Analysis for the Mechanism of Accelerated Corrosion on Low Alloy Steel in Air-Solution Alternating Condition*1

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In this study, the iron rust layer formed on the low alloy steel under air-solution alternating conditions was investigated by cross-sectional observation and analysis, and the mechanism of the accelerated corrosion of the steel under alternating conditions was clarified. The observations and analysis showed that the multilayered iron rust layer composed of the red rust layer (γ-FeOOH), rust crust layer (Fe3O4), inner crystal (Fe3O4), and inner rust layer was formed on the low alloy steel. It can be considered that the multilayered iron rust layer accelerated the cathodic reaction rate of dissolved oxygen under alternating conditions. This acceleration is the reason why the corrosion rate of the low alloy steel under alternating conditions was accelerated. [doi:10.2320/matertrans.C-M2021816]

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1. Introduction

Previous studies on atmospheric corrosion have reported that the corrosion rate of steels with a thin water film on the steel surface is faster than the corrosion that occurs in aqueous solutions.1–4) Yamamoto et al. have reported that the corrosion rate of steel at the air/solution interface is fastest because the steel at the interface always has a thin water film.5) The internal investigation of the Fukushima Daiichi Nuclear Power Station (1F) Unit 1–3 reactor confirmed that the inner wall of the reactor is currently exposed to the air/solution interface; therefore, it is possible that the corrosion rate of the inner wall composed of steel at the air/solution interface may be accelerated.6,7) However, corrosion research on the air/solution interface that simulates the 1F environment has not been carried out, and it is difficult to estimate the corrosion rate of steel at the air/solution interface inside the 1F reactor. Therefore, the authors carried out corrosion tests of steels under the simulated conditions of the air/solution interface using a rotating corrosion test equipment; it was determined that the corrosion rate of steel under the simulated conditions of the air/solution interface is more than three times faster than that of steel that is always immersed in the solution.8) It is necessary to clarify the corrosion acceleration mechanism of steel under the simulated conditions of the air/solution interface.

In this study, the corrosion tests of low alloy steel, which simulated the structural material of the 1F reactor under the simulated conditions of the air/solution interface, and the structure of the iron rust layer formed on the surface were investigated by cross-sectional observation and analysis. The purpose of this study is to clarify the structure of the iron rust layer formed under the simulated condition and to determine the mechanism of the accelerated corrosion of low alloy steel.

Fig. 1 A schematic image of the fixing jig for specimens during the corrosion tests.

2. Experimental

2.1 Rotating corrosion test equipment9)

The corrosion tests using the rotating corrosion test equipment will be explained. The steel specimens were attached to a specimen attaching jig, as shown in Fig. 1. The specimens were immersed in a test bath that was filled with dilute artificial sea water, and the jig was rotated at a constant speed by a motor. Test conditions were changed by adjusting the water level in the test bath. The first condition was that the specimens always rotate in solution (solution condition), and the second condition was that the specimens were alternately exposed to air and solution (air-solution alternating condition). It is considered that the air-solution alternating conditions simulate the air/solution interface because it was confirmed that the specimen had a thin water film during the test. The temperature of the dilute artificial seawater was maintained by installing the test bath in the thermostat equipment. The dilute artificial seawater was always kept under oxygen saturation by air bubbling, and the temperature in the solution and the concentration of the

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dissolved oxygen (DO) were measured by sensors; it was confirmed that there was no significant change.

2.2 Test conditions

JIS SQV2A (the chemical composition is shown in Table 1) equivalent low alloy steel was used to prepare specimens. The low alloy steel is a simulated material of the 1F Reactor Pressure Vessels (RPVs). The low alloy steel was cut into 40 mm × 10 mm × 2 mm strips (screw hole diameter: 3 mm). The specimen surface was polished with a #800 SiC abrasive paper and was ultrasonically cleaned in ethanol for 10 min. The corrosion tests were conducted in 200 times diluted artificial sea water for 144 h. The dilute artificial seawater was always kept under oxygen saturation by air bubbling (approximately 50 mL/min). The information on the 200 times diluted artificial sea water is as follows: the DO concentration is approximately 8.5 ppm; the chloride ion concentration is approximately 120 ppm; the pH is 6.0 ± 0.5; the temperature is 30°C. The specimen attaching jig was continuously rotated at a constant speed of one rotation every 1 min. After the corrosion tests, the specimen was immersed in ethanol and dried. Then, the specimen with an iron rust layer was molded in resin by a vacuum impregnation device. It was confirmed that the iron rust layer was sufficiently impregnated with the resin. After molding, the specimen was cut with a fine cutter, and the cross section was grinded with a SiC abrasive paper and colloidal silica before observation and analysis. A digital camera (Panasonic Inc., DMC-TZ40), a microscope (KEYENCE Inc., VHX-500), an optical microscope (Nikon Inc., ECIPSE MA200), and a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS, JEOL Ltd., JSM-7000F) were used for observation, and a micro Raman spectrometer (Raman, JASCO, NRS-3100) and an auger electron spectroscope (AES, JEOL Ltd., JAMP-9500F) were used for analysis. Because the surface analysis by AES is strongly affected by mechanical polishing, the specimen for the AES analysis was additionally polished by an ion milling device (Hitachi High Technologies Inc., ArBlade5000).

3. Results and Discussions

3.1 Appearance of specimens after corrosion tests

Figure 2 shows the appearance of the specimens after the corrosion tests. Red and black rust is observed on the specimens after corrosion tests for each condition. The red rust formed on the specimen under the solution condition is shown in Fig. 2(a); the rust easily peeled off from the surface after the immersion in ethanol after the tests. This means that the red rust formed under the solution condition was fragile. It was confirmed that black rust was formed under the red rust. The iron rust formed on the specimen after the tests under the air-solution alternating conditions shown in Fig. 2(b) has red and black rust regions, and there are severely rusted regions. A large amount of red rust was accumulated at the bottom of the test bath after the test under both conditions.

3.2 Cross-sectional observation by the microscope

Figure 3 shows the cross-sectional microscopy images after the corrosion test. The cross-sectional image of the specimen exposed under the solution condition shown in Fig. 3(a) shows that there is a black iron rust layer on the surface of the specimen that is too thin to be observed with a microscope. The red rust, which is observed in Fig. 2(a), was completely peeled off when immersed in ethanol. Smith et al.\(^{10}\) and Mcenaney et al.\(^{11}\) reported that the iron rust formed on the surface of the steel exposed to flowing solution has an outer layer of γ-FeOOH (red rust) and an inner layer of Fe₃O₄ (black rust). This suggests that the iron rust formed on the specimen under the condition when the specimen always rotates in solution has a γ-FeOOH outer layer and an Fe₃O₄ inner layer. Figure 3(b) shows the cross-sectional image of the specimen exposed under the air-solution alternating conditions. It is determined that a thick iron rust

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<th>Chemical composition of the low alloy steel.</th>
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<td>Mn</td>
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<td>SQV2A</td>
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Fig. 2 Digital camera images of the specimens after immersion for 144 h (a) in solution and (b) in air-solution alternating condition by a rotating corrosion test equipment.

Fig. 3 Cross-sectional optical images of the specimens after the corrosion test (a) in solution and (b) in air-solution alternating condition.
layer forms on the specimens under the alternating conditions, and the thickness is greater than 1 mm.

3.3 Cross-sectional observation by optical microscopy and SEM

Figure 4 shows optical microscopy and SEM images of the cross section of the specimen after the corrosion test under the air-solution alternating conditions. The cross-sectional images show the resin, iron rust layer, and low alloy steel from the top. Figure 4(a) show that the iron rust layer consists of a "red rust region" at the outer most layer and of a "rust crust layer", which is composed of a black iron rust as a dense outer shell, and of an "inner crystal region", which appears white, and of an "inner rust layer" that exists at the rust/steel interface. In this study, the layer formed under the red rust region is called a rust crust layer because Smith et al.\(^{10}\) and Masuko et al.\(^{12}\) called the layer formed between the red and black rust layer as a "crust". Figure 4(b) shows the SEM, which confirms that the rust crust layer has a defect (arrow A), and that the rust crust layer is also observed in the inner crystal region (arrow B). High-resolution SEM observations confirm that the rust crust layer is composed of nanoparticles that are smaller than 1 µm.

Figure 5(a) shows the high-resolution cross-sectional SEM images of the specimen after the corrosion tests under the air-solution alternating condition, and the observation area indicates that area 1 is surrounded by a red broken line shown in Fig. 4(b). Area 1 shows the red rust region, rust crust layer, and inner crystal region. It is observed that the contrast in the SEM secondary electron image between the rust crust layer and the inner crystal is the same. SEM back scattered electron composition observation was carried out, and the contrast of the back scattered electron composition image between the rust crust layer and the inner crystal was also the same. It is assumed that the crust layer and the inner crystal will have the same composition of iron rust because the contrast of the back scattered electron composition image is strongly influenced by the composition. Figure 5(b) is an expanded image of the inner crystal shown in Fig. 5(a). There are many crystals formed by needle like small particles in the inner crystal region. The corrosion tests under alternating conditions were carried out for 24, 144, and 500 h. These tests showed that the thickness of the red rust layer and the rust crust layer did not change; only the inner crystal region became thicker. Using a multimeter, it was confirmed that the crust layer and the low alloy steel were electrically connected via the inner crystal even if the thickness of the inner crystal region became thicker than 1 mm after 500 h of corrosion tests under alternating conditions.

Fig. 4 Cross-sectional images of the specimen after the corrosion tests in air-solution alternating condition which obtained (a) by the metallurgical microscope and (b) by the SEM.

Fig. 5 Cross-sectional SEM images (a) at the red rust/rust crust interface and (b) at the inner crystal region of the specimen after the corrosion tests in air-solution alternating condition.
3.4 Raman analyses

Figure 6 shows the Raman spectra of the red rust and the rust crust layer. The peaks at 251, 380, 524, 651, and 1059 cm\(^{-1}\) were observed in the Raman spectrum of the red rust, as shown in Fig. 6(a). These peaks correspond well with the peaks in the Raman spectrum of \(\gamma\)-FeOOH (255, 380, 528, 654, and 1056 cm\(^{-1}\)).\(^{13}\) The peaks at 312, 545, and 663 cm\(^{-1}\) are observed in the Raman spectrum of the rust crust layer, as shown in Fig. 6(b). These peaks correspond well to the peaks in the Raman spectrum of Fe\(_3\)O\(_4\) (i.e., 319, 550, and 676 cm\(^{-1}\)).\(^{13}\) On the basis of the Raman analyses of the iron rust layer formed under the air-solution alternating conditions, it is assumed that the red rust is \(\gamma\)-FeOOH, and the rust crust layer is Fe\(_3\)O\(_4\).

3.5 EDS analyses

Figure 7 shows the cross-sectional SEM images of the specimen after the corrosion test under alternating conditions, and the observation area is the area 2 surrounded by a blue broken line shown in Fig. 4(b). The steel near the inner rust layer/steel interface has a black contrast, which is attributed to the re-deposited resin during polishing by the Ar ion beam. Table 2 shows the EDS point analyses of the inner crystal region and the inner rust layer shown in Fig. 7. The abovementioned analyses show that the inner crystal is mostly composed of Fe and O, and the alloy components are lower than the standard values of the low alloy steel shown in Table 1. However, the inner rust layer has a lower O content and a higher Cl content than those of the inner crystal, and the alloy components (e.g., Mn, Cu, and Cr) are higher than the standard values. Morcill et al.\(^{14}\) and Misawa et al.\(^{15}\) have reported that a concentrated layer of alloy components is formed between the base steel and iron rust when a thick iron rust layer is formed on the weathering steel. Therefore, it is assumed that the inner rust layer is formed owing to the concentration of alloy components. Shimizu et al.\(^{16}\) have reported that chloride ions are concentrated at the iron rust/steel interface and form a Cl-concentrated site called a “nest” when a thick iron rust layer is formed on the steel. Therefore, in this study, the concentration of chloride ion is high at the inner rust layer/steel interface during the corrosion tests.

3.6 AES analyses

Figure 8 shows the cross-sectional SEM images (acquired by an SEM instrument mounted on an AES instrument) of the rust crust layer/inner crystal interface of the specimen after the corrosion test under the alternating conditions. It can be seen that the crust layer and the inner crystal have the same contrast as in Fig. 8, and the crystal appears to form from the crust layer. Table 3 shows the atomic concentration ratio between Fe\(^{2+}\) and Fe\(^{3+}\) at each point in Fig. 8. The atomic concentration ratio was calculated using a method in which
the spectra obtained by AES analysis were converted by waveform separation calculation using the standard spectra of FeO (Fe$^{2+}$) and Fe$_2$O$_3$ (Fe$^{3+}$).\textsuperscript{17,18} The atomic ratio of red rust in Table 3 indicates that 90% of Fe in the red rust is Fe$^{3+}$; these results correspond well with the result obtained by Raman in Fig. 6(a) that the red rust is γ-FeOOH. The atomic ratio of the rust crust layer and inner crystal correspond well with the ideal ratio of Fe$_3$O$_4$ shown in Table 3. Therefore, it is assumed that the rust crust layer and the inner crystal are both Fe$_3$O$_4$. The cross-sectional observation and analysis in this study confirm that the red rust is γ-FeOOH, the crust layer and internal crystals are Fe$_3$O$_4$, and the internal iron rust layer is iron rust with concentrated alloy components.

3.7 Corrosion mechanism under solution conditions

The corrosion mechanism of the low alloy steel under solution conditions is explained by the schematic diagram of the iron rust layer formed on the steel under solution conditions shown in Fig. 9. During the initial stage of corrosion, the anodic reactions of iron and the Fe$^{2+}$ oxidation reaction [i.e., eqs. (1) and (2)], and the cathodic reaction of oxygen reduction [i.e., eq. (3)] occurred on the steel surface when the steel was immersed in dilute artificial seawater.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1)
\]

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad (2)
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (3)
\]

The concentration of OH$^-$ and Fe$^{3+}$ near the surface of the steel is increased after the immersion. This means that pH increases near the steel surface during the immersion in solution, and the environment near the surface easily forms iron hydroxide, according to the potential-pH diagram.\textsuperscript{19} Mcenaney \textit{et al.}\textsuperscript{11} have reported that γ-FeOOH preferentially precipitates on steel under saturated oxygen conditions. Therefore, it is assumed that the γ-FeOOH layer is formed on the surface by the reaction shown in eq. (4).

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{FeOOH} + \text{H}_2\text{O} \quad (4)
\]

As reported by Evans\textsuperscript{20,21} and Giloy \textit{et al.}\textsuperscript{22} γ-FeOOH is gradually reduced to thermodynamically stable Fe$_3$O$_4$ by the reaction shown in eq. (5).

\[
6\text{FeOOH} + 2e^- \rightarrow 2\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{OH}^- \quad (5)
\]

Mcenaney \textit{et al.}\textsuperscript{11} have reported that γ-FeOOH is easily reduced to Fe$_3$O$_4$ under low oxygen conditions. Thus, γ-FeOOH is reduced to Fe$_3$O$_4$ at the low oxygen site such as the bottom side of the γ-FeOOH layer, as shown in Fig. 9(c). Through those processes, the iron rust layer with an inner layer of Fe$_3$O$_4$ and an outer layer of γ-FeOOH forms in the low alloy steel under solution conditions. Cross-sectional SEM observations confirmed that the Fe$_3$O$_4$ layer formed under solution conditions had a rough structure with many pores and did not have a structure that the rust crust layer had.

3.8 Corrosion mechanism under air-solution alternating conditions

The corrosion mechanism of the low alloy steel under air-solution alternating conditions will be explained by the schematic diagram of the iron rust layer formed on the steel under air-solution alternating condition shown in Fig. 10. Under these conditions, it is assumed that the redox reaction in eqs. (1)–(3) occurs during the initial stage of corrosion, and then the γ-FeOOH layer is formed, as shown in Fig. 10(a). The steel surface has a thin water film during corrosion tests under alternating conditions. Nishikata \textit{et al.}\textsuperscript{23} have reported that the oxygen reduction reaction in eq. (3) is accelerated when the steel has a water film thinner than 1 mm because the oxygen mass transfer is promoted. Therefore, the reaction rate of alternating conditions is faster than that of solution conditions owing to the acceleration of the oxygen reduction reaction; the γ-FeOOH generation reaction in eq. (4) is also increased. Mcenaney \textit{et al.}\textsuperscript{11} have reported that the reduction reaction rate of γ-FeOOH to Fe$_3$O$_4$ in eq. (5) is accelerated owing to an increase in the γ-FeOOH generation. Therefore, the formation rate of Fe$_3$O$_4$ in the lower part of γ-FeOOH is also accelerated under the air-solution alternating conditions. It has been reported that many Fe$_3$O$_4$ nanoparticles form aggregates\textsuperscript{24} high-resolution SEM observations confirmed that Fe$_3$O$_4$ nanoparticles aggregated to form the rust crust layer at the γ-FeOOH/Fe$_3$O$_4$ interface. Because the dissolved oxygen concentration

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<tr>
<td>Fe$^{2+}$</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>1 Red rust</td>
<td>9.32</td>
</tr>
<tr>
<td>2 Rust crust layer</td>
<td>39.99</td>
</tr>
<tr>
<td>3 Inner crystal</td>
<td>36.54</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>33.33</td>
</tr>
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</table>

Table 3 Cross-sectional AES point analysis of the specimen after the corrosion test.
inside the rust crust layer may be lower than that on the outside, the pH may decrease owing to the hydrolysis of dissolved iron ions, as shown in eq. (6).

$$3\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e^- \quad (6)$$

Kanzaki\(^{25)}\) has reported that the aggregation and dispersion of Fe\(_3\)O\(_4\) nanoparticles has a pH dependence and that nanoparticles aggregate more at pH 9 and disperse less at pH 5. Therefore, it can be estimated that the rust crust layer, which is formed from the aggregates of Fe\(_3\)O\(_4\) nanoparticles, was dispersed into the inner crystal owing to the decreasing pH inside the rust crust layer; then the internal crystal region is formed, as shown in Fig. 10(c).

3.9 Corrosion acceleration mechanism of low alloy steel under air-solution alternating conditions

A schematic diagram of the corrosion acceleration mechanism of low alloy steel under air-solution alternating conditions is shown in Fig. 11. In the schematic diagram, the inner crystal region is simplified, and the inner rust layer is omitted for the sake of explanation. The oxygen reduction reaction in eq. (3) occurs at the outside of the rust crust layer when the thick iron rust layer with a multilayered structure is formed on the steel, as shown in Fig. 11. The oxygen reduction reaction remained fast even when the rust layer was thick because the rust crust layer functioned as a reaction surface. The rust crust layer supplied electrons because the crust layer and base steel were electrically connected via the inner crystal, which has high electrical conductivity.\(^{26)}\) This means that the generation rate of $\gamma$-FeOOH always remained at high level, which suggests that the reduction rate of $\gamma$-FeOOH to Fe\(_3\)O\(_4\) shown in eq. (5) was also high. Therefore, the iron rust layer which has a multilayered structure was formed when the low alloy steel was exposed under air-solution alternating conditions, and the structure accelerated the corrosion rate of the steel under alternating conditions.

4. Summary

The corrosion tests of low alloy steel, which is a simulated material of the 1F RPVs structural material, was carried out under air-solution alternating conditions, and the structure of the iron rust layer formed on the steel was analyzed by cross-sectional observation and analysis. The observation and analytical results clarified the reason why the corrosion rate of steel accelerated under air-solution alternating conditions, as follows.

(1) The iron rust layer formed under alternating conditions is thicker than that under solution conditions.

(2) Multilayered iron rust formed under alternating conditions consists of the red rust layer composed of $\gamma$-FeOOH, of the rust crust layer composed of Fe\(_3\)O\(_4\), and of the inner crystal composed of Fe\(_3\)O\(_4\); the inner rust layer was formed by the concentration of alloy elements.

(3) The iron rust layer, which has a multilayered structure, forms when the low alloy steel is exposed under the air-solution alternating conditions, and the structure accelerates the cathodic oxygen reduction rate and the corrosion rate of steel under alternating conditions.

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