Atmospheric Rust Formation Process on Fe–Cr and Fe–Ni Alloys under Wet/Dry Cycles Observed by Synchrotron Radiation X-ray Diffraction

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In situ observation of initial process of rust formation on Fe–5 mass%Cr and Fe–9 mass%Ni alloys using SPring-8 synchrotron radiation was carried out under wet/dry cycling with 3.5% Na₂SO₄ and NaCl solution films. It was shown that the rust constituents detected during the quite initial wet/dry cycles were Fe(OH)₂ and Fe(OH)₃ independent of alloying elements. Most characteristic X-ray diffraction peaks obtained under the Na₂SO₄ solution film are indexed as those from goethite, α-FeOOH, both in the Fe–Cr and Fe–Ni alloys. In the case of the Fe–Cr alloy, coexistence of Cr³⁺ ion in the Na₂SO₄ film weakened the α-FeOOH diffraction peaks probably due to formation of ultrafine goethite crystals. Akaganéite, β-FeOOH, appears only under the NaCl solution film. Especially, the Fe–Ni alloy forms a considerable amount of akaganéite, which can be interpreted in terms of formation of the monoclinic akaganéite.

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1. Introduction

Iron and steel have been a beneficial material to human-kind, but unfortunately are easily oxidized back to original ore by touching with the atmospheric environment containing oxygen and water in the earth. This atmospheric corrosion has made it difficult to avoid degradation of steel materials. In recent decades, a large number of steel infrastructure has been constructed and weathering of the materials should become age-long problems. Thus it has been strongly required to protect steels against atmospheric corrosion environments.

A rust layer on a steel surface is generally considered to be responsible for protection of the steel against corrosives in atmospheric environment. It is well known that the rust layer, so called “protective” rust layer, formed on a weathering steel which contains a small amount of Cr, P and Cu has strong protective ability for atmospheric corrosion of the steel due to its densely packed microstructure and cation selectivity. In the last decade, it has been elucidated that the inner stable and protective rust layer which covered the surface of a weathering steel for more than a quarter of a century mainly consists of nano-particles of Cr-goethite, α-FeOOH phase containing Cr. Most recently, X-ray absorption fine structure study showed that Cr in this protective Cr-goethite forms negatively charged CrO₄³⁻ ion which brings characteristic cation selectivity of the protective rust layer. Dillmann et al. and Hœrle et al. have well reviewed recent structural studies on the protective rust layer.

Although beneficial effect of the protective rust layer has been well recognized, the corrosion resistance of this conventional weathering steel is not enough as a structural materials in salinity environments containing Cl⁻ ion. For this reason, an advanced weathering steel containing considerable amount of Ni as an alloying element has been developed. But the role of Ni on the protective effect of the rust layer in salinity environments is not clear to date.

Atmospheric corrosion proceeds under very small thickness of electrolyte where a small amount of corrosion can appreciably change the composition of the solution and the solubility limit of a corrosion product can be very quickly attained causing very early coverage of the steel surface by the corrosion product. This process is the initial stage of rust formation. In order to understand the effect of alloying element, such as Cr and Ni mentioned above, on the protective performance of rust layer, it is necessary to know how those alloying elements affect the formation process of rust layer.

In order to allow assessments of atmospheric corrosion behavior of steel, outdoor exposure experiments have usually been performed. Because outdoor exposure experiments are inevitably affected by wide variety of environmental parameters, sophisticated indoor research technique which controls and varies only a few selected environmental parameters with fixing the other ones is advantageous to study the effect of alloying element on the formation process of rust layer. Moreover, it is also desirable to employ an Fe-based binary alloy to emphasize the role of an alloying element on the rust formation process.

In the present study, we selected laboratory experiments under well-defined conditions for atmospheric corrosion studies. In situ observation of initial process of rust formation on Fe-based binary alloys was carried out under wet/dry cycling using energy dispersive X-ray diffraction technique with special attention to the effect of alloying Cr and Ni.

2. Experimental Method

2.1 Specimen

Specimens employed were Fe–5 mass%Cr and Fe–9 mass%Ni alloys, prepared by vacuum melting of 99.9%
purity materials, with dimensions of 10 mm × 10 mm × 3 mm. The specimens were polished by series of emery papers until #600, and were cleaned by alcohol between each step.

2.2 Corrosion chamber

Figure 1 shows schematic illustration of specially designed corrosion chamber. This chamber is made of transparent acrylic resin, so that the specimen on mount of sample inside the chamber can be seen. This corrosion chamber is set on the diffractometer installed in the experimental hatch of SPring-8 synchrotron radiation facility in Hyogo, Japan.

The chamber possesses two water receptacles. Relative humidity inside the chamber can be controlled by water injection to and draining from the receptacles, and by changing the flow rate of dry air in an air cylinder. Temperature at the experimental hatch was kept at 300 ± 1 K. The relative humidity and temperature were recorded by a thermohygrometer. X-ray windows are made of Kapton.

2.3 Experimental procedure

The specimen surface was covered with 100 × 10⁻⁶ m thick electrolyte film which was obtained by pouring solution at 1 × 10⁻¹ L/m² by hamilton syringe. A 3.5% Na₂SO₄ or NaCl solution was employed to form the electrolyte film. The specimen covered with the electrolyte film was placed in the corrosion chamber. The sample surface normal was oriented to be 1° from the vertical, then X-rays impinges on the sample surface with 1° incident angle. Relative humidity was increased up to 95%, so that the thickness of the electrolyte film on specimen was kept constant. After the 2 h wet stage, relative humidity was decreased below 30%. In this dry stage, the electrolyte film was evaporated within 1 h. At the beginning of the next wet stage, 1 × 10⁻¹ L/m² distilled water was poured in the dry surface of the steel. X-ray diffraction measurement was continuously and repeatedly performed during the cyclic wet and dry stages.

2.4 X-ray diffraction measurement

The X-ray diffraction experiments were carried out at BL14B1 in SPring-8. Since this beamline was installed at the bending magnet section, white X-rays with rectangular cross section of 50 × 10⁻⁶ m vertical and 500 × 10⁻⁶ m horizontal can be used. X-ray diffraction measurements were carried out with energy dispersive mode with a Si solid-state detector. The incident angle and 2θ were fixed at 1.0° and 3.5°, respectively. The diffraction measurement with 5 min integrated time was successively repeated. The corrosion chamber was surrounded by Pb shield to reduce the background level.

3. Results

3.1 Initial form of rust detected

The relative humidity inside the corrosion chamber successfully increased during the wet stage and then decreased in the subsequent dry stage, as shown in Fig. 2. During this wet and dry cycling, the rust constituents detected especially during the quite initial wet/dry cycles were Fe(OH)₃ and Fe(OH)₄ independent of alloying elements and of ion species in the electrolyte film. An example of the X-ray diffraction spectra during the first several wet and dry cycling is shown in Fig. 3, where the observed diffraction peaks are compared with JCPDS diffraction standard. Obtained d-values indicated in the figure were found to deviate slightly from the bibliographic data, probably due to less crystallization in the initial stage of corrosion. Fe(OH)₃ would be formed by oxidation of Fe(OH)₂. Those initial corrosion products were subsequently transformed mainly to polymorphs of FeOOH, depending on alloying elements and ion species in the electrolyte film. In addition, very weak peak of γ-Fe₂O₃ and peaks due to fluorescent X-ray were also observed.

3.2 Rust constituents depending on alloying element

3.2.1 Fe–Cr alloy

Figure 4 shows the X-ray diffraction spectra of the rust layer on the Fe–Cr alloy covered with the 3.5% Na₂SO₄ solution film after the 7th cycles. Even though only weak diffraction peaks were detected, the strongest peak was due to formation of α-FeOOH. This indicates that detectable crystal phase was α-FeOOH but most of the rust constituents covering the entire surface of the specimen may consist of nano-phase materials which cannot be detected by X-ray diffraction spectroscopy.

The X-ray diffraction spectra of the rust layer on the Fe–Cr alloy covered with the 3.5% NaCl solution film are shown in Fig. 5 after the 7th wet/dry cycles. Strong γ-FeOOH peak
was observed as well as weak peaks originated from $\alpha$-FeOOH and $\beta$-FeOOH. Since the peak height of $\alpha$-FeOOH was comparable to that observed under the 3.5% Na$_2$SO$_4$ solution film, crystal growth of $\mu$-FeOOH might be suppressed more in the 3.5% Na$_2$SO$_4$ solution film than in the 3.5% NaCl solution film. The observation of $\beta$-FeOOH is consistent with the fact that $\beta$-FeOOH is often recognized by exposure experiments of steels in a salinity environment. 10)

3.2.2 Fe–Ni alloy

The X-ray diffraction spectra of the rust layer on the Fe–Ni alloy covered with the 3.5% Na$_2$SO$_4$ solution film are shown in Fig. 6 after the 7th wet/dry cycles. Most characteristic diffraction peaks are identified as $\alpha$-FeOOH and a certain amount of $\gamma$-FeOOH is probably formed. From the present experiments, it can be concluded that the preferential formation of $\alpha$-FeOOH under the 3.5% Na$_2$SO$_4$ solution film is a common result for both the Fe–Cr and Fe–Ni alloys.

Figure 7 shows the X-ray diffraction spectra of the rust layer on the Fe–Ni alloy covered with the 3.5% NaCl solution film after the 7th wet/dry cycles. It was clearly found that formation of $\beta$-FeOOH was predominant under the 3.5% NaCl solution film. Usually, mass fraction of $\beta$-FeOOH is less than that of $\alpha$-FeOOH after long-term exposure of a conventional weathering steel to high-salinity environments. 10) Moreover, it was shown in Fig. 5 that only weak peak due to $\beta$-FeOOH was observed in the Fe–Cr alloy. Thus, it can be said that the predominant formation of $\beta$-FeOOH in the rust layer on the Fe–Ni alloy is highly likely caused by relatively larger amount of Ni addition as an alloying element.

4. Discussion

At the initial wet/dry cycles, Fe(OH)$_2$ and Fe(OH)$_3$ were first formed and then these initial corrosion products were transformed mainly to polymorphs of FeOOH. This transformation process can be understood by considering initial dissolution of Fe$^{2+}$ ion from the Fe-based alloys and subsequent oxidation and dehydration. During FeOOH
diffraction peaks was succeeding to Fe(OH)$_3$ or Fe(OH)$_2$ peaks as the strongest ones, FeOOH was not well crystallized yet so that we could see separation or shift of the diffraction peak from its bibliographic value, as can be seen at the 5th wet and dry stage indicated at the righthand side of the spectrum. Observed diffraction peaks are compared with JCPDS diffraction standard indicating candidate oxide, d-value, crystal plane hkl and relative intensity I$_r$. Fluorescent X-rays originated from Pb shield, Ta slit and W collimator were also observed.

Fig. 5 X-ray diffraction spectra of corrosion products formed on Fe–5 mass%Cr alloy under 3.5% NaCl solution film between 8th and 10th wet/dry cycles. Each spectrum was obtained at the corresponding time in the wet or dry stage indicated at the righthand side of the spectrum. Observed diffraction peaks are compared with JCPDS diffraction standard indicating candidate oxide, d-value, crystal plane hkl and relative intensity I$_r$. Fluorescent X-rays originated from Pb shield, Ta slit and W collimator were also observed.

Tamura et al.\textsuperscript{12)} showed that with lower concentration of SO$_4^{2-}$ ion air oxidation of Fe(OH)$_2$ suspension results in formation of Fe$_2$O$_3$, and that α-FeOOH is preferentially formed at SO$_4^{2-}$ ion concentration of 0.1 kmol/m$^3$. In the present experiment, concentration of SO$_4^{2-}$ ion was higher than 0.1 kmol/m$^3$, thus the preferential formation of α-FeOOH on the Fe-based alloys is consistent with their arguments.

However, α-FeOOH diffraction peaks in the Fe–Cr alloy were very weak compared with those in the Fe–Ni alloy covered with the 3.5% Na$_2$SO$_4$ solution film. We have examined the X-ray absorption fine structure spectra of the rust layer formed on weathering steel exposed to an atmosphere for 17 years and pointed out that Cr$^{3+}$ in the rust layer is coordinated with O$^{2-}$ and is located in the double chains of vacant sites in the network of FeO$_6$ octahedra as a surface-adsorbed and/or intergranular ion in α-FeOOH crystal.\textsuperscript{13)} Due to this Cr$^{3+}$ effect, ultrafine crystals of α-FeOOH are formed. By considering this effect, the weaker α-FeOOH diffraction peaks in the Fe–Cr alloy can be
solution film.

The crystal symmetry of akaganéite (FeO(OH)) usually observed in the rust layer on a conventional weathering steel exposed to the atmosphere is tetragonal. However, it has been pointed out by Post and Buchwald (14) that akaganéite found in an iron-nickel meteorite is monoclinic one with containing Ni and Cl, Fe_{7.6}Ni_{0.4}O_{h.35}(OH)_{k.65}Cl_{1.25}. In addition, Yamashita et al. (15) pointed out that the rust layer formed on a weathering steel containing 0.5% Cr–0.3% Cu–0.06% P–0.5% Ni under a NiSO_4 solution film contains the monoclinic akaganéite after an immersion experiment in a NaCl solution. On the basis of JCPDS diffraction data, the unit cell dimension of the monoclinic akaganéite with a = 1.0603 nm, b = 0.3035 nm, c = 1.0512 nm and β = 90.22° (JCPDS 421315) is only slightly different from that of the tetragonal akaganéite with a = 1.0535 nm and c = 0.3030 (JCPDS 341266). Therefore, the peak positions in the X-ray diffraction spectra of the monoclinic akaganéite is almost identical to those of the tetragonal akaganéite. This implies that the monoclinic akaganéite would show the FeO(OH) pattern observed in Fig. 7.

Those arguments imply that the preferential formation of akaganéite in the Fe–Ni alloy is probably due to coexistence of Ni^{2+} and Cl⁻ ions in the electrolyte film covering the alloy surface; namely coexistence of Ni^{2+} and Cl⁻ ions in atmospheric corroding surface of an Fe-based alloy might result in formation of a considerable amount of the monoclinic akaganéite.

As has been mentioned above concerning an advanced weathering steel, addition of a certain amount of Ni as an alloying element to a weathering steel can improve its corrosion resistance in salinity environments. Supposing that this improvement effect of Ni is due to a structural modification of the rust layer formed on the steel, it can be expected that a characteristic rust phase is formed in the surface rust layer. If a certain amount of the monoclinic akaganéite was formed on the Fe–Ni alloy, this monoclinic akaganéite might be the characteristic rust phase with improvement effect on the corrosion resistance in salinity environments. Since the monoclinic akaganéite intrinsically contains Cl⁻ ion in its crystal as has been pointed out by Post and Buchwald, (14) it is expected that the formation of the monoclinic akaganéite makes aggressively corrosive Cl⁻ ion inactive by fixing it up in the rust layer. This results in higher corrosion resistance of the Fe–Ni alloy, therefore of the advanced weathering steel with containing Ni, in a salinity environment.

5. Conclusions

In situ observation of initial process of rust formation on the Fe–Cr and Fe–Ni alloys under wet/dry cycles with the Na_2SO_4 and NaCl solution films has been discussed. The concluding remarks are summarized as follows.

(1) The rust constituents detected during the quite initial wet/dry cycles are Fe(OH)_2 and Fe(OH)_3 independent of alloying elements.

(2) Most characteristic diffraction peaks obtained under the Na_2SO_4 solution film are due to goethite, α-FeOOH, both in the Fe–Cr and Fe–Ni alloys. Because of the
Cr\(^{3+}\) effect, \(\alpha\)-FeOOH diffraction peaks in the Fe–Cr alloy are weaker than those in the Fe–Ni alloy.

(3) Akaganeite, \(\beta\)-FeOOH, appears only under the NaCl solution film. Especially, the Fe–Ni alloy forms a considerable amount of akaganeite, which can be interpreted in terms of formation of the monoclinic akaganeite.

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