering steel (COR-TENT) [2], which contains mainly 0.56 % Cr, 0.29 % Cu, 0.15 % Ni, 0.5 % Mn, 0.47 % Si, and 0.11 % P as chemical composition, was donated from Chikuma Kozai Co., Ltd. The steel plate with 1 mm in thickness was cut to 80 mm x 60 mm each piece. Oil and stain on test plates were removed and cleaned by ethanol. Test plates were placed in a plastic container and sprayed with various test solutions. Corrosion tests were carried out based on JIS H8502 method. The outline is as follows; Test plates are sprayed with various test solutions, kept in dry atmosphere at 60 °C for 2 hours, and kept in wet atmosphere at 50 °C for 10 hours. It takes 12 hours for one cycle. The corrosion products used for measurement of X-ray diffraction (XRD) and Mössbauer spectra were obtained after 3 cycles (36 hrs.), 6 cycles (72 hrs.), 10 cycles (120 hrs.) and 20 cycles (240 hrs.), respectively. Powder samples were scrubbed off from the corroded plates.
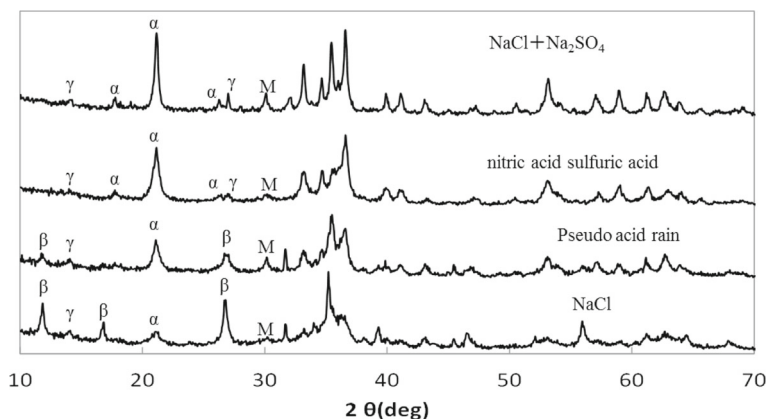
Fig. 2 XRD patterns of rust produced after 20 splay cycles test of weathering steel. Specific peaks: α; α-FeOOH, β; β-FeOOH, γ; γ-FeOOH, M;γ-Fe$_2$O$_3$ (or Fe$_3$O$_4$) · Sharp peak at 32° : NaCl

Test solutions for spray are as follows: Solution (1) of 5 % NaCl; 15 g of sodium chloride was dissolved in distilled water (300 mL). Solution (2) of pseudo acid rain containing Cl$^-$ ions; 46.8 mL of 0.1 mol/L nitric acid and 8.26 mL of 10 % sulfuric acid were added to 300 mL of 5 % NaCl solution. The pH of solution was adjusted to 3.5 by adding 10 % NaOH solution. Solution (3) of acid without chloride ions; HNO$_3$ + H$_2$SO$_4$; 46.8 mL of 0.1 mol/L nitric acid and 8.26 mL of 10 % sulfuric acid were added to 300 mL of distilled water. The pH was adjusted to 3.5 by adding 10 % NaOH solution. Solution (4) of 5 % NaF; 15 g of sodium fluoride was dissolved in distilled water (300 mL). Solution (5) of 5 % NaCl + Na$_2$SO$_4$; 15 g of sodium chloride and 36.9 g of sodium sulfate were dissolved in distilled water (300 mL).

XRD patterns were measured with Rigaku Ultima IV equipped with a Cu target and a monochromater, and analyzed by using a Rietveld method (Rietan-2000 program) [5, 6] to identify the crystalline products quantitatively. Mössbauer spectra were measured at room temperature (RT) and low temperatures using a ^{57}Co (Cr) source and a conventional instrument with a cryostat. Doppler velocity was calibrated using Mössbauer data of α-Fe foil.

3 Result and discussion

Test plates were corroded according to test cycles step by step. Black portions were observed at the early stage. The color became yellow brown with test cycles. Yellow brown materials became dominant with the progress of the cycle. Figure 1 shows the XRD patterns of corrosion products generated with spray cycles of 5 % NaCl solution. It is well known that β-FeOOH is formed under the influence of chloride ions [3, 4]. XRD peaks of Fe$_3$O$_4$(or γ-Fe$_2$O$_3$), α-FeOOH and γ-FeOOH were detected, which developed according to the progress of the test cycles. Especially β-FeOOH was the dominant component after 3 cycles. The XRD peaks of α-FeOOH were broadened due to the fine grains.

Table 1 Quantitative analysis of crystal phases in corrosion products various solution by Rietveld method

Solution comp.	$\alpha-$FeOOH	$\gamma-$FeOOH	$\gamma-$Fe$_2$O$_3$	$\beta-$FeOOH	R
1) 5 % NaCl solution	36 %	14 %	10 %	40 %	2.00
2) Pseudo acid rain (pH = 3.5)	56 %	1 %	20 %	24 %	1.14
3) Nitric + sulfuric acid solution (pH = 3.5)	72 %	15 %	13 %	0 %	1.38
4) 5 % NaCl + Na$_2$SO$_4$	74 %	1 %	25 %	0 %	1.49
5) Coastal : 9 years[a]	65 %	7 %	6 %[b]	22 %	1.63

[a]A. Matsubara, Materials Science & Technology, no.8 supplement, p.126 (2003)

[b]He identified this as Fe$_3$O$_4$

Figure 2 shows the XRD patterns of rust produced after 20 cycles under four atmospheric conditions. β-FeOOH, α-FeOOH, γ-FeOOH and γ-Fe$_2$O$_3$ (or Fe$_3$O$_4$) were observed under 5 % NaCl spray condition. Under the pseudo acid rain condition (2), the portion of β-FeOOH was relatively small, and α-FeOOH and γ-Fe$_2$O$_3$ were dominant as compared with the XRD pattern under 5 % NaCl spray condition. The ratio of the products depended on the anions in the spray solutions. β-FeOOH was not produced under the spray condition of HNO$_3$+ H$_2$SO$_4$ solution. It is remarkable that β-FeOOH was not produced under the condition of 5 % NaCl + Na$_2$SO$_4$ solution. It is considered that the iron ion interacts with SO$_4^{2-}$ stronger than Cl$^-$ because the stability constant of SO$_4^{2-}$ is larger than that of Cl$^-$ in aqueous solutions. Not so much rust was produced under the NaF spray condition although the surface color became shiny dilute green.

The XRD pattern of Fe$_3$O$_4$ is very similar to that of γ-Fe$_2$O$_3$. It was hard to distinguish two compounds by XRD. The black color of the rust produced in the early stage of test cycles may indicate Fe$_3$O$_4$, which is often produced in mild steel [4]. The analyzed results by the Rietveld method are listed in Table 1 [6]. As reference [7], the component and relative amounts of rust produced on new weathering steel (containing mainly 3 % Ni, 4 % Cu, and 1 % Mn) exposed in coastal area for 9 years also are added in Table 1. Matsubara's results showed 22 % β-FeOOH in addition to α−FeOOH, γ-FeOOH, and Fe$_3$O$_4$. However, Fe$_3$O$_4$, which he identified by XRD, is considered to be γ-Fe$_2$O$_3$ as described in next paragraph. We identified the unclear XRD peaks (Fe$_3$O$_4$ or γ-Fe$_2$O$_3$) as γ-Fe$_2$O$_3$. The component ratio obtained by pseudo acid rain containing NaCl is similar to that of rust on new weathering steel exposed in coastal area.

All RT Mössbauer spectra of rusts produced by spraying NaCl, acid, and pseudo acid (Cl$^-$) solutions gave broad peaks as shown in Fig. 3. We analyzed the spectra by hyperfine field (B$_{hf}$) distributions. In addition to two distinguishable doublets, at least two main peaks were observed in the hyperfine field distributions. In the spray condition of 5 % NaCl solution, paramagnetic doublets were strongly present in the spectra. They are considered to be mainly due to the β-FeOOH and γ-FeOOH included in the rust products. With respect to the acid rain atmosphere, α-FeOOH, γ-FeOOH, and γ-Fe$_2$O$_3$ (or Fe$_3$O$_4$) were identified by XRD. It is well known that Mössbauer spectra of Fe$_3$O$_4$ consist of two sextets (46 T and 49 T) due to tetrahedral (Fe^{3+}) and octahedral sites (Fe^{2+} and Fe^{3+} mixed valence states) of the Fe$_3$O$_4$ crystal structure. The Mössbauer spectrum observed shows only the sextet with B$_{hf}$ = 49 T, isomer shift (IS) = 0.37 mm/s, due to γ-Fe$_2$O$_3$. Weak hyperfine field distributions were observed in the tails of the large peak in the magnetic field distributions. They are considered to be due to small grains of γ-Fe$_2$O$_3$ because the characteristic two sextets
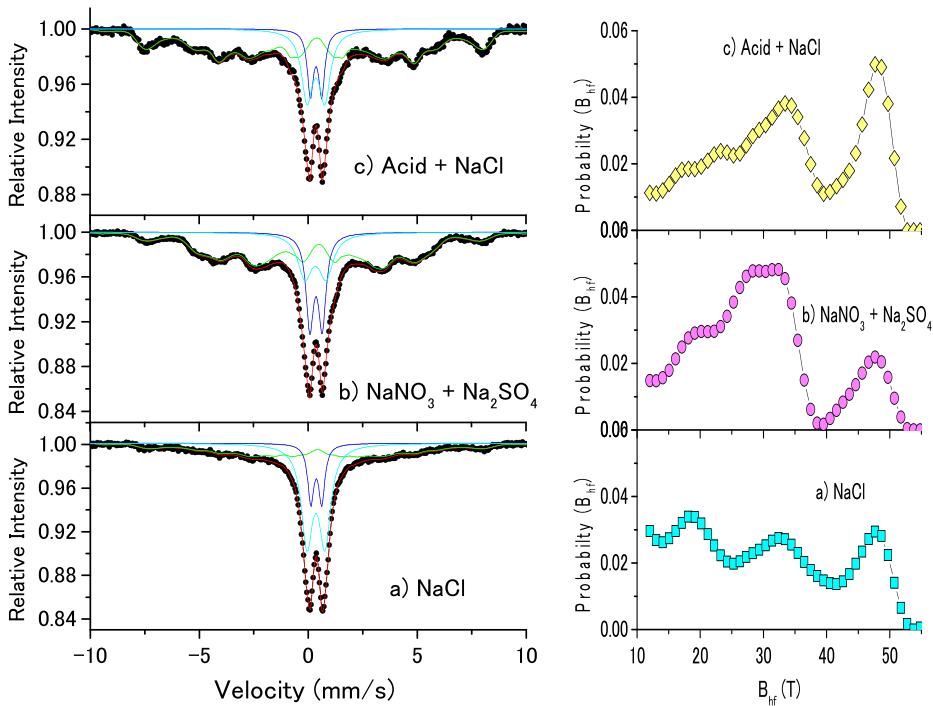
Fig. 3 Room temperature Mössbauer spectra and hyperfine field distributions of rust on weathering steel produced by spraying **a**) 5 % NaCl solution, **b**) $HNO_3 + H_2SO_4$ (pH=3.5) solution and **c**) pseudo acid rain (pH=3.5) containing Cl^-
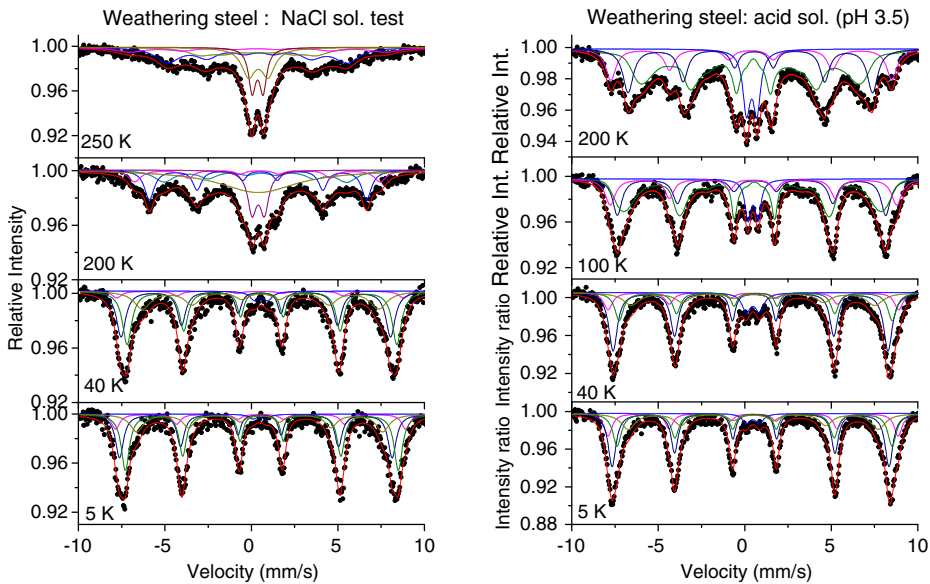

Fig. 4 Low temperature Mössbauer spectra of rust on weathering steel, which is produced by spaying (*left*) 5 % NaCl solution and (*right*) pseudo acid (Cl^-) solution (after 20 cycles)

Table 2 5 K Mössbauer parameters of rust on weathering steel corroded by spraying 5 % NaCl solution and pseudo acid rain (after 20 cycles)

Sample	IS(mm/s)	QS(mm/s)	B_{hf}(T)	LW(mm/s)	Intensity (%)	Compound
5 % NaCl	0.50	0.00	52.0	0.59	10.3 %	$\gamma-Fe_2O_3$
	0.37	−0.24	49.0	0.59	30.3 %	$\alpha-FeOOH$
	0.58	0.00	48.9	0.59	40.5 %	$\beta-FeOOH$
	0.47	−0.00	44.1	0.95	17.4 %	$\gamma-FeOOH+$
	0.59	0.77	0.59	–	1.5 %	Fine FeOOH
Pseudo acid rain (Cl⁻)	0.50	0.00	52.0	0.55	19.6 %	$\gamma-Fe_2O_3$
	0.44	−0.24	49.6	0.55	38.9 %	$\alpha-FeOOH$
	0.58	0.00	49.1	0.55	22.3 %	$\beta-FeOOH$
	0.54	−0.00	43.8	0.80	15.5 %	γ-FeOOH
	0.57	0.88	–	0.57	3.7 %	+Fine FeOOH

of Fe_3O_4 were not observed in these rusts. Fe_3O_4 were often detected inside the rust layers of weathering steel by X-ray scattering Mössbauer spectrometry [8]. A small amount of Fe_3O_4 may have already changed into γ-Fe_2O_3 when scrubbing after 20 test cycles even if Fe_3O_4 is produced at the initial stage of corrosion. It is known that Fe_3O_4 is formed at the interface of mild steel beneath γ-FeOOH and Fe hydroxides in NO_3^- solution [9].

Collapsed sextets with small $B_{hf} = 34$ T and lower B_{hf} were observed in RT Mössbauer spectra as shown in Fig. 3. These tailing peaks are assigned to fine grains of α-FeOOH. α-FeOOH is originally observed as sextet peaks with tailing because of the needle shaped crystals. One of two paramagnetic doublets is considered to be due to γ-FeOOH, and another doublet with a large QS is FeOOH due to non-crystalline or $Fe_2O_3xH_2O$ [8]. In the case of the rust produced by spraying NaCl and pseudo acid (Cl⁻) solutions, the doublets are considered to contain the peaks due to β-FeOOH as shown clearly in the XRD patterns

Mössbauer spectra of rust produced under spray cycles of 5 % NaCl and pseudo acid (Cl⁻) solutions were measured at low temperatures as shown in Fig. 4. The doublets observed at RT transform into broad magnetic sextets at 250 K. Since Neel temperature of β-FeOOH is 293 K, the new sextets are due to the magnetic component of β-FeOOH. Another doublet remaining at 40 K is considered to be due to fine FeOOH. The doublet of γ-FeOOH changes into a sextet because the Neel temperature is ca. 50 K. 5 K Mössbauer spectra were decomposed into four magnetic components and a paramagnetic one. The first sextet with the largest $B_{hf} = 52$ T is assigned to γ-Fe_2O_3. The second sextet with $B_{hf} = 49$ T and QS = -0.24 mm/s is due to α-FeOOH. The third sextet with 49 T and QS= 0.0 mm/s is due to β-FeOOH, and the fourth broad sextet with 44 T is to γ-FeOOH. It is considered from XRD results that the fourth sextet and a doublet contain components due to fine FeOOH, especially for the rust produced by spraying pseudo acid solution. The rusts produced under 5 % NaCl and the pseudo acid rain (Cl⁻) solution conditions are not inherently different, but the grain size and composition ratio are different as shown in Table 2.

Kamimura and Nasu reported 10 K Mössbauer spectra of rust on weathering steel corroded under the atmosphere at a non-coastal area for 15 years [10]. α-FeOOH, γ-FeOOH, and γ-Fe_2O_3 were identified as the rust of weathering steel, and no amorphous phases were detected [11]. Perez et al [12] studied the corrosion of carbon steel and weathering steel in NaCl solution of three different concentrations. Fundamentally Fe_3O_4 is easily produced on

carbon steel and γ-Fe_2O_3 on weathering steel. Our results of the rust produced by wet and dry cyclic conditions are similar to the results obtained by Perez et al. [12].

4 Conclusion

Rust on weathering steel, corroded under wet-dry cycle atmosphere using various solutions, was characterized by Mössbauer spectrometry and XRD. The quantities of the components in the rust were analyzed by the Rietveld method of XRD pattern analysis.

A black color compound generated in an initial corrosion stage might be Fe_3O_4, but Mössbauer spectra of the scraped samples showed the existence of γ-Fe_2O_3.

Fine α-FeOOH, γ-FeOOH and γ-Fe_2O_3 are fundamentally produced under wet and dry cyclic atmospheric conditions, containing no chloride ions. β-FeOOH is additionally formed in the presence of chloride ions. β-FeOOH is an undesirable compound against the performance of weathering steel.

The amount of β-FeOOH produced in pseudo acidic rain solution (containing chloride, nitric and sulfate ions at pH = 3.5) was relatively smaller than that in 5 % NaCl solution. Further, no β-FeOOH was formed under the wet dry cyclic condition of $NaCl + Na_2SO_4$ solution. Thus, it is found that the addition of SO_4^{2-} remarkably prevents the formation of β-FeOOH. The corrosion of weathering steel did not proceed so strongly under cyclic splay of NaF solution.

These results suggest that the corrosion of weathering steel could be controlled by addition of proper anions.

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