Characterization of Nanostructure of Rusts Formed on Weathering Steel

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Nano-scale structures of rusts formed on the weathering steel surface were investigated. It has been shown that the key structure is an Fe(O, OH)\textsc{6} network, which is different from crystalline FeOOH. Atomic structures were analyzed quantitatively by a combination of X-ray absorption fine structure (XAFS) analysis including \textit{in situ} observation under wet conditions, X-ray diffraction (XRD), and transmission electron microscopy (TEM). It has been shown that the Fe(O, OH)\textsc{6} network structure evolves in the process of corrosion and a small amount of alloying elements such as chromium modifies the evolution process and the final morphology of rust.

KEY WORDS: weathering steel; rust; corrosion; atomic structure; iron oxyhydroxide; network structure; X-ray absorption fine structure.

1. Introduction

Improvement of the corrosion resistance of steel without coating is very important from the viewpoint of life-cycle assessments of materials. Although low-alloy steel is believed to corrode under moisture, a protective rust layer is known to form on the surface of the steel to which small amounts of chromium and copper are added.\(^1\) This steel is called weathering steel and used as structural materials. In order to make clear the corrosion resistance mechanism, the atomic level structure of rust is of great interest. The rust mainly consists of iron oxyhydroxide, FeOOH, typically \(\alpha\)-FeOOH and \(\gamma\)-FeOOH,\(^2\)\(^-\)\(^6\) of which the crystalline structures are shown in Fig. 1. Their structures are composed of FeO\textsc{6} octahedrons and intercalated hydrogen. However, the atomic structures in actual rust formed on steel do not always keep the long-range order observed in crystals, because of small grain size and insufficient crystal growth. Because it is difficult to analyze the rusts by only conventional electron microscopy techniques, their nano-structures have never been understood yet in spite of their importance in understanding the corrosion resistance of weathering steel.

In this work, X-ray absorption fine structure (XAFS\(^7\)\(^-\)\(^8\)) analysis, X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used for characterizing nano-structures and microstructures of rusts formed on a weathering steel and a relevant alloy. Experimental results were discussed on the basis of nano-structures of rusts and a new concept of “Fe(O, OH)\textsc{6} network” composed of octahedrons of FeO\textsc{6} octahedrons and intercalated hydrogen, is proposed.

2. Experimental

Weathering steel and Fe–5mass%Cr alloy were prepared and corroded under different conditions (Table 1). A weathering steel (WS) was exposed to air in a rural area for different periods (Table 2), and rusts formed on the steel surface were analyzed by XAFS, XRD and TEM. Rusts formed on the surface of an Fe–5mass%Cr alloy (CR) were also analyzed in order to investigate the effect of chromium addition more clearly, especially in an initial stage of corrosion. Colloidal rust, CR (WET), was prepared by immersing this alloy in seawater for two weeks, and rust powder, CR (DR Y), was prepared by filtering and drying the colloidal rust at room temperature. Commercial \(\alpha\)-FeOOH (STD-\(\alpha\)) and \(\gamma\)-FeOOH (STD-\(\gamma\)) reagents were also analyzed for comparison.

The atomic structures in terms of short-range order (SRO) around iron and chromium in rusts were analyzed by measuring Fe K and Cr K XAFS spectra, respectively. Colloidal rust, which is formed at the sample surface in seawater for several days, were analyzed by a special XAFS cell for a liquid sample,\(^9\) as shown in Fig. 2. In measuring XAFS spectra in the transmission geometry, the thickness of the liquid containing colloidal rust was optimized by a micrometer, since the spectral intensities depend on the liquid density.

XAFS spectra of rust formed on the sample surface exposed for a long time were measured in the reflection geometry as shown in Fig. 3, in which the fluorescence X-ray spectra were measured by a 19-element SSD (solid state detector).\(^10\) Cr K XAFS spectra in these measurements provide information on the atomic structure around a small
amount of chromium in a sample. The size of the beam was about 1 by 1 mm$^2$ at the sample. Measurements of Fe K and Cr XAFS spectra were carried out at beam lines BL-7C$^{11}$ and BL-12C$^{10}$ at the Photon Factory, KEK, Tsukuba, Japan. XAFS spectra in the form $k^3\chi(k)$, where $k$ is the wave number, were analyzed using the program REX (Rigaku Corporation).

The atomic structures in terms of long-range order (LRO) were investigated by X-ray diffraction (XRD). The thickness of rusts on specimens range from about 50 (corrosion for 0.5 year) to more than 200 \( \mu \text{m} \) (corrosion for 15 years). At first, XRD patterns were measured for the outer layer of rusts on specimens, then the outer layer was mechanically removed in order to expose the inner layer and XRD patterns were measured for the inner layer. The rest of the rust was covered by a sheet of lead to eliminate the diffraction from the outer layer.

The microstructure of rust formed on the weathering steel was observed by field-emission transmission electron microscopy (TEM) at 200 keV. TEM samples were sliced using focused Ga ion beams with 30 keV, so that areas near the interface between the rust layer and the steel substrate could be observed. An energy-dispersive X-ray analyzer attached in TEM was also used for analyzing the chemical composition of local area in rust.

Table 1. Compositions of samples.

| Specimen | Cu (mass%) | Cr (mass%) | Ni (mass%) | Mn (mass%) | P (mass%) | Si (mass%) | C (mass%) |
|----------|------------|------------|------------|------------|-----------|------------|-----------|
| WS       | 0.28       | 0.55       | 0.15       | 0.49       | 0.081     | 0.51       | 0.10      |
| MS       | --         | --         | --         | 0.60       | 0.020     | 0.30       | 0.15      |
| GR       | --         | 5.00       | --         | --         | --        | --         | --        |

WS: weathering steel, MS: mild steel, GR: Fe-5wt.%Cr alloy

Table 2. Corrosion conditions of samples.

| Specimen | Corrosion Conditions | Specimen | Corrosion Conditions |
|----------|----------------------|----------|----------------------|
|          |                       | WS       | W35Y                  |
|          |                       | MS       | WS35Y (exposed indoors) |
|          |                       |          | W35Y                  |
|          |                       |          | WS35Y                 |
|          |                       |          | W35Y                  |
|          |                       |          | W35Y (exposed indoors) |
|          |                       |          | W35Y                  |
|          |                       |          | W35Y                  |
|          |                       |          | W35Y                  |
|          |                       |          | W35Y                  |

$w$: week, $y$: year

Fig. 1. Atomic structures of crystalline (a) $\alpha$-FeOOH and (b) $\gamma$-FeOOH, where only octahedrons of FeO$_6$ are shown.

Fig. 2. Cell for in situ XAFS measurements of liquid sample.

Fig. 3. Experimental set-up for XAFS measurements in reflection-geometry.
3. Results and Discussion

3.1. Change of Atomic Structure of Rusts during Corrosion: Formation of \("\text{Fe(O, OH)}_6\) Unit and Its Evolution

Changes in the \(\text{Fe(O, OH)}_6\) network during corrosion under atmosphere were evaluated in terms of the radial distribution function (RDF) obtained by Fourier transformation of \(\text{Fe K XAFS}\) spectra. Figure 4 shows a typical result of RDF obtained. Figure 4 shows RDF around chromium for CR2W (DRY), where RDF and the imaginary part are shown by solid and thin lines, respectively. RDF show peaks around the distance \(=0.16, 0.25, \) and \(0.34\) nm, and the imaginary part also shows peaks at the same positions. These peaks show the distances between the absorbing atom (Cr) and the nearest (1st NN), the second nearest (2nd NN), and the third nearest (3rd NN) neighboring atoms. Since the phase shift in the spectra was not taken into account in the present RDF’s, the atomic distance appears to be shorter than the real one.

Figure 5 shows characteristic RDF’s of rust formed on the surface of the Fe–5%Cr alloy under different conditions: the colloidal rust formed in seawater: CR2W (WET), the rust powder: CR2W (DRY), and the rust formed on the CR surface exposed to air indoors for 15 years: CR15Y. The RDF for crystalline \(\alpha\)-FeOOH is also shown in Fig. 5. Each peak in the RDF may basically correspond to the atomic distances observed in crystalline \(\alpha\)-FeOOH and \(\gamma\)-FeOOH, which is obtained from crystallographic data and given in Table 3,\(^{12}\) although the distance obtained in RDF is slightly short because of the phase shift. The first peaks located at about 0.15 nm in the RDF’s are attributed to the first nearest neighbor (1st NN) correlation of Fe–O. The peaks at about 0.27 and 0.32 nm in RDF’s correspond to the second (2nd NN) and the third nearest neighbors (3rd NN) correlation of Fe–Fe and Fe–O, respectively. The fact that the 1st NN peaks in the RDF’s of all rust samples are as high as that of crystalline \(\alpha\)-FeOOH (STD-\(\alpha\)) indicates that the octahedron of \(\text{Fe(O, OH)}_6\) units are formed in these rusts. However, the heights of the 2nd NN and the 3rd NN peaks in the rusts are weaker than those in \(\alpha\)-FeOOH. This suggests that the periodic arrangement of \(\text{Fe(O, OH)}_6\) units is slightly disordered, compared to that of crystalline \(\alpha\)-FeOOH having a long-range order.

Small but significant differences among these samples were found in the 3rd NN peak region; the 3rd NN peak height in CR15Y is higher than that in CR2W (DRY) and CR2W (WET). In addition, the 3rd NN peak positions in CR2W (WET) and CR2W (DRY) seem to be close to that in \(\gamma\)-FeOOH, while the 3rd NN peak position of CR15Y is near that in \(\alpha\)-FeOOH. These results suggest that the \(\text{Fe(O, OH)}_6\) network of the rust changes depending on corrosion conditions such as its atmosphere and exposing time.

The atomic structure of the rusts formed on WS after corrosion for longer periods were analyzed by XRD. Figure 6 shows X-ray diffraction patterns of the inner rusts of specimens corrodes in longer periods: (from top) STD-\(\alpha\), WS15Y, WS5Y, WSHY, STD-\(\gamma\).

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**Table 3.** Atomic distance of crystalline \(\alpha\)-FeOOH and \(\gamma\)-FeOOH.

| Pair           | Distance (nm) | N | Pair           | Distance (nm) | N |
|----------------|---------------|---|----------------|---------------|---|
| Fe–O (1st NN) | 0.1954        | 2 | Fe–O (1st NN) | 0.1973        | 2 |
| Fe–O           | 0.2068        | 2 | Fe–O           | 0.1978        | 2 |
| Fe–O           | 0.2088        | 2 | Fe–O (2nd NN) | 0.2135        | 2 |
| Fe–Fe          | 0.3024        | 2 | Fe–Fe          | 0.3060        | 2 |
| Fe–Fe          | 0.3265        | 4 | Fe–Fe          | 0.3099        | 4 |
| Fe–Fe          | 0.3465        | 4 | Fe–Fe          | 0.3870        | 2 |
| Fe–O (2nd NN)  | 0.3253        | 2 | Fe–O (2nd NN) | 0.3641        | 4 |
| Fe–O           | 0.3600        | 2 | Fe–O           | 0.3678        | 2 |

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WS15Y, WSSY, WSHY, STD-γ. The peak ratios of α-FeOOH 110/γ-FeOOH 020 are about 0.5 (WSHY), 0.6 (WSSY), and 1.2 (WS15Y). The similar tendency was also observed in the peak ratios α-FeOOH 110/γ-FeOOH 020 of the outer rusts, but it was smaller than that of the inner rusts at each period of corrosion. These results show that the Fe(O, OH)₆ network of the inner rusts changes from the one similar to γ-FeOOH into the one similar to α-FeOOH during corrosion exposed to air, and the transformation proceeds at the inner part of rusts.

Most of diffraction peaks of the rusts are broader than those of crystalline phases. The grain size (d) of the inner rust of WS15Y was calculated from the width of 110 peak using Scherrer equation as follows:

\[ d = \frac{0.9 \lambda}{W \cos \theta_b} \]  \hspace{1cm} (1)

where λ is the wave length of X-ray, and W is the width of scattering peak in radian unit. The result of curve-fitting showed that the grain-size distribution has two peaks around \( d = 15 \text{ nm} \) and \( d = 5 \text{ nm} \), as shown in Fig. 6. Grain-size distributions of the rusts formed on weathering and mild steel were reported using XRD and Mössbauer spectroscopy, showing that the particle size is about 5–25 nm in diameter. On the other hand, the diffraction pattern from the position b showed clear diffraction spots, which were also assigned to those of α-FeOOH but the crystallite size is much larger than that in position a, being about 100 nm. Only small fraction of the rust showed the morphology like the position b. It was shown to be characteristic morphology that rust formed in the weathering steel is mainly composed of very small α-FeOOH, which is contrary to the fact that the crystallite size of rust formed on mild steel is about 1 μm.

An energy-dispersive X-ray analyzer attached in TEM was used for analyzing the chemical composition of rust. The results showed that chromium is enriched by about 5–10 mass% at the position a, whereas chromium enrichment was hardly detected at the position b. It has also been shown that the thickness of the chromium enriched layer increases as exposure time increases: about 100–500 nm in WSHY, more than a few μm in WS15Y, and 10 μm in WS31Y. These results show that the amount of chromium in a fine rust having the Fe(O, OH)₆ network similar to α-FeOOH increases as exposure time increases and that enriched chromium in the network acts as a refinement of grains. This enrichment in micro-scale were also observed in macro-scale by electron probe micro analysis, showing that the particle size is about 5–25 nm in diameter. The enrichment in a scale of 0.1–10 μm may evolve in a scale of more than 100 μm during corrosion for a long period.

The present TEM observation has revealed that the inner rusts formed on weathering steel is mainly composed of small grains having a structure similar to α-FeOOH. The amount of chromium in the fine rust increases as exposure time increases, suggesting that enriched chromium in the network acts as a refinement of grains.

### 3.3. Local Structure around Chromium

Cr K XAFS spectra for sample CR and WS were measured to investigate the influence of an addition of chromium on the Fe(O, OH)₆ network formation. RDF around chromium at early stage of corrosion: CR2W (DRY) is shown in Figs. 4 and 5. The results show that peak heights of the 2nd NN and the 3rd NN peaks are much lower than those of the same specimen CR2W (DRY) (at the middle in Fig. 5). Another significant difference was observed in the...
position of the 2nd NN peak of RDF around chromium; it is much smaller than that of the 2nd NN peak of RDF around iron. Detailed analysis has shown that the distance of Cr–Fe(Cr) neighboring is 12% smaller than that of the Fe–Fe neighboring. Figure 9 shows a structure model of rusts containing chromium in its Fe(O, OH)$_6$ network, which is determined based on these results.\(^{12}\)

These difference between RDF’s obtained around chromium and iron indicates that the octahedrons of Cr(O, OH)$_6$ unit may be formed in the rust at the early stage of corrosion, but that the unit was strongly deformed or chromium atoms occupy another type of site from iron atoms. It is also shown that correlation between the Cr(O, OH)$_6$ and the neighboring Cr(O, OH)$_6$ or Fe(O, OH)$_6$ units is lower than that of between Fe(O, OH)$_6$ and Fe(O, OH)$_6$ units. This suggest that the Cr(O, OH)$_6$ unit works as a heterogeneous site in the network.

Theses effects of chromium are also likely to be found in rusts formed on the surface of the weathering steel after corrosion for long periods. XAFS spectra were measured for inner layer of rusts, where the enrichment of chromium in fine grains was observed as discussed.

Figure 10 shows time-evolution of RDF obtained by Fourier transformation of the Cr K and Fe K (the bottom one) XAFS spectra for rusts at the middle and the final stages of corrosion. Reference XAFS spectra for a metallic chromium foil (Cr foil), a bulk weathering steel (WS bulk) before corrosion, which were measured in the reflection geometry, are shown in Fig. 10 for comparison. In addition, the spectrum for $\alpha$-FeOOH (STD-$\alpha$) taken in the transmission geometry is also shown. The RDF of WS (bulk) appears to be similar to that of metallic chromium, since they have the same structure that is body centered cubic structure. The RDF of WSHY is equivalent to the atomic structure of a mixture of the initial rust and the metallic substrate. This is because signals from the steel substrate overlap to those from the thin rust in reflective XAFS measurements. However, it is interesting to note that the octahedrons of Cr(O, OH)$_6$ unit is formed in the rusts at the early stage of corrosion (2 weeks–0.5 year), as observed in the 1st NN peak of the RDF. As exposure time increases, the RDF seems to approach to the shape of $\alpha$-FeOOH, as seen in WSSY and WS15Y. However, the atomic distance observed in the 2nd NN peak corresponding to Cr–Fe correlation, about 0.23 nm, is smaller than the value observed in peaks of Fe–Fe correlation in the RDF’s of $\alpha$-FeOOH and the actual rust, about 0.27 nm, as shown in Figs. 5 and 10. These experimental results indicate that Cr(O, OH)$_6$ units in the rust are strongly distorted compared with the surrounding atomic arrangements consisting of mainly Fe(O, OH)$_6$ units in the rusts and that chromium atoms occupy another type of site from iron atoms.\(^{12}\)

3.4. Formation Process of the Fe(O, OH)$_6$ Network

On the basis of the results of present study, time-evolution of the atomic structure of the rust is discussed in terms of an Fe(O, OH)$_6$ network.\(^{12}\) This is illustrated in Fig. 11, where Fe(O, OH)$_6$ and Cr(O, OH)$_6$ units are denoted by triangles with dots and crosses, respectively.

At the initial stage of corrosion of steel, iron atoms form Fe(O, OH)$_6$ units in water or in air with moisture, resulting in formation of colloidal rusts. The Fe(O, OH)$_6$ units in the rusts may be similar to the structural components as found in FeOOH of Fig. 1. The RDF results, as shown in Figs. 4 and 5, have indicated that there is clear 1st NN and 2nd NN correlations in CR2W (WET), but the 3rd NN correlation is only observed after drying in CR2W (DRY). These results suggest that in a wet-dry process, the initial Fe(O, OH)$_6$ units evolve to form the Fe(O, OH)$_6$ network which is similar to that of crystalline $\gamma$-FeOOH. As the corrosion progresses after about half a year, the Fe(O, OH)$_6$ network may change from $\gamma$-FeOOH like to $\alpha$-FeOOH like, which have reportedly very fine grain size about 5–15 nm in diameter in Mossbauer spectroscopy (Fig. 7).\(^{13}\)

Chromium addition results in formation of Cr(O, OH)$_6$ units having different structures from Fe(O, OH)$_6$, as shown in Fig. 9. Thus, the Cr(O, OH)$_6$ units may influence the evolution of Fe(O, OH)$_6$, so as to distort the Fe(O, OH)$_6$ network. This is related to the fact that the final size distribution of $\alpha$-FeOOH formed in the weathering steels is smaller than that in mild steel. In particular, this tendency may be remarkable in an inner layer of rust formed on the surface of the weathering steel, where chromium is considerably enriched. Actually, the previous works\(^{3–6,12–14}\) reported that inner rust formed on the weathering steel is composed of very fine $\alpha$-FeOOH and enrichment of chromium is related to the formation of such fine $\alpha$-FeOOH. Therefore, the pre-
sent experimental results may explain the mechanism of refinement of \( \alpha \)-FeOOH in the rust by chromium addition.

Evolution of the \( \text{Fe(O, OH)}_6 \) network during corrosion can be considered from the viewpoint of an electrochemical reaction. Anodic reaction in corrosion is simply expressed as follows:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe(OH)}_2 \rightarrow \text{FeOOH} \quad \text{............(2)}
\]

This reaction accompanies several phenomena such as nucleation, growth, coagulation, adhesion and ripening, and a combination of these reactants, which influence the corrosion rate.\(^6\),\(^15\)

When these reactions are considered as a sum of nucleation and grain-growth, the total rate of reaction \( (v) \) can be written as follows:

\[
v = N \exp\left(-E_{\text{Nucl.}}/kT\right) \exp\left(-E_{\text{Growth}}/kT\right) \quad \text{............(3)}
\]

where \( N \) is the number of reaction sites, and \( E_{\text{Nucl.}} \) and \( E_{\text{Growth}} \) are activation energy of nucleation and growth of reaction products, respectively. At the initial stage of corrosion, the \( \text{Fe(O, OH)}_6 \) units nucleate from \( \text{Fe}^{2+} \). Since alloying elements such as chromium may increase the atomic level heterogeneity in rusts as described above, they possibly increase the number of reaction sites. It is also expected that the nucleation energy of the \( \text{Cr(O, OH)}_6 \) unit is different from that of the \( \text{Fe(O, OH)}_6 \) and that this may decrease \( E_{\text{Nucl.}} \). The increase of \( N \) and decrease of \( E_{\text{Nucl.}} \) may enhance nucleation, which induces refinement of rust particles.

Also, it has been proposed in previous works\(^3\)–\(^6\) that rust of very fine crystallites is expected to be protective against diffusion of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) along the grain boundaries. Thus, the formation of fine rust results in reduction of the corrosion reaction rate, and this is understood as an increase of \( E_{\text{Growth}} \) in this model.

In such a manner, chromium addition is considered to modify the process of evolution of the \( \text{Fe(O, OH)}_6 \) network.

4. Conclusion

Fe K and Cr K X-ray absorption fine structure (XAFS) analyses with X-ray diffraction (XRD) and transmission electron microscopy (TEM) have been used for studying the atomic structure and microstructure of rusts formed on a weathering steel and an iron-chromium alloy. The main conclusions are as follows:

1. The atomic structure of the rust is expressed by the \( \text{Fe(O, OH)}_6 \) network, which evolves in the process of corrosion.

2. A small amount of an alloying element such as chromium modifies the evolution process and the morphology of rust. In particular, chromium addition decreases the size of \( \alpha \)-FeOOH and produces heterogeneous sites in the \( \text{Fe(O, OH)}_6 \) network.

3. The change of the \( \text{Fe(O, OH)}_6 \) network affects the process of the corrosion reaction, resulting in a different morphology after corrosion for a long period: very fine grains as found in the inner rusts formed on the weathering steel.

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