Atomic-Scale Structure and Morphology of Ferric Oxyhydroxides Formed by Corrosion of an Iron–Silicon Alloy

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Quantitative X-ray structural analysis using an in-house X-ray diffraction apparatus has been used for characterizing the atomic-scale structure of the γ-FeOOH (lepidocrocite) particles prepared by dipping a pure iron and an iron-silicon alloy into aqueous solutions containing sodium chloride. The morphology of the γ-FeOOH particles was observed by transmission electron microscopy (TEM), and their bonding structure were analyzed using Fourier transform infrared spectroscopy (FT-IR). The realistic atomic-scale structures in the γ-FeOOH particles were estimated by fitting the interference functions with the help of the reverse Monte Carlo (RMC) simulation technique. The results showed that the linkages of fundamental FeO₆ octahedral units in the particles were deviated from the ideal crystal structure. The structural deviation is considered to be due to the incorporation of foreign ions during the formation of these particles in the aqueous solutions.

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1. Introduction

Atmospheric corrosion of steel occurs by exposure to humid air at room temperature, and corrosion products are formed through dissolution and precipitation of ferric and ferrous ions from the surface of steel.¹ The species and fraction of the constituents of corrosion products are governed by the amounts of ferrous and ferric ions, foreign ions and so on.²,³ Anodic and cathodic reactions occur on the surface of steel under environments, and corrosion products are formed from ferric, ferrous and hydroxyl ions through these reactions.²,³ The corrosion rate of steel is influenced by the properties of corrosion products formed on the steel surface, as seen a protective rust layer on weathering steel.⁴–⁶ Thus, the structure and properties of corrosion products are of great importance.

Ferric oxyhydroxides, γ-FeOOH and α-FeOOH, are known to be the main components of corrosion products formed by atmospheric corrosion and to turn into γ-Fe₂O₃.⁷,⁸ The structure of ferric oxyhydroxides is described using the linkages of FeO₆ octahedral units, and the octahedral units are linked by corners, edges or faces to form different structural arrays, which are maintained even in the amorphous state.⁹ As the linkages of the octahedral units are correlated with the morphology and stability of ferric oxyhydroxides, the influences of foreign cations and anions on the atomic-scale structure of ferric oxyhydroxides have been focused.¹⁰–¹³ Thus, it is required that the influence of foreign ions on the atomic-scale structures of corrosion products formed on the surface of iron-based alloys or steel is clarified.

The extended X-ray absorption fine structure (EXAFS) measurements¹⁴–¹⁶ and other methods have been used for characterizing the local structure of corrosion products, but structural information obtained by EXAFS seems to be too short-range to discuss the linkage of the FeO₆ octahedral units in the structure of the ferric oxyhydroxides. Recently, quantitative X-ray structural analysis using ordinary and anomalous X-ray scattering (AXS) along with reverse Monte Carlo (RMC) simulation, which was verified for various states, such as liquids and aperiodic systems,¹⁷–¹⁹ have been used successfully for characterizing the atomic-scale arrangement of ferric oxyhydroxides. The structural analysis showed that the linkages of FeO₆ octahedral units are influenced by the incorporation of foreign cations and anions during the formation of ferric oxyhydroxides.¹⁰ On the other hand, as anions are mainly composed of relatively light elements, the quantitative X-ray structural analysis along with other spectroscopic methods is effective in the atomic-scale structure of corrosion products.

Silicon is one of the most important alloying elements in steel, which may influence the structure of corrosion products. Thus, the objective of this work is to show a method for preparing corrosion products of one specific kind of ferric oxyhydroxide, γ-FeOOH, by dipping a pure iron and an iron silicon alloy into aqueous media containing different salts, and to characterize the influence of foreign atoms, especially silicon, on the atomic-scale structure of corrosion products of γ-FeOOH using quantitative X-ray structural analysis coupled with RMC simulation. The morphologies of the corrosion products were observed by transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR) was used to study the influence of foreign ions on the structure.

2. Experimental

2.1 Sample preparation

Commercial γ-FeOOH (99% above) manufactured by Kojundo Chemical Lab. Co., Ltd. was used as pure γ-FeOOH particles, in order to compare the structure and morphology of practical corrosion products. This is because the pure γ-FeOOH particles were relatively well crystallized, and they are hereafter referred to as γ-FeOOH.

Sheets of a pure iron and an iron–2 mass% silicon alloy of about 0.3 mm in thickness were used as starting material for preparing corrosion products formed in aqueous media. The sheets were cut and dipped into 20 ml aqueous solutions
containing 2 mass% sodium chloride (NaCl). Corrosion products consisting mainly of γ-FeOOH particles were formed in open 150 mL glass bottles for 14 days at room temperature. The γ-FeOOH particles were filtered and dried at room temperature. The corrosion products, prepared from the pure iron and the iron-silicon alloy in the solution, are referred to as γ-Fe-Rust and γ-FeSi-Rust, respectively.

2.2 Measurements

X-ray diffraction measurements were carried out using an X-ray diffractometer apparatus with a Mo Kα radiation of 17.447 keV (50 kV, 30 mA). The X-ray scattering intensity was measured with a wide range of wave vectors, in order to obtain an accurate interference function for samples. The atomic-scale structure of γ-FeOOH particles was described using the partial distribution functions calculated from the interference functions obtained by statistical optimization through RMC simulation technique.17–19 The RMC routine is essentially identical to that used in our previous work.10 The super cells of γ-FeOOH were assigned dimensions of 3.756 × 3.870 × 3.684 nm³. The simulation was accomplished with initial configurations of 4320 atoms (1440 for iron and 2880 for oxygen) for γ-FeOOH, positioned in each super cell. The atomic configurations of iron and oxygen were estimated in this work, as X-ray scattering intensities by the partial pair distribution functions calculated from the atomic-scale structure of γ-FeOOH, presumably by the absorption of foreign ions. Peaks of γ-FeOOH are broader than those for γ-Fe-Rust and γ-FeSi-Rust, and their linkages appear to be significantly distorted in γ-Fe-Rust and γ-FeSi-Rust are distorted compared to the case of γ-FeOOH.

The experimental ordinary interference functions $Q(\langle Q \rangle)$ for γ-FeOOH, γ-Fe-Rust and γ-FeSi-Rust are shown as dots in Figs. 2(a), (b) and (c), respectively. The realistic atomic-scale arrangements in these samples were estimated by fitting the interference functions through the RMC simulation technique. The interference functions computed by the RMC method were compared with the experimental interference functions so new atomic configurations in the super cell were generated through the random movement of atomic positions for structural optimization. The interference functions were calculated by repetition of acceptance and rejection on the basis of comparison with the previous configuration data. When the interference functions so new atomic configurations in the super cell were generated through the random movement of atomic positions for structural optimization. The interference functions were calculated by repetition of acceptance and rejection on the basis of comparison with the previous configuration data. When the interference functions of Fe–O, Fe–Fe, and O–O pairs in γ-FeOOH, γ-Fe-Rust, and γ-FeSi-Rust estimated by RMC simulation.

3. Results and Discussion

3.1 X-ray diffraction profiles and interference functions

Figures 1(a), (b), and (c) show the X-ray diffraction profiles for γ-FeOOH, γ-Fe-Rust and γ-FeSi-Rust, respectively. The reference lines for γ-FeOOH, given in the JCPDS database, are also shown for comparison. The results show that the fundamental structures of these samples are the γ-FeOOH structure, however the structures of γ-Fe-Rust and γ-FeSi-Rust are distorted compared to the case of γ-FeOOH.

Figures 2 and 3 show the partial pair distribution functions of Fe–O, Fe–Fe, and O–O pairs in γ-FeOOH, γ-Fe-Rust, and γ-FeSi-Rust estimated by RMC simulation. The experimental ordinary interference functions $Q(\langle Q \rangle)$ for γ-FeOOH, γ-Fe-Rust and γ-FeSi-Rust are shown as dots in Figs. 2(a), (b) and (c), respectively. The realistic atomic-scale arrangements in these samples were estimated by fitting the interference functions through the RMC simulation technique. The interference functions computed by the RMC method were compared with the experimental interference functions so new atomic configurations in the super cell were generated through the random movement of atomic positions for structural optimization. The interference functions were calculated by repetition of acceptance and rejection on the basis of comparison with the previous configuration data. When the difference between the experimental results and calculated values was smaller than that of the previous configuration, the new configuration was accepted. The results of the RMC simulation are shown as solid lines in Fig. 2. The computed interference functions are in good agreement with the experimental results.
y\text{-}Fe\text{-}Rust and y\text{-}FeSi\text{-}Rust, as shown in Fig. 3(c). These results indicate that the linkages of FeO$_6$ octahedral units are distorted, which may arise from the incorporation of chloride and silicate in aqueous solutions.

The realistic atomic arrangements calculated by RMC simulation for γ-FeOOH, γ-Fe-Rust, and γ-FeSi-Rust are shown in Figs. 4(a), (b) and (c), respectively. The γ-FeOOH structure consists of double chains of edge-shared octahedral units parallel to the $b$-axis, and the double chains share edges with adjacent double chains forming corrugated sheets of octahedral units. The atomic arrangements in γ-FeOOH are similar to those in the ideal γ-FeOOH structure. On the other hand, the shape of FeO$_6$ octahedral units in γ-Fe-Rust and γ-FeSi-Rust and the linkages of FeO$_6$ octahedral units are distorted.

### 3.3 Transmission electron micrographs

As the atomic-scale structure of ferric oxyhydroxide is reflected by its microscopic morphology, the particles were observed using a transmission electron microscope. Transmission electron micrographs of γ-FeOOH, γ-Fe-Rust, and γ-FeSi-Rust are shown in Figs. 5(a), (b) and (c), respectively. The morphologies of these samples are plate-shaped, which results from the layered structure of γ-FeOOH shown in Fig. 4. The size and aspect ratio are different in γ-FeOOH, γ-Fe-Rust, and γ-FeSi-Rust. In addition, the morphologies of γ-FeOOH particles, as show in Fig. 5, are likely to be correlated the atomic-scale distortion detected in quantitative X-ray diffraction analysis. As differences in the atomic-scale structure and morphology may be induced by foreign ions incorporated in the samples, FT-IR of the γ-FeOOH particles were measured.

### 3.4 Infrared spectra

Figures 6(a), (b) and (c) show the IR spectra in the 500–1500 cm$^{-1}$ region of γ-FeOOH, γ-Fe-Rust and γ-FeSi-Rust, respectively. Four main absorption peaks are observed at approximately 1142, 1023, 750, and 583 cm$^{-1}$, which is characteristic of the bonding structure in γ-FeOOH$^{20-22}$ The absorption band at approximately 1142 cm$^{-1}$ is assigned to the in-plane Fe–O–H bending vibration, and it is shifted to a
The absorption band at approximately 583 cm$^{-1}$ is attributed to Fe–O vibration related to the displacement of oxygen ions (O$^{2-}$), and this band becomes smaller in γ-FeOOH and γ-FeSi-Rust. These results indicate that the bonding structures in in-plane Fe–O–H bending and Fe–O vibration are changed in the particles formed by corrosion of the pure iron and the iron–silicon alloy. In addition, the adsorption band at approximately 910 cm$^{-1}$ is observed in Fig. 5(c), which is caused by Fe–O–Si bending vibration.$^{20,21}$

Thus, the incorporation of foreign ions, presumably silicate ions from alloying elements, in ferric oxyhydroxide is suggested by FT-IR spectra. This result corresponds to the structural and morphological results obtained by quantitative X-ray diffraction method and transmission electron microscopy. In this study, the influence of the foreign ions to the X-ray scattering was neglected for the structural calculation, since the atomic position of the anions in the unit cell is not identified and they are of relatively light elements. Nevertheless, the atomic-scale structures estimated by RMC simulation in this study are believed to be sufficiently reasonable.

4. Conclusion

Quantitative X-ray structural analysis along with RMC simulation, TEM, and IR were used for characterizing the influence of foreign ions, mainly silicate ions, on the atomic-scale structure and morphology of γ-FeOOH particles, which are formed by corrosion of iron alloys.

(1) The pair distribution functions and atomic arrangements estimated using quantitative X-ray diffraction profiles and the RMC simulation indicated that the structure and linkages of FeO$_6$ octahedral units in γ-FeOOH are distorted by the incorporation of the foreign ions, presumably silicate ions from alloying elements.

(2) Absorption bands observed in FT-IR spectra are attributed to the presence of foreign ions in γ-FeOOH particles. The incorporation of the foreign ions in the particles is considered to lead to morphological changes, as observed by TEM.

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