Mössbauer Spectroscopic Study of Rust Formed on a Weathering Steel and a Mild Steel Exposed for a Long Term in an Industrial Environment

Takayuki Kamimura¹, Saburo Nasu², Takashi Tazaki^{2, *}, Kaori Kuzushita^{2,*} and Shotaro Morimoto²

¹Corporate Research and Development Laboratories, Sumitomo Metal Industries, Ltd., Amagasaki 660-0891, Japan ²Division of Materials Physics, Department of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

The rusts formed on mild steel (15-year exposure) and weathering steel (32-year exposure) exposed to an industrial environment have been characterized by means of X-ray diffraction technique and ⁵⁷Fe Mössbauer spectroscopy. By using an X-ray diffraction method, it is suggested that the rusts formed on both steels consist of the crystalline α -FeOOH, γ -FeOOH and an X-ray amorphous phase, which gives no peak to X-ray diffraction pattern. The amount of the X-ray amorphous phase exceeds 50% of the total amount of the rust. The ⁵⁷Fe Mössbauer spectra observed at 10 K indicate that the rust contains only α -FeOOH, γ -FeOOH and Fe_{3- δ}O₄ (γ -Fe₂O₃) for mild steel, and only α -FeOOH and γ -FeOOH for weathering steel. The X-ray amorphous substance in the rust layer formed on mild steel possesses the structures of mainly α -FeOOH showing superparamagnetism owing to its small particle size, and Fe_{3- δ}O₄ (γ -Fe₂O₃). They are contained both in the inner rust layer and in the outer rust layer. The X-ray amorphous phase in the rust layer formed on weathering steel is mainly α -FeOOH.

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1. Introduction

An understanding of the mechanism of atmospheric corrosion of steel requires a study of the corrosion products (rust) formed on the steel surfaces. It has been widely reported that they consist of iron oxyhydroxides, such as α -FeOOH, β -FeOOH, γ -FeOOH, and magnetite as crystalline substances, and so-called "X-ray amorphous substance".^{1–10)} Their formation strongly depends upon the environment where steels are exposed. β -FeOOH, for instance, is formed in the case of existence of chloride.

Weathering steels, which contain a small amount of Cu, Cr, P and Ni, form protective rust layers as corrosion proceeds under atmospheric conditions. It is believed that the protective rust layer is composed of double layers of outer and inner rusts, and the inner rust layer is dense enough to protect the permeation of the corrosives. Under various environmental conditions it is therefore of great importance to investigate rust formed on steels because the formed rust layers, which may act as coatings, greatly affect the corrosion resistance. To investigate rust is also of great importance from a viewpoint of electrochemical behavior of weathering steels, especially under the initial wet/dry cycles. Because the rust is reduced just after wetting of the dry surface as cathodic reaction by the negative electrode potential, and during drying the oxygen reduction as cathodic reaction takes place on the reduced rust surface in the pore system of the rust.^{11–22)}

In spite of the importance of the rust on the corrosion behavior of steels, limited numbers of studies have mentioned the rust constituents formed on the steel surfaces. The crystalline rust, which is detected by X-ray diffraction technique, has been well characterized, and the composition change of the crystalline rust with the exposure duration have

been reported for the weathering steels.^{2,3,23,24} In addition, some different structures of the X-ray amorphous substance have been proposed such as spinel type iron substance,^{4,5)} Fe(OH)₃,²⁵⁾ and δ -FeOOH¹⁰⁾ by other authors. Recently, several pieces of literature on the investigation of the rust formed on steels exposed to atmosphere have been reported by means of Mössbauer spectroscopy²⁶⁻³¹⁾ because it has a great advantage for identification of poorly crystalline or amorphous corrosion products.^{32–37)} Cook et al.²⁶⁾ and Yamashita et al.²⁷⁾ pointed out that the X-ray amorphous substance formed on the weathering steels exposed for 16 years in a rural environment having ISO site corrosion class C3 (S0, P0,T3)³⁸⁾ is mainly Cr substituted α -FeOOH, of which crystal size is less than 15 nm. Okada et al.³⁹⁾ have investigated the inner rust, which was tightly adhered to the bulk steel, formed on the weathering and mild steels exposed in a "semi-rural" type of environment. They pointed out that α -FeOOH is the major component in the inner rust of both steels, and the difference in the structures of the inner rust between the mild and the weathering steels is its particle size distribution; α -FeOOH particle in the rust on weathering steel has a continuous distribution, while that on mild steel does not. The above literature deals with the rust formed in the semi-rural or rural environment. It is well known that the superior performance of weathering steel is generally obtained in the relatively severe conditions, where the pollutant such as SO_x is contained in the atmosphere; the great difference in corrosion loss between weathering steel and mild steel is observed in the industrial environment.⁴⁰⁾ We have investigated the rust formed on the weathering steel in an industrial region for 15 years by means of Mössbauer spectroscopy and the following results can be summarized.³⁰⁾ The X-ray amorphous phase in the rust layer is mainly α -FeOOH which shows a paramagnetic doublet due to the superparamagnetism occurring

^{*}Graduate Student, Osaka University.

for small particles at room temperature. The outer layer also contains a considerable amount of the superparamagnetic α -FeOOH (spm. α -FeOOH). The particle size of α -FeOOH is widely distributed and the inner layer contains relatively well-crystallized α -FeOOH compared to the outer layer.

In the present study, to clarify the difference in the rust constituents between those formed on the weathering steel and those on the mild steel in an industrial environment, where the weathering steel shows superior corrosion resistance to the mild steel, the constituents of corrosion products formed on a mild steel exposed to an industrial environment for 15 years are characterized by means of Mössbauer spectroscopy, and compared to the results previously obtained for the rust formed on the weathering steel.³⁰⁾ Furthermore, the rust formed on weathering steel exposed to an industrial environment for 32 years is also characterized in order to investigate the phase-change of the rust with the exposure duration.

2. Experimental

2.1 Atmospheric rusting and preparation of specimens

Plates of mild steel and weathering steel $(60 \times 100 \times 4 \text{ mm}^3)$ were exposed at Amagasaki, JAPAN at an angle of 30° facing south for 15 years and 32 years, respectively. This site, located approximately 5 km inland from the coast but having below 0.01 mdd (mg/dm²/day) of the deposition rate of chloride, is considered industrial having ISO site corrosion class C3 (S0, P1, T4). This site is identical to that in the previous report.³⁰⁾ The chemical compositions of the steels used for the exposure test and also used in the previous report³⁰⁾ are listed in Table 1. The specimens after the exposure were cut perpendicular to the plate surface with a dimension of 15×10 mm². A scrap of steel was first affixed to the surface of the specimens with rust by hard adhesives (Torr Seal manufactured by varian) so that the rust on the steel is not scraped off by subsequent polishing procedures, and the specimens were then fixed by an epoxy resin. The cross-section of the fixed specimen was mechanically polished by emery papers (grades 400-1500) and then with a diamond paste. The rust layers formed on the steel surface were also scraped off by a razor until the steel surface appeared, and then they were ground into powder. The powdered rust samples were desiccated for a week in advance of the subsequent analyses.

2.2 Analysis of the powdered rust and cross-section of rust

The powdered samples were characterized by means of X-ray diffraction technique (XRD). The XRD measurements and the quantitative determination by peak intensities of rust

were carried out according to the same procedure reported previously.³⁰⁾ The cross-section of the surface rust layers was investigated by the observation of the reflection behavior of polarized light in an optical microscope using a Nikon Model OPTIPHOT2-POL.

The ⁵⁷Fe Mössbauer measurements for the powdered rust samples were performed in transmission geometry in the temperature range between 300 K and 5 K using a ⁵⁷Co γ -ray source in Rh. The outer (10–20 µm in thickness) and the inner (60–80 µm in thickness) rust were divided by the same procedure in the previous paper.³⁰⁾ The velocity scale is relative to α -Fe at 300 K. Obtained spectra were analyzed by using a thin foil approximation. Distribution analyses of the Mössbauer parameters have been performed by using a NORMOS DIST program developed by Brand.⁴¹⁾

3. Results

3.1 Constituent of rust

The surface of the mild steel exposed for 15 years and the weathering steel exposed for 32 years were covered with dark-brown rust, whose average thickness was approximately $60-90\,\mu\text{m}$. Figure 1 shows the cross-section of the rust. It was found by microscopic observation, using reflected polarized light and crossed nicols, that the rust layer formed on the weathering steel exposed for 32 years is mainly composed of optically isotropic region (darkened), and only outer surface of the rust is optically active (illuminated). On the other hand, the rust formed on the mild steel is composed of the mottled structure consisting of the optically active and isotropic corrosion products. For the mild steel the big cracks reaching the steel substrate were clearly observed, whereas no crack was observed for the weathering steel, which is the same tendency for the weathering steel exposed for 15 years.³⁰⁾ Those cracks can be mostly formed during the sample preparation of cutting and/or polishing procedure since they were not detected by the surface observation before cutting the samples. It should be therefore noted that the rust formed on the mild steel is fragile, and in other words, the rust formed on the weathering steel can be adherent and tight.

From the X-ray diffraction patterns, the rust layers formed on the mild steel and the weathering steel were mainly composed of α -FeOOH and γ -FeOOH as crystalline constituents, and Fe₃O₄ can be hardly detected in the rust of both steels as shown in Fig. 2. The quantitative phase-analysis obtained from the diffraction intensities indicated that the rust contained 20% of α -FeOOH, 15% of γ -FeOOH and 65% of the X-ray amorphous substance for the mild steel, and 25% of α -FeOOH, 10% of γ -FeOOH and 65% of the X-ray amorphous

Table 1 Chemical compositions of the steels tested (mass%).

	С	Si	Mn	Р	S	Cu	Ni	Cr
Mild steel (15-years exposure)	0.12	0.32	1.47	0.023	0.004	0.01	0.02	0.04
Weathering steel ³⁰⁾ (15-years exposure)	0.11	0.24	0.75	0.014	0.005	0.33	0.12	0.49
Weathering steel (32-years exposure)	0.10	0.50	0.50	0.018	0.014	0.55	0.53	0.91



Fig. 1 Cross-section of the rust formed on the weathering steel for 32 years (a) and the mild steel exposed for 15 years (b) by polarizing microscope.



Fig. 2 Typical X-ray diffraction patterns of the rust formed on the steels. (a) Weathering steel exposed for 32 years, (b) Mild steel exposed for 15 years.

substance for the weathering steel.

3.2 Mössbauer spectroscopy of the inner and the outer rust

Figures 3 and 4 shows ⁵⁷Fe Mössbauer spectra obtained from powdered samples scrapped from the inner and the outer rust formed on the weathering steel exposed for 32 years, together with the results from the distribution analysis of the hyperfine magnetic field at 78 K at the right of the figures. The line profile of the individual lines of sextets of the distributions was assumed to be Lorentzian and their width was fixed to 0.4 mm s^{-1} for the fitting. The spectra obtained were similar to those for the weathering steel exposed for 15 years.³⁰⁾ The room temperature spectrum of the inner rust shows a superposition of an intense quadrupole-split doublet and a magnetically split-sextet. This magnetically split-component is divided into two sextets with strong and weak intensities. Analysis was done by a least-square-fit with a thin foil approximation. The former sextet is clearly due to α -Fe having a magnetic hyperfine field $B_{int} = 33 \text{ T}$ at room temper-

ature, which was contaminated during the scraping of the rust. The latter sextet is assigned to be α -FeOOH. The room temperature spectra for the outer rust show only an intense quadrupole-split. These results mean that the inner rust contains relatively well-crystallized α -FeOOH, and agree with the results obtained for the rust formed on the weathering steel exposed for 15 years.³⁰⁾ For the spectra of the inner and the outer rusts at 78 K, the intensity of the central doublet decreased and the intensities of the sextets increased. These results suggest that the central paramagnetic component at 78 K may be due to the paramagnetic γ -FeOOH whose Néel temperature is reported to be $73 K^{42}$ or $35 K^{43}$ and also due to the spm. α -FeOOH^{26–28,30} whose Néel temperature is much higher than 78 K. This result is significant and leads to evidence of the existence of superparamagnetic small particles in the rust layer formed on the weathering steel exposed for 32 years. As shown at the right in Figs. 3 and 4, the hyperfine magnetic field of the sextet due to α -FeOOH is widely distributed at 78 K. These results may correspond to the wide distribution of the particle size of α -FeOOH. The central doublet obtained at 78 K cannot be clearly identified because it may contain smaller particles, which show paramagnetism even at 78 K. For the spectra of the inner and the outer rust at 5 K the central doublet completely vanished, which implies that the superparamagnetic fluctuation of the magnetic moments in a nano-scaled particle of hydroxides may become static at 5 K. The spectra observed at 5 K were analyzed into two sextets by a least-square-fit; one is due to α -FeOOH having $B_{int} = 50$ T, and the other is due to γ -FeOOH having $B_{int} = 45$ T. It should be concluded that there is no phase-change of rust formed on the weathering steels exposed for 15 years and 32 years.

Figures 5 and 6 show the ⁵⁷Fe Mössbauer spectra obtained from powdered samples scrapped from the inner and the outer rust formed on the mild steel, together with the results from the distribution analysis of the hyperfine magnetic field at RT and 78 K at the right of the figures, respectively. The spectra obtained were different from that for the weathering steels. The room temperature spectrum of the inner rust shows a superposition of an intense quadrupole-split doublet and a magnetically split-sextet. In addition, another broad sextet was observed, which has a large full-width at half-maximum (FWHM) and does not show the sharp spectrum. This sextet having a large hyperfine field of approximately 50 T was never observed for the rust formed on the weathering steels. The room temperature spectra for the outer rust also show an intense quadrupole-split doublet and a broad sextet having a large hyperfine field of approximately 50 T. For the spectra of the inner and the outer rust layer at 78 K, the broad sextet observed at RT became sharpened, and the intensity of the central doublet decreased and the intensities of the new sextet lines increased. These results suggest that the central paramagnetic component at 78 K may be due to the paramagnetic

 γ -FeOOH and the spm. α -FeOOH as mentioned above. This leads to evidence of the existence of superparamagnetic small particles in the rust layer for the rust formed on the mild steel. Therefore the rust formed on the mild steel also contains a considerable amount of the spm. α -FeOOH. As shown at the right in Figs. 5 and 6, the hyperfine magnetic field of the sextet due to α -FeOOH is widely distributed at 78 K. These results may correspond to the wide distribution of the particle size of α -FeOOH, as mentioned above. The remarkable differences in the distribution of the hyperfine magnetic field were not observed between the mild steel and the weathering steel in this study. For the spectra of the inner and the outer rust layer at 10 K the central doublet completely van-



Fig. 3 Typical transmission Mössbauer spectra of the inner rust formed on the weathering steel exposed for 32 years. The velocity is relative to α -Fe. Right: hyperfine magnetic field distributions used to fit the spectra on the left.

ished. The spectra observed at 10 K were analyzed into three sextets by a least-square-fit; one is due to γ -Fe₂O₃ having $B_{\text{int}} = 52$ T, another is due to α -FeOOH having $B_{\text{int}} = 50$ T, and the other can be γ -FeOOH having $B_{\text{int}} = 47$ T, which is slightly larger than B_{int} reported for the synthesized γ -FeOOH^{42,44} and the obtained γ -FeOOH in the rust formed on the weathering steel as mentioned above. It is therefore undeniable that a small amount of ferrihydrite may contribute to this spectrum, whereas the Mössbauer spectrum of ferrihydrite is not yet clear.^{45–47}

4. Discussion

4.1 X-ray amorphous substance in rust formed on mild steel

Magnetite (Fe₃O₄) and magnetite (γ -Fe₂O₃) were not observed in the rust formed on the mild steel used in this study by means of XRD as shown in Fig. 2. The crystal structure of these two iron oxides is cubic (inverse-spinel structure). The lattice parameters are close to each other, and therefore they cannot be distinguished easily only by XRD. The Mössbauer spectra obtained for the rust formed on the mild steel clearly



Fig. 4 Typical transmission Mössbauer spectra of the outer rust formed on the weathering steel exposed for 32 years. The velocity is relative to α -Fe. Right: hyperfine magnetic field distributions used to fit the spectra on the left.

shows the existence of 3rd substance except α -FeOOH and γ -FeOOH. As has mentioned, α -FeOOH and γ -FeOOH were detected by XRD as crystalline. From the hyperfine parameters of the 3rd substance at 10 K, it is likely that it is assigned to γ -Fe₂O₃, because the spectra of the site for Fe(II + III) of B-site in Fe₃O₄ were not clearly observed at RT. For the spectra observed at RT the broad sextet due to γ -Fe₂O₃ is superposed on the intense doublet. This cannot be observed in the rust formed on the weathering steel at all. It is proven from the spectra at 10 K that there is no presence of intrinsic amorphous phase in the rust. It should be pointed out that the rust may contain a considerable amount of non-stoichiometric substances. It is known that Fe₃O₄ is partly oxidized and then

it can be expressed as $Fe_{3-\delta}O_4$ ($0 < \delta < 1/3$, $\delta = 1/3$ corresponds to γ -Fe₂O₃.). Since the spectra from Fe(II + III) at B-site in Fe₃O₄ were not observed at RT as shown in Figs. 5 and 6, δ is thought to be mainly close to 1/3 (corresponding to γ -Fe₂O₃). However it is probable that the rust contains Fe_{3-\delta}O₄ having various values ($0 < \delta < 1/3$). This may result in the broad spectrum and widely distributed hyperfine magnetic field at RT, shown in Figs. 5 and 6 on right hand side. From the above-mentioned discussion, it may therefore be concluded that one of the X-ray amorphous substance in the rust formed on the mild steel is γ -Fe₂O₃ (Fe_{3-\delta}O₄).

The intensity of paramagnetic doublet is large at RT but decreases at 78 K, and the contribution of the magnetically



Fig. 5 Typical transmission Mössbauer spectra of the inner rust formed on the mild steel exposed for 15 years. The velocity is relative to α -Fe. Right: hyperfine magnetic field distributions used to fit the spectra on the left.

split-sextet, on the other hand, increases at 78 K. It should be noted from these results that the rust formed on the mild steel contains a considerable amount of spm. α -FeOOH. An intense quadrupole-split doublet, except for γ -Fe₂O₃ at RT, is due to γ -FeOOH and the spm. α -FeOOH. It is therefore concluded that the spm. α -FeOOH is also one of the X-ray amorphous substances in the rust layer formed on the mild steel. Furthermore, those γ -Fe₂O₃ and the spm. α -FeOOH are even contained in the outer rust layers.

Figure 7 shows the comparison of the mass fraction of α -FeOOH, γ -FeOOH and γ -Fe₂O₃ in the rust formed on the mild steel obtained by XRD and Mössbauer spectroscopy at 10 K. Quantitative analysis of Mössbauer spectra was performed by using the data of recoilfree fractions $[f(\alpha\text{-FeOOH})/f(\gamma\text{-FeOOH}) = 0.98$, $f(\gamma\text{-Fe}_2O_3)/f(\gamma\text{-FeOOH}) = 0.92$ at 77 K] reported by Oh and Cook.⁴⁸⁾ The mass fraction of γ -FeOOH by different quantitative determination is almost identical, and this also supports that the X-ray amorphous substance is mainly the spm. α -FeOOH and γ -Fe}_2O_3 in the rust formed on the mild steel. The remarkable point obtained from Fig. 7 is that approximately half of the X-ray amorphous substance is γ -Fe}_2O_3, and the residual is the spm. α -FeOOH. It is concluded again that the X-ray amorphous substance in the rust formed on the mild steel is composed of α -FeOOH and γ -Fe}_2O_3 although the rust may somewhat contain a small amount of γ -



Fig. 6 Typical transmission Mössbauer spectra of the outer rust formed on the mild steel exposed for 15 years. The velocity is relative to α -Fe. Right: hyperfine magnetic field distributions used to fit the spectra on the left.



Fig. 7 Comparison of the mass fraction of rust obtained by X-ray diffraction and by Mössbauer spectroscopy for the rust formed on the mild steel. Note that mass fraction of Mössbauer spectroscopy was calculated from the data of the recoil-free fraction of γ -FeOOH, α -FeOOH and γ -Fe₂O₃ by Oh and Cook,⁴⁸ that is, $f(\alpha - \text{FeOOH})/f(\gamma - \text{FeOOH}) = 0.98$ and $f(\gamma - \text{Fe}_2\text{O}_3)/f(\gamma - \text{FeOOH}) = 0.92$ at 77 K.



Fig. 8 Comparison of the mass fraction of the rust obtained by X-ray diffraction and by Mössbauer spectroscopy for the rust formed on the weathering steels. (a) Weathering steel exposed for 32 years [XRD], (b) Weathering steel exposed for 32 years [Mössbauer spectroscopy], (c) Weathering steel exposed for 15 years [Mössbauer spectroscopy]³⁰) Note that mass fraction of Mössbauer spectroscopy was calculated from the data of the recoil-free fraction of γ -FeOOH and α -FeOOH by Oh and Cook,⁴⁸) that is, $f(\alpha - \text{FeOOH})/f(\gamma - \text{FeOOH}) = 0.98$ at 77 K.

FeOOH, which can not be detected by means of XRD owing to its small particles.

Figure 8 shows the comparison of the mass fraction of α -FeOOH and γ -FeOOH in the rust formed on the weathering steel obtained by XRD and Mössbauer spectroscopy at 5 K. The mass fraction of γ -FeOOH by different quantitative determination is almost identical, and this also supports that the X-ray amorphous substance is mainly the spm. α -FeOOH. It is concluded that the X-ray amorphous substance is mainly composed of α -FeOOH for the rust formed on the weathering steel exposed for 32 years. The mass fraction of α -FeOOH and γ -FeOOH for the weathering steel exposed for 32 years is slightly different from that for 15 years,³⁰⁾ as shown in Fig. 8(c). It is likely that the mass fraction of α -FeOOH

slightly increases with an increase of the exposure duration. This tendency agrees with the results obtained by Yamashita *et al.*,²⁾ although their quantitative phase-determination was done only by X-ray diffraction intensities. The increase in the mass fraction of α -FeOOH in the rust with an increase of the exposure duration was not observed for the weathering steels exposed for 15 years³⁰⁾ and 32 years by X-ray diffraction method, however the results by Mössbauer spectroscopy indicated the increase tendency of the mass fraction of α -FeOOH with an increase of the exposure duration. The systematic investigation is needed to clarify the each mass fraction change of rust with the exposure duration.⁴⁹⁾

4.2 Difference between rust constituents formed on mild and weathering steels

It was found that the X-ray amorphous substance in the rust is α -FeOOH for the weathering steel and α -FeOOH and Fe_{3- δ}O₄ (γ -Fe₂O₃) for the mild steel. The exposure site is identical, and therefore the difference of the rust constituents is caused by the alloying elements such as Cu, Cr, Ni and P. When one considers the process of the rust formation, the solid state transformation of rust should also be taken into account.⁵⁰⁾

Misawa et al.^{7,50} reported the detailed formation mechanism of iron oxides and oxyhydroxides. The fact that rust formed on the mild steel contains $Fe_{3-\delta}O_4$ may indicate one possible rusting process, in which the rust can be formed via green rust. $Fe(OH)_2$ is first generated by the anodic dissolution during the atmospheric corrosion.⁵¹⁾ It is gradually oxidized to green complex or green rust, which are the complex compounds of Fe(II) and Fe(III). Fe(OH)₂ has a hexagonal close-packed structure of oxygen, and therefore it seems impossible that Fe_3O_4 and γ -FeOOH is formed directly from Fe(OH)₂ because they have a cubic close-packed structure. Therefore, $Fe(OH)_2$ is first converted to the intermediate phase (green rust) having both hexagonal and cubic layers of closed packed oxygen, and then converted to Fe₃O₄ and γ -FeOOH. In the case of formation of Fe_3O_4 , two oxygen ions per three molecules of Fe(OH)₂ must be removed with dehydration and deprotonation. If the oxidation proceeds slowly and the oxidation time is long enough to remove oxygen from crystal and rearrange oxygen and iron in crystal lattice, the Fe_3O_4 phase may be constructed. If the oxidation proceeds fast and the structural rearrangement of green rust cannot be completed, γ -FeOOH can be formed having the distorted cubic packing of oxygen. From the above-mentioned process of Fe₃O₄ and γ -FeOOH, the added alloying elements may affect the oxidation process of $Fe(OH)_2$. In other words, they can affect the rearrangement of crystal structure. It was reported that Cu, which is one of the most effective elements on the atmospheric corrosion of steel, can affect the oxidation of the Fe(II)-complexes by catalytic effect, $^{51)}$ and therefore $\gamma\text{-}$ FeOOH can be formed without a formation of Fe₃O₄ for the rust formed on the weathering steel.

The other formation process of Fe_3O_4 is the reduction of the rust already formed on steels during the atmospheric corrosion. The atmospheric corrosion is electrochemical in nature.⁵²⁾ It is widely reported that rust is electrochemically highly active,^{13–18)} and therefore the rust on the corroding steel surfaces is affected by the potential of steel. Due to the variation in thickness of the electrolyte layer during exposure to the atmosphere the rate of oxygen reduction should vary periodically and this should result in a periodic variation of the corrosion potential.

Stratmann et al.^{14,18)} have investigated the reduction behavior of rust in detail by means of in-situ Mössbauer spectroscopy. They demonstrated that the rust reduction behavior is affected by pH, the concentration of Fe²⁺ and potential. α -FeOOH is thermodynamically stable and not easily reduced, although it is partly reduced at a very negative potential below -0.5 V SHE. On the other hand, γ -FeOOH is easily reduced. γ -FeOOH is reduced and {Fe.OH.OH} is formed probably on the surface of γ -FeOOH as an intermediate.¹⁴⁾ At the negative potential such as -0.4 V SHE, which is nearly the corrosion potential of Fe and, that is, the potential near the steel/rust interface, γ -FeOOH is reduced to Fe₃O₄. They also demonstrated that the formed Fe_3O_4 by the reduction of γ -FeOOH is oxidized back not to γ -FeOOH but γ -Fe₂O₃. The added elements are expected to affect the reduction behavior of γ -FeOOH. In fact, Cu-incorporated γ -FeOOH is not easily reduced as compared to γ -FeOOH.⁵³⁾ Furthermore from the results of the potential measurements of the steels exposed for a long period,⁵⁴⁾ the negative value of potential is observed for the mild steel, while the more noble potential is observed for the weathering steel because of the inhibition of the anodic reaction by the protective rust layer. This could result in the reduction of γ -FeOOH and the formation of Fe₃O₄, which can be partly oxidized to γ -Fe₂O₃ during a long period of exposure for the mild steel. From the results on the cross-section of the rust as shown in Fig. 1, the rust formed on the mild steel seems to be fragile. This may be related to the formation of $Fe_{3-\delta}O_4$. If the formed γ -FeOOH is reduced to Fe_3O_4 , the volume change can be expected. If Fe₃O₄ is formed and therefore the pore structure in the rust is changed, the subsequent corrosion can be accelerated since Fe₃O₄ having a good electric conductivity may act the cathodic site. From a viewpoint of the reduction of rust, it is possible that even the rust formed on weathering steels can also contain $Fe_{3-\delta}O_4$ if the corrosion potential stays at a very negative value; the thick water layer forms repeatedly or for a long time on the steel surface, or the atmosphere contains a large amount of air-borne salt particles and protective rust cannot be formed.

It is still unclear whether Fe₃O₄ and γ -FeOOH are formed simultaneously at the rusting process or the initial corrosion products is γ -FeOOH as has been stated by Misawa *et al.*,⁷⁾ and then the formed γ -FeOOH is partly reduced to Fe₃O₄ after the subsequent corrosion process, whereas it is certain that the added elements can be greatly related to both processes.

5. Conclusions

The rust layers formed on the mild steel (15-year exposure) and the weathering steel (32-year exposure) exposed to an industrial environment have been characterized by means of Xray diffraction technique and Mössbauer spectroscopy. The conclusions obtained are summarized as follows:

(1) The large cracks reaching the steel substrate are clearly observed for the mild steel, whereas no crack is observed for the weathering steel. The rust formed on the weathering steel is presumably adherent and tight, and the outer rust is also adherent and tight.

(2) The rust constituents formed on weathering steels are not changed after a long exposure; they are only α -FeOOH and γ -FeOOH.

(3) The X-ray amorphous substance in the rust formed on the weathering steel exposed for 32 years is α -FeOOH having the small particle size.

(4) The X-ray amorphous substance in the rust layer formed on the mild steel, which gives no peak of X-ray diffraction pattern, is mainly α -FeOOH showing superparamagnetism owing to its small particle size, and Fe_{3- δ}O₄ (γ -Fe₂O₃). They are contained both in the inner rust layer and in the outer rust layer.

(5) Two possible formation processes of $Fe_{3-\delta}O_4$ on the mild steel are discussed. One is the oxidation of $Fe(OH)_2$ via green rust, and the other is the reduction of already formed γ -FeOOH during the atmospheric corrosion of steel.

REFERENCES

- T. Misawa, M. Yamashita, Y. Matsuda, H. Miyuki and H. Nagano: J. Iron Steel Inst. Japan 79 (1993) 69–75.
- M. Yamashita, H. Miyuki, T. Matsuda, H. Nagano and T. Misawa: Corros. Sci. 36 (1994) 283–299.
- M. Yamashita, H. Miyuki, H. Nagano and T. Misawa: Zairyo-to-Kankyo 43 (1994) 26–32.
- 4) H. Okada: J. Soc. Mater. Sci. Japan 17 (1968) 705-709.
- H. Okada, Y. Hosoi, K. Yukawa and H. Naito: J. Iron Steel Inst. Japan 55 (1969) 355–365.
- T. Misawa, K. Hashimoto and S. Shimodaira: Corros. Engineering Japan 23 (1974) 17–27.
- T. Misawa, K. Asami, K. Hashimoto and S. Shimodaira: Corros. Sci. 14 (1974) 279–289.
- 8) T. Misawa: Corros. Engineering Japan **32** (1983) 657–667.
- 9) H. Kihira, S. Ito and T. Murata: Corros. Sci. 31 (1990) 383–388.
- 10) J. T. Keiser and C. W. Brown: Corros. Sci. 23 (1983) 251–259.
- M. Stratmann, K. Bohnenkamp and H.-J. Engell: Welkst. Korros. 34 (1983) 604–612.
- M. Stratmann, K. Bohnenkamp and T. Ramchandran: Corros. Sci. 27 (1987) 905–926.
- 13) A. Kuch: Corros. Sci. 28 (1988) 221–231.
- 14) M. Stratmann, K. Bohnenkamp and H.-J. Engell: Corros. Sci. 23 (1983) 969–985.
- 15) U. R. Evans and C. A. J. Taylor: Corros. Sci. 12 (1972) 227-246.
- 16) I. Suzuki, Y. Hisamatsu and N. Masuko: J. Electrochem. Soc. 127 (1980) 2210–2215.
- I. Suzuki, N. Masuko and Y. Hisamatsu: Corros. Engineering Japan 23 (1974) 141–149.
- 18) M. Stratmann and K. Hoffmann: Corros. Sci. 29 (1989) 1329-1352.
- 19) M. Stratmann and J. Müller: Corros. Sci. **36** (1994) 327–359.
- 20) M. Stratmann and H. Streckel: Corros. Sci. 30 (1990) 697-714.
- 21) T. Kamimura and M. Stratmann: Corros. Sci. 43 (2001) 429-446.
- 22) J. W. Schults, S. Mohr and M. M. Lohrengel: J. Electroanal. Chem. 154 (1983) 57–68.
- 23) T. Kamimura, M. Yamashita, H. Uchida and H. Miyuki: J. Japan. Inst. Metal 65 (2001) 922–928.
- 24) M. Yamashita, A. Maeda, H. Uchida, T. Kamimura and H. Miyuki: J. Japan. Inst. Metal 65 (2001) 967–971.
- 25) J. Dünwald and A. Otto: Corros. Sci. 29 (1989) 1167–1176.
- D. C. Cook, R. Balasubramanian, S. J. Oh and M. Yamashita: Hyperfine Interact. 122 (1999) 59–70.
- 27) M. Yamashita, T. Misawa, H. E. Townsend and D. C. Cook: J. Japan Inst. Metals 64 (2000) 77–78.
- 28) M. Yamashita, T. Misawa, S. J. Oh, R. Balasubramanian and D. C. Cook: Zairyo-to-Kankyo 49 (2000) 82–87.
- 29) J. F. Marco, M. Gracia, J. R. Gancedo, M. A. Martín-Luengo and G. Joseph: Corros. Sci. 42 (2000) 753–771.
- 30) T. Kamimura and S. Nasu: Mater. Trans., JIM 41 (2000) 1208-1215.
- S. Music, G. P. Santana, G. Šmit and V. K. Garg: Journal of Alloys and Compounds 278 (1998) 291–301.

- 32) K. Nomura, M. Tasaka and Y. Ujihira: Corrosion 44 (1988) 131–135.
- 33) H. Leidheiser, Jr. and S. Music: Corros. Sci. 22 (1982) 1089–1096.
 34) A. K. Sigh, T. Ericsson, L. Häggström and J. Gullman: Corros. Sci. 25
- (1985) 931–945.
- 35) D. C. Cook: Hyperfine Interactions. 28 (1986) 891.
- 36) K. Nomura and Y. Ujihira: Hyperfine Interactions 29 (1986) 1467– 1470.
- 37) J. Davalos, M. Gracia, J. F. Marco and J. R. Gancedo: Hyperfine Interactions 69 (1991) 871–874.
- International Standards Organization, "Corrosion of Metals and Alloys Corrosivity of Atmospheres Classification", Standard 9223–92 (1992).
- 39) T. Okada, Y. Ishii, T. Mizoguchi, I. Tamura, Y. Kobayashi, Y. Takagi, S. Suzuki, H. Kihira, M. Itou, A. Usami, K. Tanabe and K. Masuda: Jpn. J. Appl. Phys. **39** (2000) 3382–3391.
- For example, K. Horikawa: Kinzoku-Hyomen-Gijutsu 34 (1983) 529– 533.
- 41) R. A. Brand: unpublished. Program is available through http://www.wissel-instruments.de.
- 42) C. E. Johnson: J. Phys. C (Solid St. Phys.) 2 (1969) 1996–2002.
- Ph. Bauer, J. M. Genin and D. Rezel: Hyperfine Interactions 28 (1986) 757–760.
- 44) S. Nasu, T. Kamimura and T. Tazaki: Hyperfine Interactions, to be pub-

lished.

- 45) E. Murad and J. H. Johnston: Iron oxides and oxyhydroxides, in: G. J. Long (Ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Vol. 2, (Plenum Publ. Co., New York-London, 1987) pp. 507–582.
- 46) J. F. Marco, M. Gracia, J. R. Gancedo, M. A. Martín-Luengo and G. Joseph: Corros. Sci. 42 (2000) 753–771.
- 47) S. Nasu, T. Kamimura and T. Tazaki: unpublished data.
- 48) S. J. Oh and D. C. Cook: J. Appl. Phys. 85 (1999) 329-332.
- 49) T. Kamimura, T. Doi, T. Tazaki, K. Kuzushita, S. Morimoto and S. Nasu: Proc. 2nd Int. Conf. on Environment Sensitive Cracking and Corrosion Damage (2001) pp. 190–196.
- 50) T. Misawa, K. Hashimoto and S. Shimodaira: Corros. Sci. 14 (1974) 131–149.
- 51) T. Misawa, T. Kyuno, W. Suëaka and S. Shimodaira: Corros. Sci. 11 (1971) 35–48.
- 52) For example, M. Stratmann: Ber. Bunsen-ges. Phys. Chem. **94** (1990) 626–639.
- 53) M. Schneider and M. Stratmann: Ber. Bunsen-ges. Phys. Chem. 96 (1992) 1731–1736.
- 54) K. Kashima, S. Hara and H. Miyuki: Proc. 2nd Int. Conf. on Environment Sensitive Cracking and Corrosion Damage (2001) pp. 197–203.