Atomic-scale Structure of Ferric Oxyhydroxide Formed from Fe–Si Alloy in Aqueous Solutions Containing Different Salts

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(Received on February 13, 2006; accepted on June 5, 2006)

Quantitative X-ray structural analysis coupled with reverse Monte Carlo (RMC) simulation was performed for characterizing the atomic-scale structure of γ -FeOOH (lepidocrocite) particles. These particles were formed by dipping pure iron or Fe–2mass%Si alloy into aqueous solutions containing Na_2SO_4 or NaCl. The realistic atomic-scale structures of γ -FeOOH particles were estimated by fitting ordinary interference functions through the RMC simulation technique. The results revealed that the fundamental FeO_6 octahedral structural units and their linkages were distorted in the γ -FeOOH particles formed from the Fe–Si alloy. This distortion was considered to be caused by the incorporation of silicate species into these particles. Transmission electron microscopy and Fourier-transform infrared (FT-IR) spectroscopy were employed for observing the morphology of the particles and for characterizing their bonding structure, respectively. Further, the amount of γ -FeOOH particles formed was measured in order to investigate their formation processes. The changes in the pH and oxidation-reduction potential (ORP) of the solutions were monitored during the formation of γ -FeOOH particles. Inductively coupled plasma analyses were also performed for determining the amounts of iron and silicon in supernatant solutions. The results indicated that the formation process of γ -FeOOH particles in the solutions was influenced by the addition of silicon to iron.

KEY WORDS: ferric oxyhydroxide; lepidocrocite; X-ray diffraction; atomic-scale structure.

1. Introduction

Atmospheric corrosion of iron-based alloys and steel is triggered by exposure to humid air, and corrosion products are formed on their substrates by various anodic and cathodic reactions that occur under various environments.¹⁾ The species and fractions of the constituents of corrosion products are governed by pH, oxidation rate, light, temperature, concentration of ferrous and ferric ions, foreign elements in the system, and so on.²⁾ In general, the actual corrosion process begins with the formation of ferrous ions through the oxidation of iron in aqueous solutions. The resulting corrosion products mainly comprise ferric ions and foreign cations and anions from alloying elements and the atmosphere.^{1,2)} The corrosion processes of steel are influenced by a layer of corrosion products formed on its surface. Typically, a protective layer formed on the surface of weathering steel reduces the corrosion rate.^{3–9)} Therefore, the atomic-scale structure and morphology of corrosion products are very important for understanding the corrosion mechanism. This is because they are closely related to the corrosion process on the surface of iron-based alloys and steel.

Ferric oxyhydroxides are one of the most important corrosion products, and γ -FeOOH is known to be a representative ferric oxyhydroxide formed on iron-based alloys and

steel during atmospheric corrosion. These oxyhydroxides are formed by dissolution and recrystallization through the ololation and oxolation of FeO_6 octahedral units^{1,10,11)} that are maintained even during the amorphous state in the corrosion process.¹²⁾ The atomic-scale structures of ferric oxyhydroxides are fundamentally described based on the linkages of FeO_6 octahedral units; these units are linked by corners, edges, faces, or combinations of these linkages to form different structural arrays.^{1,2,12)} The linkages of the local structure are influenced by cations and anions during the formation of ferric oxyhydroxides. It is possible that the atomic-scale structures of ferric oxyhydroxides are correlated with their morphology and stability.^{13,14)} It is reported that some elements strongly affect the formation and atomic-scale structures of ferric oxyhydroxides.^{15–23)} Therefore, the influence of cations and anions on the atomic-scale structures of ferric oxyhydroxides formed by iron-based alloys and steel under various environments are strongly required in order to understand the relation between the atomic-scale structures and corrosion process.

Recently, quantitative X-ray structural analysis using ordinary and anomalous X-ray scattering (AXS) coupled with reverse Monte Carlo (RMC) simulation, which was verified in various states such as liquids, glasses, and aperiodic systems,^{24–27)} was successfully performed for the characterization of the atomic-scale structures of ferric oxyhydrox-

ides.^{13–15,21,22)} However, the anions in corrosion products such as carbonates, silicates, and sulfates are composed of relatively light elements that cannot be easily identified by X-ray scattering. Thus, the application of the AXS measurement with synchrotron radiations is limited to some extent. In this regard, quantitative X-ray structural analysis coupled with RMC simulation using in-house equipment and other spectroscopic methods is significantly more effective for investigating the influence of anions on the atomic-scale structure of corrosion products; this is proved in our previous reports.¹⁵⁾

Silicon is one of the most important elements of steel and is often used as an alloying element in order to improve corrosion resistance.^{28–30)} It is known that during atmospheric corrosion, silicate ions are formed by the oxidation of silicon present in steel.^{31,32)} However, the influence of silicon in iron-based alloys and steel on the formation and atomic-scale structures of ferric oxyhydroxides during the actual corrosion process has not yet been clarified. Actually, the corrosion products, which are formed through the repetition of wetting and drying processes during atmospheric corrosion, are complicated and somewhat different from the corrosion products formed in aqueous solutions. However, the atomic-scale structural characterization of ferric oxyhydroxides formed in aqueous solutions is very effective to investigate an influence of silicon on the structure of specific corrosion products without other factors in the atmospheric corrosion. Such an initial layer of ferric oxyhydroxides formed on the surface of steel may also affect subsequent corrosion process. With this background, we studied the atomic-scale structures of ferric oxyhydroxides formed from Fe–Si alloy in aqueous solutions. In this study, quantitative X-ray structural analysis using in-house X-ray diffraction equipment with Mo K α radiation coupled with RMC simulation was used for investigating the atomic-scale structure of γ -FeOOH particles. These particles were formed from Fe–Si alloy substrates by reaction with solutions of 2 mass% Na₂SO₄ and NaCl. The morphologies of these particles were observed by transmission electron microscopy, and the changes in their bonding structure were analyzed by infrared spectroscopy. Furthermore, in order to characterize the reaction field of nucleation and growth of the solid particles of γ -FeOOH in the solutions, the solutions were analyzed using different methods. The changes in the pH and oxidation-reduction potential (ORP) of the solutions were monitored during the reaction. The amount of γ -FeOOH particles formed was measured, and inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses were performed in order to investigate the changes in the content ratio of silicon to iron dissolved in supernatant solutions.

2. Experimental

2.1. Sample Preparation

Ingots of pure iron (99.99%) and Fe–2mass%Si alloy were produced by vacuum induction melting of electrolytic iron and pure silicon. They were rolled and shaped into samples with dimensions of 30 mm×25 mm×1 mm. They were then dipped into 20 mL aqueous solutions of 2 mass% Na₂SO₄ and NaCl in open 100 mL glass bottles up to 14 d

at room temperature. Colloidal particles, which primarily comprised γ -FeOOH, were filtered through a 0.2 μ m membrane filter in order to separate solid particles from the supernatant solutions of the suspensions. The solid particles were washed with distilled water and dried for 48 h at room temperature in air. Hereafter, γ -FeOOH particles formed from pure iron and the Fe–Si alloy in the solution of 2 mass% Na₂SO₄ are referred to as γ -Fe/Na₂SO₄ and γ -Fe–Si/Na₂SO₄, respectively. γ -FeOOH particles formed from pure iron and the Fe–Si alloy in the solution of 2 mass% NaCl are referred to as γ -Fe/NaCl and γ -Fe–Si/NaCl, respectively.

2.2. Characterizations

X-ray diffraction measurements were performed using in-house X-ray diffraction equipment with Mo K α radiation of 17.447 keV (50 kV, 30 mA), Rigaku RINT-2200. The scattering X-ray intensity was measured in a wide range of wave vectors in order to determine accurate interference functions of the samples. The realistic atomic-scale structures of γ -FeOOH particles were determined by fitting the experimental interference functions with those calculated using statistical optimization; in this optimization, the atomic positions were changed from the initial configurations in an ideal structure by the RMC simulation technique.^{13–15,24–27)} In this simulation, the supercells of γ -FeOOH were determined with dimensions of 3.756 nm×3.870 nm×3.684 nm in order to ensure that the crystal was composed of a sufficient number of atoms for computational accuracy. The simulation was accomplished with initial configurations of 4 320 atoms (1 440 for iron and 2 880 for oxygen) positioned in the supercell of γ -FeOOH. The atomic-scale structures were described using FeO₆ octahedral units and their linkages in γ -FeOOH particles by using partial distribution functions. The typical periodic boundary conditions, in which the cell is surrounded by its images, were applied and the interference functions were calculated to obtain the quantitative structural information related to nearest-neighbor correlations. Detailed methods of these measurements and characterizations are described elsewhere.²⁴⁾

A transmission electron microscope, JEOL JEM-1200EX II, was used for observing the microscopic morphology of the solid particles. A Fourier-transform infrared spectroscope (FT-IR), DIGILAB FTS 7000, was used for characterizing the influence of silicon on the bonding structure of γ -FeOOH particles formed in the solutions. The amount of solid particles, particularly those of γ -FeOOH, formed at different times was weighted. The changes in the pH and ORP of the suspensions with reaction time were monitored using a TOA DKK IM-55G ion meter. A platinum electrode, which was referred to Ag/AgCl in 3.33 mol/dm^{−3} KCl solution, was used for ORP measurement. The contents of iron and silicon in the separated supernatant solutions were analyzed using ICP-AES equipment, Perkin-Elmer Optima 3300.

3. Results and Discussion

3.1. Atomic-scale Arrangements of Different γ -FeOOH Particles

Figures 1(a)–1(d) show the X-ray diffraction patterns as a function of 2θ for γ -Fe/ Na_2SO_4 , γ -Fe-Si/ Na_2SO_4 , γ -Fe/ NaCl , and γ -Fe-Si/ NaCl , respectively; these particles were obtained by the reaction in the solutions of 2 mass% Na_2SO_4 and NaCl . The reference lines for γ -FeOOH mentioned in the JCPDS database are also shown in Fig. 1. The fundamental structure of these samples was identical to that of γ -FeOOH indicated by the reference lines, and the other phases were not observed in all X-ray diffraction patterns. However, the diffraction patterns revealed that the intensity ratios of the diffraction peaks of γ -Fe-Si/ Na_2SO_4 and γ -Fe-Si/ NaCl differed from those of γ -Fe/ Na_2SO_4 and γ -Fe/ NaCl . These results indicate that the short-range and/or middle-range structures in γ -Fe-Si/ Na_2SO_4 and γ -Fe-Si/ NaCl were changed; this may be attributed to the effect of silicon during the formation of γ -FeOOH particles.

The experimental and calculated interference functions $Q_i(Q)$ for γ -Fe/ Na_2SO_4 , γ -Fe-Si/ Na_2SO_4 , γ -Fe/ NaCl , and γ -Fe-Si/ NaCl are shown in Figs. 2(a)–2(d), respectively. The experimental ordinary interference functions obtained from the X-ray diffraction patterns are shown as dots. The realistic atomic-scale arrangements of γ -Fe/ Na_2SO_4 , γ -Fe-Si/ Na_2SO_4 , γ -Fe/ NaCl , and γ -Fe-Si/ NaCl were determined by fitting the interference functions computed by the RMC method, which are shown as solid lines in Fig. 2, with the experimental interference functions. New atomic configurations in the supercell were generated by randomly changing the atomic positions for structural optimization in the crystal. The interference functions were calculated by accepting or rejecting these configurations based on a comparison with previous configuration data. When the difference between the experimental and calculated values was less than that in the previous configuration, the new configuration was accepted; otherwise, it was rejected. This iterative process was accomplished with sufficient time until a reasonable convergence was obtained by statistical optimization. In all cases, the computed interference functions were in good agreement with the experimental results, although some deviations from the experimental data occurred possibly due to the relatively simple assumptions of this RMC simulation. For the calculation, the contribution of silicon in X-ray scattering was assumed to be negligible because its atomic position in the unit cell could not be identified and it could not be easily detected by X-ray scattering since it is a relatively light element. However, the atomic-scale structures determined by the RMC simulation in this study were considered to be quite reasonable because they were calculated from precise measurements.

Figures 3(a)–3(c) show the partial pair distribution functions of the pairs of Fe–O, Fe–Fe, and O–O in γ -Fe/ Na_2SO_4 and γ -Fe-Si/ Na_2SO_4 . These functions were calculated from the new atomic configurations by statistical optimization between the experimental and calculated interference functions through the RMC simulation technique. The partial pair distribution functions of the pairs of Fe–O, Fe–Fe, and O–O in γ -Fe/ NaCl and γ -Fe-Si/ NaCl are shown in Figs. 4(a)–4(c). These functions suggest that the structures of γ -

Fig. 1. X-ray diffraction patterns as a function of 2θ for (a) γ -Fe/ Na_2SO_4 , (b) γ -Fe-Si/ Na_2SO_4 , (c) γ -Fe/ NaCl , and (d) γ -Fe-Si/ NaCl . These particles were obtained by the reaction in the solutions of 2 mass% Na_2SO_4 and NaCl using in-house X-ray diffraction equipment with Mo $K\alpha$ radiation of 17.447 keV. The reference lines for γ -FeOOH mentioned in the JCPDS database are also shown.

Fig. 2. Experimental and calculated interference functions $Q_i(Q)$ estimated by the RMC simulation for (a) γ -Fe/ Na_2SO_4 , (b) γ -Fe-Si/ Na_2SO_4 , (c) γ -Fe/ NaCl , and (d) γ -Fe-Si/ NaCl . Dots and solid lines indicate experimental and calculated values, respectively.

FeOOH particles depend on the presence of silicon in iron instead of the species of the salts in the solutions. Some deviations are observed in the peaks of the partial pair distribution functions of Fe–O, $g_{\text{Fe-O}}$, that are located around 0.2 nm, between γ -Fe-Si/ Na_2SO_4 and γ -Fe-Si/ NaCl . Moreover, the distribution profiles of γ -Fe-Si/ Na_2SO_4 and γ -Fe-Si/ NaCl are broader than those of γ -Fe/ Na_2SO_4 and γ -Fe/ NaCl . This indicates that the fundamental FeO_6 octahedral units are distorted and the iron-oxygen neighboring correlations in γ -Fe-Si/ Na_2SO_4 and γ -Fe-Si/ NaCl are distributed, possibly by the influence of silicate ions. The pair distribution functions of Fe–Fe, $g_{\text{Fe-Fe}}$, for γ -Fe-Si/ Na_2SO_4

Fig. 3. Partial pair distribution functions of the pairs of (a) Fe–O, (b) Fe–Fe, and (c) O–O estimated by the RMC simulation for γ -Fe/ Na_2SO_4 and γ -Fe-Si/ Na_2SO_4 obtained by the reaction for 14 d in the solution of 2 mass% Na_2SO_4 .

Fig. 4. Partial pair distribution functions of the pairs of (a) Fe–O, (b) Fe–Fe, and (c) O–O estimated by the RMC simulation for γ -Fe/ NaCl and γ -Fe-Si/ NaCl obtained by the reaction for 14 d in the solution of 2 mass% NaCl .

and γ -Fe-Si/ NaCl differ significantly from those of γ -Fe/ Na_2SO_4 and γ -Fe/ NaCl , as shown in Figs. 3(b) and 4(b). The peaks of $g_{\text{Fe-Fe}}$ for γ -Fe-Si/ Na_2SO_4 and γ -Fe-Si/ NaCl are broader than those for γ -Fe/ Na_2SO_4 and γ -Fe/ NaCl . Some differences are also observed in the pair distribution functions of O–O, $g_{\text{O-O}}$, between γ -Fe/ Na_2SO_4 and γ -Fe-Si/ Na_2SO_4 and between γ -Fe/ NaCl and γ -Fe-Si/ NaCl . Therefore, these distribution profiles clearly indicate that the distance of the fundamental FeO_6 octahedral units and their linkages related to the middle-range order in the crystal are distorted by the incorporation of silicate ions during the formation process of γ -FeOOH particles in the solutions of Na_2SO_4 and NaCl .

Figures 5(a)–5(d) show the realistic atomic arrange-

Fig. 5. Atomic arrangements of (a) γ -Fe/ Na_2SO_4 , (b) γ -Fe-Si/ Na_2SO_4 , (c) γ -Fe/ NaCl , and (d) γ -Fe-Si/ NaCl determined by the RMC simulation. The arrangements are described using FeO_6 octahedral structural units.

ments in the crystal estimated by the RMC simulation for γ -Fe/ Na_2SO_4 , γ -Fe-Si/ Na_2SO_4 , γ -Fe/ NaCl , and γ -Fe-Si/ NaCl , respectively. γ -FeOOH exhibits a layered structure in which four formula units exist in an orthorhombic unit cell. The anions are stacked in cubic close-packing arrays, and Fe ions occupy the octahedral interstices. The fun-

damental structures can be described using FeO_6 octahedral units. The structure of $\gamma\text{-FeOOH}$ comprises double chains of edge-sharing FeO_6 octahedral units. These double chains share edges with adjacent double chains to form corrugated sheets of FeO_6 octahedral units; they are linked only by hydrogen bonds, which have not been shown. The atomic arrangements of $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe}/\text{NaCl}$ indicate that the linkages of FeO_6 octahedral structure units are similar to those of the ideal $\gamma\text{-FeOOH}$ structure, although some structural distortion in the linkages of FeO_6 occurs due to the incorporation of unwanted anions during the formation of $\gamma\text{-FeOOH}$ particles. On the other hand, the fundamental FeO_6 octahedral units in $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe-Si}/\text{NaCl}$ are distorted and their linkages deviate from those of $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe}/\text{NaCl}$. Thus, it is likely that the resulting atomic-scale structures are influenced by the incorporation of silicate species in the formation process of $\gamma\text{-FeOOH}$ particles. In real corrosion processes, foreign species such as cations and anions dissolved in the solutions may influence not only the local structure but also morphology of the corrosion products by the incorporation in the corrosion products. Thus, such distorted atomic-scale structure of corrosion products may result in the formation of a relatively dense rust layer on the surface of iron-based alloys, which is believed to tend to suppress the diffusion or permeation of oxygen, other foreign species through the rust layer,¹⁴⁾ although further experiments are required for verify such a mechanism. Furthermore, the present method for estimating the atomic-scale arrangements is considered to be useful for discussing the formation processes of corrosion products and for understanding the corrosion mechanism in various aqueous solutions that contain foreign species.

3.2. Transmission Electron Microscopy and Infrared Spectroscopy

The transmission electron micrographs of $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$, $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$, $\gamma\text{-Fe}/\text{NaCl}$, and $\gamma\text{-Fe-Si}/\text{NaCl}$ produced by the reaction for 14 d are shown in Figs. 6(a)–6(d), respectively. The solid particles of $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe}/\text{NaCl}$ exhibited plate-like morphologies. On the other hand, the particle sizes of $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe-Si}/\text{NaCl}$ decreased slightly and the aspect ratio of solid particles was greater than that of $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe}/\text{NaCl}$. Electron probe microanalysis revealed that the molar ratios of silicon to iron in $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe-Si}/\text{NaCl}$ were 0.037 and 0.043, respectively. Therefore, the morphological changes of $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe-Si}/\text{NaCl}$ were attributed to the incorporation of silicate species during the formation of $\gamma\text{-FeOOH}$ particles in the solutions of 2 mass% Na_2SO_4 and NaCl .

Figures 7(a)–7(d) show the FT-IR absorption spectra in the range of 500–1500 cm^{-1} for $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$, $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$, $\gamma\text{-Fe}/\text{NaCl}$, and $\gamma\text{-Fe-Si}/\text{NaCl}$, respectively. For these samples, three main absorption peaks were observed around 1150, 1020, and 750 cm^{-1} , which were similar to those of pure $\gamma\text{-FeOOH}$ particles.^{33–35)} The absorption bands of $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe-Si}/\text{NaCl}$ decreased and broadened; this may be due to poor crystallinity. In the spectra of $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$ and $\gamma\text{-Fe-Si}/\text{NaCl}$, new absorption bands were observed around 900 and 700 cm^{-1} . They

Fig. 6. Transmission electron micrographs of (a) $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$, (b) $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$, (c) $\gamma\text{-Fe}/\text{NaCl}$, and (d) $\gamma\text{-Fe-Si}/\text{NaCl}$.

Fig. 7. FT-IR absorption spectra of $\gamma\text{-Fe}/\text{Na}_2\text{SO}_4$, $\gamma\text{-Fe-Si}/\text{Na}_2\text{SO}_4$, $\gamma\text{-Fe}/\text{NaCl}$, and $\gamma\text{-Fe-Si}/\text{NaCl}$ obtained by the reaction in the solutions of 2 mass% (a) Na_2SO_4 and (b) NaCl .

may be attributed to the Fe–O–Si linkage of the particles, which occurred due to the incorporation of silicate species during the formation of $\gamma\text{-FeOOH}$ particles in the solutions of 2 mass% Na_2SO_4 and NaCl .^{23,32)} This result was in good agreement with our previous results of the influence of silicate ions on the conversion process of ferric hydroxide to $\beta\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$.^{20,23)}

3.3. Formation of Particles and Changes of Aqueous Solutions

Figure 8 shows the changes in the amount of solid particles formed at different reaction times in the solutions of 2 mass% Na_2SO_4 and NaCl . These results indicate that the formation rate of $\gamma\text{-FeOOH}$ particles decreases in the Fe–Si alloy irrespective of the type of solution. Thus, silicon in the alloy may affect the formation of $\gamma\text{-FeOOH}$ particles in the solutions possibly by the formation of silicate ions, although a small amount of adhesive particles is formed on the surfaces of pure iron and the Fe–Si alloy. Therefore, it is considered that silicon dissolved in the solution influences the formation of corrosion products in the aqueous solu-

Fig. 8. Changes in the amount of solid particles formed at different reaction times by the reaction of pure iron and Fe-Si alloy substrates with the solutions of 2 mass% Na_2SO_4 and NaCl.

Fig. 9. Variations in pH as a function of reaction time. The variations were observed during the reaction of pure iron and Fe-Si alloy substrates with the solutions of 2 mass% Na_2SO_4 and NaCl.

tions.

Figure 9 shows the variation of pH during the reaction in the solutions of 2 mass% Na_2SO_4 and NaCl. In the case of pure iron, the pH increases in the initial stage and then decreases slightly. It appears to be stable from 4 to 12 h and increases thereafter. This tendency is similar between the solutions of 2 mass% Na_2SO_4 and NaCl. In the case of the Fe-Si alloy, the pH increases in the initial stage; thereafter, it increases gradually in comparison with that in the case of pure iron. During the reaction, the pH level is maintained higher than that in the case of pure iron.

These reactions should be interpreted with the elemental reaction of the dissolution and precipitation of ferrous and ferric ions. γ -FeOOH particles in water are formed or precipitated from ferrous ions dissolved in it, according to the following reactions.^{1,2)}

Metallic iron is dissolved in the solutions according to the anodic reaction given in Eq. (1), while the cathodic reaction

Fig. 10. Variations in ORP as a function of reaction time. The variations were observed during the reaction of pure iron and Fe-Si alloy substrates with the solutions of 2 mass% Na_2SO_4 and NaCl.

given in Eq. (2) is balanced with the anodic reaction. Then, it is considered that the pH increases through the formation of OH^- ions by the cathodic reaction. These reactions correspond to the increase in the pH observed in the initial stage, as shown in Fig. 9. When the content of ferrous or ferric ions increases in the aqueous solution and they react with oxygen, FeOOH particles may be precipitated according to Eq. (3). It should be noted that the reaction of Eq. (3) is simplified, as ferric oxyhydroxides are formed through intermediated products, like green rusts consisting of ferrous and ferric ions.²⁾ The formation or precipitation of ferric oxyhydroxides affects the pH value, as given in Eq. (3). Actually, the pH value decreases in the case of pure iron that is reacted for approximately 10 h, as shown in Fig. 9, when the amount of FeOOH particles increases, as shown in Fig. 8. Since these reactions occur heterogeneously in the solution in a complicated manner, further precise analyses of the suspensions should be required to characterize the elementary reactions. Nevertheless, a possible mechanism for interpreting the influence of silicate ions on the reactions and structures of resulting ferric oxyhydroxides may be discussed. In the case of Fe-Si alloy, silicate ions may be formed during its dissolution in the aqueous solution, which corresponds to the oxidation of silicon, like the reaction of Eq. (1) in the case of iron, where the emission of electrons is balanced with the consumption of electrons as given in Eq. (2). As a result, the pH value of the solution in the case of the Fe-Si alloy may be higher than that for the case of pure iron, although further experiments are required to confirm this model.

In relation to the above changes in the pH, the variations in the ORP of the solutions are shown in Fig. 10. It is known that the ORP increases during the formation of ferric oxyhydroxides from ferrous ions, which is closely correlated with the content of oxygen dissolved in the solution.³⁶⁻⁴⁰⁾ However, the oxidation of iron and consumption of oxygen take place simultaneously during the reactions, and ferrous ions formed from metallic iron are also oxidized to form ferric oxyhydroxides by the reaction with oxygen in the solution. Fundamentally, the ORP value is determined by the oxidation of iron and consumption of oxygen in the solution, as shown in Eqs. (1), (2), and (3). In this study, the ORP decreases during the reaction; this may

be attributed to the simultaneous formation of ferrous ions and ferric oxyhydroxides by the consumption of oxygen in the solution. In both solutions of the Fe–Si alloy, the ORP value decreases in the initial stage and is maintained below that of pure iron during the reaction. This results indicates that the oxidation potential in both solutions of Fe–Si alloy is weaker than that in the solutions of pure iron regardless of the kinds of salts. The reason why the ORP value is maintained at lower value in both solutions of the Fe–Si alloy can not be explained simply based on the results of ORP variation, because the reactions of Eqs. (1), (2), and (3) occur simultaneously in complicated manners. Nevertheless, the overall results of pH and ORP, as shown in Figs. 9 and 10, suggest that the rate of oxidation from Fe^{2+} to Fe^{3+} for the formation of ferric oxyhydroxides seems to decrease in the solutions of 2 mass% Na_2SO_4 and NaCl in the Fe–Si alloy. Therefore, the variations in the pH and ORP indicate that the formation rate of γ -FeOOH particles is reduced in the solutions by the addition of silicon; this may be consistent with the results of the change in the amount of γ -FeOOH particles, as shown in Fig. 8. Fundamentally, silicate ions are formed by the oxidation of silicon dissolved in the aqueous solution,^{31,32)} and thus it is considered that the inhibition of γ -FeOOH formation is correlated with the presence of silicate ions during the formation of ferric oxyhydroxides in the solution of Na_2SO_4 and NaCl.

The contents of iron and silicon in the initial stages were analyzed in order to consider the formation process of γ -FeOOH particles from the Fe–Si alloy in the solutions of 2 mass% Na_2SO_4 and NaCl. **Figures 11(a)** and **11(b)** show the content ratio of silicon to iron and the dissolved iron content of the supernatant solutions of γ -Fe–Si/ Na_2SO_4 and γ -Fe–Si/NaCl as a function of reaction time, respectively. The variation in the content of iron dissolved in the solution up to 10 h may be due to significant changes in the solubility of ferrous and ferric ions.²⁾ It should be noted that it is

difficult to measure the iron content of the supernatant solutions accurately because the ferrous ions are easily oxidized by oxygen in the solution. While the dissolved iron content of the solution is very low, the content of silicon or silicate ions is relatively high despite the fact that the amount of silicon in the Fe–Si alloy is 2 mass%. Therefore, it is considered that the silicate ions dissolved in the solutions of 2 mass% Na_2SO_4 and NaCl are involved in the formation of γ -FeOOH particles. The incorporation of silicate species may lead to the inhibition of γ -FeOOH formation, as shown in Fig. 8. This may affect the atomic-scale structure and morphology of the particles with variations in the pH and ORP of the solutions.

4. Concluding Remarks

Quantitative X-ray structural analysis coupled with RMC simulation, transmission electron microscopy, and infrared spectroscopy was performed to characterize the atomic-scale structure and morphology of γ -FeOOH particles. These particles were formed by dipping pure iron and Fe–Si alloy in aqueous solutions containing different salts. The solutions were also characterized by the measurements of pH and ORP and inductively coupled plasma analyses. The main conclusions are summarized as follows:

(1) The pair distribution functions and atomic arrangements determined by the structural analysis revealed that the fundamental FeO_6 octahedral units and their linkages were strongly distorted in the γ -FeOOH particles formed from the Fe–Si alloy. This distortion was due to the incorporation of silicate ions during the formation of γ -FeOOH particles.

(2) Transmission electron micrographs revealed that the morphology of the γ -FeOOH particles formed from the Fe–Si alloy differed from that of the particles formed from pure iron. FT-IR spectra also revealed that new absorption bands were formed in the γ -FeOOH particles produced from the Fe–Si alloy; this suggested the presence of silicate ions in the particles. These results were consistent with those of the atomic-scale structural analysis.

(3) The formation rate of the γ -FeOOH particles formed from the Fe–Si alloy was less than that of the particles formed from pure iron. Correspondingly, the ion content of the solution in which the Fe–Si alloy was dipped differed from that in the case of pure iron. The distortion of the atomic-scale structure of the γ -FeOOH particles formed from the Fe–Si alloy may be related to the formation process in the solution.

Acknowledgement

The authors would like to express their gratitude to Prof. E. Matsubara and Prof. A. Muramatsu for their valuable discussions. This study was supported by the Grant-in-Aid for Scientific Research Fund of the Japan Society for Promotion of Science (No. 17206075) and the grant of the Iron and Steel Institute of Japan.

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Fig. 11. (a) Content ratio of silicon (Si) to iron (Fe) dissolved in the supernatant solutions of γ -Fe–Si/ Na_2SO_4 and γ -Fe–Si/NaCl in the initial stages and (b) iron content in the solution as a function of reaction time.

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