In-situ X-ray Diffraction of Corrosion Products Formed on Iron Surfaces

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In-situ X-ray diffraction measurements by synchrotron radiation and conventional X-ray source have been carried out for identifying constituent species of corrosion products, which were formed on the surface of a pure iron and an iron-5 mass% nickel alloy by reaction with aqueous solutions containing sodium chloride or sodium sulfate. A cell has been prepared for in-situ diffraction measurements of the corrosion products. Diffraction patterns from the corrosion products showed that major constituent species of the corrosion products was γ-FeOOH, and the fraction of minor species of α-FeOOH and Fe₃O₄ in the corrosion products depended on corrosion conditions, such as wetting and drying processes, anion species in aqueous solutions and nickel in the sample. An oxide scale thermally formed on the iron surface was also found to affect the formation of corrosion products.

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1. Introduction

The surface of carbon steel and low-alloyed steel is corroded by exposure to humid air at about room temperature, and this phenomenon is called atmospheric corrosion. The corrosion products or rust formed on these steels surface consist of iron oxides, such as ferric oxyhydroxides and hydroxides, and their properties and formation processes have been discussed from various points of view. The structure and properties of corrosion products are still of great importance, because the corrosion products themselves strongly influence corrosion processes of steel. Typically, a protective rust layer is formed on the surface of weathering steel, and the layer is known to considerably reduce the corrosion rate of weathering steel.

The mechanism of atmospheric corrosion has been discussed on the basis of electrochemical reactions, and electrochemical methods and other techniques were utilized for studying reaction processes in atmospheric corrosion. It was considered in these works that the anodic metal dissolution reaction is balanced by the cathodic reaction during corrosion, and the reduction and re-oxidation of corrosion products of ferric and ferrous ions can occur in water. In order to prove these reactions in corrosion, in-situ Mössbauer spectroscopy was employed to analyze the resultant corrosion products. The results showed that γ-FeOOH in corrosion products are transformed to Fe₃O₄ by reduction. Mössbauer spectroscopy has also been used for identifying species containing iron in corrosion products and analyzing their fine structures. The other analytical methods, such as electron probe microanalysis, transmission electron microscopy, infrared spectroscopy and Raman spectroscopy, are also applied for analyzing corrosion products formed on the steel surface. These results provide interesting information on the composition, morphology and structure of corrosion products. However, in-situ measurements by these methods are still limited, because corrosion products are formed on the iron surface under humid condition.

On the other hand, the X-ray diffraction method must be effective for in-situ analysis of constituent species in corrosion products formed by reaction with aqueous solution. Practically, X-ray diffraction with synchrotron radiation for characterizing corrosion products enables us to provide useful structural information. This prompts us to systematically carry out in-situ X-ray diffraction analysis of corrosion products formed under various conditions.

The purpose of this work is to establish a method for in-situ X-ray diffraction measurement of constituent species in corrosion products formed under various conditions, and to obtain the experimental results concerning several factors influencing the formation of constituent species in corrosion products. Since the beam time of synchrotron radiation was limited, conventional X-ray diffraction measurement were also made. A cell was prepared for in-situ diffraction measurements, in which aqueous solution was reacted with iron substrates under humid atmosphere. In order to study the effect of anion species in aqueous solution and alloying element on corrosion processes, aqueous solutions containing chloride or sulfate ions and an iron-nickel alloy were used. As steel sheets are sometimes covered with an oxide scale formed thermally, the effect of a thin oxide scale on the formation of corrosion products was also investigated.

2. Experimental

2.1 Sample preparation

Small ingots of pure iron and iron-5 mass% nickel were prepared by vacuum melting and they were rolled to about 0.5 mm in thickness. These sheets were cut to 20 mm square, and annealed at about 1073 K under vacuum. Finally, these sheets were mechanically polished. These iron and iron-5% nickel samples are hereafter referred to as PFe and FeNi, respectively.

About 0.2 ml of aqueous solutions containing 2 mass% sodium chloride (NaCl) or 2 mass% sodium sulfates (Na₂SO₄) were dropped onto the polished sample surfaces, as shown Fig. 1(a). After the samples were kept for about
3.6 × 10^6 s under about 100% relative humidity at room temperature, a wet area of the solution was expanded and corrosion products were formed on the sample surfaces, as shown in Fig. 1(b). Then, the samples were transferred to a cell covered with Kapton films, which was designed for in-situ diffraction measurements as shown in Fig. 2. The high humidity was held using wet clothes neighboring to the samples. After in-situ diffraction measurements under humid atmosphere, corrosion products were dried using silica gel in the cell, of which a view is shown in Fig. 1(c).

Some samples were oxidized at 773 K for 600 s in air, in order to study the effect of an oxide scale on the formation of corrosion processes. About 3 μm thick oxide scale was formed on sample surfaces by the oxidation. Since the formation of corrosion products was restricted on a center part of the surface of oxidized samples, diffractions from a few different areas were measured.

2.2 Measurements

Diffraction measurements were mainly carried out by high brilliant synchrotron radiation in BL14B1 of SPring-8 in Japan Synchrotron Radiation Research Institute, Hyogo, Japan. The synchrotron radiation with wavelength of 0.20416 nm was selected by a monochromator. The cell for in-situ diffraction measurements was first attached to be horizontal on a goniometer, and then it was tilted according to the 0–2θ scan mode in diffraction measurements. Diffraction patterns from about 1 mm × 4 mm area of corrosion products were obtained.

Since the beam time for in-situ experiments using synchrotron radiation is limited, an in-house X-ray apparatus was also used for measuring diffraction patterns form corrosion products, which were dried after corrosion. The apparatus used was Rigaku RINT-Ultima with a Cr target. Sample planes in the cell were kept to be horizontal on a sample stage, and a diffraction pattern was measured in the 0–2θ scan mode by moving the X-ray source and counter. Diffraction patterns denoted by Cr Kα in this work are results obtained by the in-house apparatus. About 5 mm × 10 mm area of the center of a sample was analyzed in these diffraction measurements.

As the wavelength of synchrotron radiation selected was slightly different from that of Cr Kα used in the in-house X-ray apparatus, diffraction patterns shown in this work are plotted against the scattering wave vector of \( Q = 4\pi \sin \theta / \lambda \), where \( \lambda \) is the wavelength. The positions of diffraction peaks were compared with d-values given by JCPDS database.

3. Results and Discussion

3.1 Corrosion products formed on the iron surface by aqueous solution with sodium chloride or sodium sulfate

Figure 3(a) shows an X-ray diffraction pattern from corrosion products formed on the PFe surface by aqueous NaCl solution. Most of diffraction peaks are assigned to γ-FeOOH, which frequently appears as corrosion products. Although the population of the peak heights is deviated from that given by JCPDS database, the deviation is considered to arise from a change of the measured position in the sample by tilting the sample stage and so on. This is because corrosion products were formed and floated in the aqueous solution.
Small diffraction peaks detected in this pattern are likely to be assigned to $\alpha$-FeOOH and Fe(OH)$_2$, and a peak from the iron substrate was also observed.

On the other hand, a diffraction pattern from corrosion products, which was dried after corroded by the aqueous solution, is given in Fig. 3(b). Heights of diffraction peaks, which are assigned to $\alpha$-FeOOH and Fe$_3$O$_4$, were increased relative to those for $\gamma$-FeOOH during the drying process. This indicates that $\alpha$-FeOOH and Fe$_3$O$_4$ were formed as new constituent species in corrosion products, and Fe(OH)$_2$ containing Fe$^{2+}$ was oxidized so as to form another species during the drying process. Thus, the formation of corrosion products are quite likely to be influenced by corrosion conditions, such as wetting and drying processes, in which dissolution and precipitation of iron ions occur.

Corrosion products were prepared by dropping aqueous Na$_2$SO$_4$ solution onto the PFe surface, in order to investigate an influence of anions in aqueous solution on species of corrosion products. Figures 4(a) and (b) show X-ray diffraction patterns from corrosion products formed on PFe by the Na$_2$SO$_4$ solution, and corrosion products subsequently dried, respectively. These diffraction patterns are fundamentally similar with each other. The diffraction pattern from the corrosion products is also similar that for corrosion products formed on the PFe surface without an oxides scale by aqueous NaCl solution, as shown in Fig. 3(a). On the other hand, the diffraction pattern from the dried corrosion products indicates that the formation of $\gamma$-FeOOH and Fe$_3$O$_4$ was suppressed compared to the case for the PFe surface without an oxides scale, as shown in Fig. 3(b). Small diffraction peaks, which are assigned to Green rust II (GRII), $\alpha$-FeOOH and NaCl, were also detected in this pattern. Appearance of a peak of NaCl suggests the precipitation of sodium and chloride ions from the solution, although the precipitation may depend on the position on the sample surface. As there is a thermally formed oxide scale between the metallic iron substrate and aqueous solution, corrosion is likely to occur by

![Fig. 3 X-ray diffraction patterns from (a) corrosion products formed on Fe in NaCl aqueous solution, and (b) corrosion products subsequently dried.](image)

![Fig. 4 X-ray diffraction patterns from (a) corrosion products formed on Fe in Na$_2$SO$_4$ aqueous solution, and (b) corrosion products subsequently dried.](image)

### 3.2 Corrosion products formed on the iron surface with an oxides scale

The iron surface is often covered with a thermally formed oxide scale as well as a native oxide layer. Since aqueous solution contacts with such an oxide scale during corrosion processes, an influence of an oxide scale on corrosion processes by aqueous solution is also of importance. In this work, corrosion products were prepared by dropping aqueous NaCl solution onto the PFe surface covered with an oxide scale of about 3µm in thickness. Although the oxide scale reduced a corroded area on the sample surface, a diffraction pattern from corrosion products was obtained using the focused condition synchrotron radiation. Figures 5(a) and (b) show diffraction patterns from corrosion products formed by aqueous NaCl solution, and corrosion products subsequently dried, respectively. These diffraction patterns are fundamentally similar with each other. The diffraction pattern from the corrosion products is also similar that for corrosion products formed on the PFe surface without an oxide scale by aqueous NaCl solution, as shown in Fig. 3(a). On the other hand, the diffraction pattern from the dried corrosion products indicates that the formation of $\alpha$-FeOOH and Fe$_3$O$_4$ was suppressed compared to the case for the PFe surface without an oxides scale, as shown in Fig. 3(b). Small diffraction peaks, which are assigned to Green rust II (GRII), $\alpha$-FeOOH and NaCl, were also detected in this pattern. Appearance of a peak of NaCl suggests the precipitation of sodium and chloride ions from the solution, although the precipitation may depend on the position on the sample surface. As there is a thermally formed oxide scale between the metallic iron substrate and aqueous solution, corrosion is likely to occur by
penetration of aqueous solution through the oxide scale. Furthermore, it may safely be said the oxygen ions in the oxide scale, more or less, contributes to the formation constituent species of corrosion products. As a result, corrosion products shown in Fig. 5 may be formed in wetting and drying processes.

While the corroded area in the PFe surface covered with an oxide scale was localized in the center part, the formation of corrosion products appeared to be suppressed in wet area around the corrosion products, in which the oxide scale seemed to be as formed. Figure 6(a) shows an X-ray diffraction pattern obtained from the PFe surface covered with an oxide scale, which was formed by annealing in air. The pattern indicates that the PFe substrate is covered with an oxide layer of α-Fe2O3 and Fe3O4. On the other hand, Figure 6(b) shows an X-ray diffraction pattern from the PFe surface covered with an oxide scale dropped with NaCl aqueous solution. The vertical scale of Fig. 6(b) is expanded to check the small peaks in the diffraction pattern. The ratio of Fe2O3 peak heights to Fe3O4 peak heights was decreased by the aqueous solution dropped on the PFe surface. This result suggests that an α-Fe2O3 layer was dissolved into the fresh aqueous solution so as to form iron ions, and the dissolved ions may be precipitated in drying process. Thus, when corrosion processes in wetting and drying processes are discussed, iron oxides existing on the iron surface, like the thermally formed oxides and initial rust layer, are considered to act as precursors of corrosion products.

3.3 Corrosion products formed iron and iron-nickel surfaces without and with an oxide scale

Alloying elements in steel are also likely to affect constituent species of corrosion products formed on steel surfaces, as the fraction of constituent species in corrosion products for weathering steel is different from that for mild steel. As nickel is one of the most important elements for suppressing corrosion, an effect of nickel on corrosion products formed on the FeNi surface was focused in this work. X-ray diffraction patterns from corrosion products formed on the FeNi surface by the NaCl solution and corrosion products dried after corroded by the solution are shown in Figs. 7(a) and (b), respectively. The diffraction pattern from corrosion products formed in wetting process is similar to that from corrosion products formed on the PFe surface, as shown in Fig. 3(a). On the other hand, small diffraction peaks, which are allocated to Green rust II (GRII) and α-FeOOH, were detected in the dried corrosion products. The diffraction peaks from α-FeOOH and Fe3O4 in this pattern are not high compared to those from corrosion products formed on the PFe surfaces in drying process. Therefore, nickel in the alloy is also considered to suppress the formation of α-FeOOH and Fe3O4 during drying process.

In addition, the oxide scale effect on corrosion products formed the FeNi surface was also studied as shown in Fig. 8. X-ray diffraction patterns from corrosion products formed by aqueous NaCl solution on the FeNi surface covered with the oxide scale and corrosion products subsequently dried are given in Figs. 8(a) and (b), respectively. The diffraction pattern from corrosion products formed by solution reveals a broad scattering profile and γ-FeOOH, indicating that
colloidal \( \gamma \)-FeOOH particles are suspended in solution and the amount of solution is relatively high in this case. The diffraction pattern from the dried corrosion products shows that major species in corrosion products were \( \gamma \)-FeOOH and \( \text{Fe}_3\text{O}_4 \), and minor diffraction peaks, which are allocated to Green rust II and \( \alpha \)-FeOOH, were observed. Diffraction peaks of \( \text{Fe}_3\text{O}_4 \) are likely to originate from not only the oxide scale but also \( \text{Fe}_3\text{O}_4 \) formed in drying process, as shown in Fig. 3(b). The relatively high peaks from \( \text{Fe}_3\text{O}_4 \) are contrast to those from corrosion products formed on the PFe surface covered with the oxide scale, as shown in Fig. 5(a). This may be related to the nickel effect on the stability of \( \text{Fe}_3\text{O}_4 \).

### 3.4 Factors affecting constituent species in corrosion products

As protective rust layers formed in weathering steel are known to consist of mainly fine \( \alpha \)-FeOOH particles, the formation mechanism of corrosion products or rust layers formed on the iron surfaces is of interest.\(^3\)-\(^6\) Therefore, formation conditions of iron oxides, including ferric oxy-hydroxides and hydroxides, will be compared with the present experimental results, although the results are concerned with corrosion products formed in one cycle of wetting and drying processes. It should be mentioning that corrosion conditions in this work are not always identical to the case for the protective rust layer formed cycled wetting and drying processes.

Cornell and Schwertmann summarized formation routes of various iron oxides from iron ions in aqueous solution.\(^2\) According to the routes, for instance, \( \alpha \)-FeOOH and \( \beta \)-FeOOH are mainly formed in aqueous solution containing \( \text{Fe}^{3+} \), while \( \gamma \)-FeOOH and \( \text{Fe}_3\text{O}_4 \) are formed in aqueous solution containing \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \). The amount of \( \text{Cl}^- \) in aqueous solution affects the formation of \( \beta \)-FeOOH, as its structure includes chlorine. Furthermore, the formation of constituent species in corrosion processes is likely to be influence by the amount of dissolved oxygen and hydrogenion, electrochemical potential in aqueous solution and so on. It should be taken into account that there are gradients of the amounts of dissolved oxygen, hydrogen ion, anions and cations in aqueous solution in practical corrosion occurring on the metallic surface. The amount of oxygen in atmospheric side of solution is likely to be higher than that in the iron substrate, whereas the amounts of cations of iron and alloying elements in the substrate side are higher than those in the atmospheric side, as illustrated in Fig. 9. The amount of aqueous solution dropped on the iron surface is cyclically changed in wetting and drying processes in practical atmospheric corrosion. Although such formation conditions of corrosion products have not been monitored experimentally, the present results clearly indicate that different iron oxides are formed in wetting and drying processes, in which anions and cations act as the precipitation of the iron oxides. Thus, a small amount of chemical species is considered to act as modifier of iron oxides, as recognized in the atomic structures of different iron oxides, which are expressed combinations of \( \text{Fe}_6\text{O}_8 \) octahedra. The \textit{in-situ} X-ray diffraction method established in this work allows us to provide further information on the formation mechanisms of various iron oxides in wetting and drying processes.
Concluding Remarks

Constituent species in corrosion products formed on the surface of a pure iron and an iron-5 mass% nickel alloy were identified by in-situ diffraction measurements with synchrotron radiation as well as conventional X-ray source. A specially designed cell was used for in-situ diffraction measurements of corrosion products formed under humid atmosphere.

The diffraction patterns show that the main constituent species in corrosion products is $\gamma$-FeOOH, and the fraction of other iron oxide species in corrosion products is influenced by conditions, such as wetting and drying processes, anion species in aqueous solution, and nickel in the samples. An oxide scale thermally formed on the sample surface also influenced corrosion processes of the iron substrate.

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REFERENCES