

# Electrochemical corrosion tests for core materials utilized in BWR under conditions containing seawater

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## Abstract

Electrochemical corrosion behavior under salt water in a type 304L stainless steel (SS) used to a part of BWR core materials was investigated to evaluate the possibility of crevice corrosion occurrence for the fuel assemblies which experienced seawater exposure in the Fukushima Daiichi Nuclear Power Plant (1F) accident. Especially, focusing on the upper end plug part having the 304L SS crevice structure, measurements of repassivation potential for crevice corrosion ( $E_{R,CREV}$ ) were carried out using the crevice test pieces fabricated by 304L SS plates. The solution conditions were determined based on the long-term water quality environment change of the 1F spent fuel pools; chloride ion concentration and temperature were selected ranging from 10 to 10000 ppm and from room temperature to 80 °C, respectively. As the results,  $E_{R,CREV}$  was lower than a spontaneous potential ( $E_{SP}$ ) when the temperature was over 50°C and the chloride ion concentration was over 2500 ppm under the saturated concentration of dissolved oxygen. This indicates that there is a possibility that crevice corrosion will occur in the crevice structure composed of the 304L SS parts of the 1F fuel assemblies which experienced seawater exposure, even though the corrosion rate should be accurately estimated and the influence of the oxide film which is formed along the 304L SS surface during reactor operation as well as the effect of dissolved oxygen concentration on the crevice corrosion behavior should be evaluated.

## 1. Introduction

As one of the decommissioning works of Fukushima Daiichi Nuclear Power Plant (1F), the new and spent fuel assemblies, which had experienced seawater exposure by emergent cooling of the spent fuel pool (SFP) and had been stored there, have been already transported to the common pool at the 1F site. These fuel assemblies were temporally exposed to solution with high chloride ion concentration (about 10000 ppm) and high temperature (around 80 °C) in the early 1F accident [1]. Then, in order to suppress corrosion occurrence, not only the concentration and temperature kept low level over a long time by conducting some countermeasures such as switching to fresh water injection and recovery of the coolant circulation system with removal function of chloride ions, but also the reduction of dissolved oxygen concentration by an addition of hydrazine and the neutralization by an boric-acid solution were carried out. For a Zircaloy-2 fuel rod of a fuel assembly, there was no report on significant corrosion occurrence under simulated SFP water conditions because it was considered that they were less likely to be attacked under those conditions due to the passive coated layer formation on Zircaloy-2 fuel rod surface [2].

On the other hand, it has been recently reported to exhibit seawater incursion to the crevice structure between the 304L SS nut of the upper end plug and tie plate (Figure 1), when detail inspections were carried out for the new fuel assemblies that had been stored in the SFP of Unit 4 [3]. Therefore, at the site having the

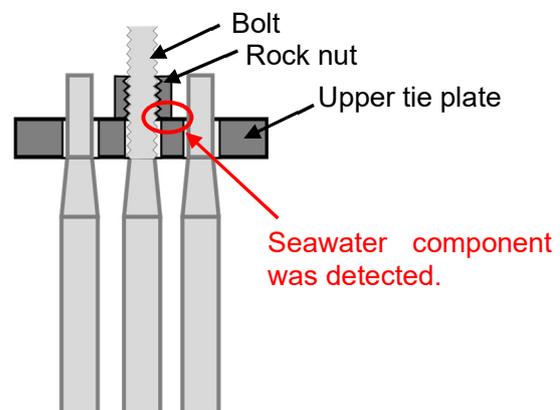


Fig.1. Schematic illustration of the upper end plug.

crevice structure in the fuel assemblies, the crevice corrosion might have occurred during the storage in the SFP and may be continuously progressed in even the common pool. Especially, the strength retention of the fuel assembly structure has been realized by the part of Zircaloy-2 bolt and 304L SS rock nut in the upper end plug, which has the crevice structure. During the future long storage of the fuel assemblies, the structure strength must be also kept suppressing fuel recriticality by fracturing of them. Therefore, the crevice corrosion behavior of 304L SS should be preferentially evaluated because it is expected that corrosion resistance of 304L SS would be lower than that of Zircaloy-2.

In this study, the effects of temperature and chloride ion concentration on crevice corrosion in the crevice structure composed of 304L SS were investigated under the simulated SFP water conditions to evaluate the possibility of the crevice corrosion occurrence. This was performed by the electrochemical method of determining the repassivation potential ( $E_{R,CREV}$ ), which corresponds to a critical potential to induce crevice corrosion, of metals [4-6]. The possibility of crevice corrosion occurrence was considered comparing the obtained  $E_{R,CREV}$  with the spontaneous potential ( $E_{SP}$ ).

## 2. Experimental Procedures

The material used is a 304L SS utilized to a nut part of upper end plug in 1F-type fuel assemblies. The chemical composition of the steel is indicated in Table 1. Two types of large and small plate specimens with sizes of 50mm × 20mm × 2mm and 20mm × 20mm × 2mm were prepared. The specimens were polished up to 600 grit and were ultrasonically cleaned using pure water before corrosion test. The contact surfaces of both specimens were fulfilled with the test solution, then the specimens were joined by a set of Ti bolt, nut and washer (Figure 2). The test solution conditions were systematically determined as parameters of the temperature and chloride ion concentration based on the water quality environment change in the SFP of the 1F accident [1]. The test temperature were room temperature (RT), 50 °C and 80 °C, and, chloride ion concentrations were 10 ppm, 100 ppm, 2500 ppm and 10000 ppm. In this study, not natural seawater but artificial seawater was used as the test solution to preventing from the complex effect of microbiological corrosion [7-8]. Assuming that the reduction of dissolved oxygen concentration by an addition of hydrazine might not be incomplete near complex structures such as a crevice structure, inert gas was not purged in these experiments.

Table 1. Chemical composition of the 304L SS used

304L SS	Fe	C	Si	Mn	P	S	Cr	Ni
(wt.%)	Bal.	0.007	0.68	1.36	0.0021	0	18.1	10.12

The crevice corrosion tests were conducted using the crevice corrosion test pieces of 304L SS and a potentiostat (SYRINX, SERM-614), and  $E_{R,CREV}$  were measured by three times in accordance with JIS G 0592 [4]. The test apparatus is shown in Figure 3. The apparatus consists of three electrodes namely the test electrode of 304L SS, the counter electrode of platinum and the reference electrode of the saturated KCl-Ag/AgCl. The procedure of crevice corrosion test is shown in Figure 4. The creviced specimen was anodically polarized at a rate of 30 mV/min up to 200  $\mu$ A of current value (Step1). The current value was kept for two hours (Step2). After that, potentiostatic polarization of up to two hours was performed (Step3). As the rise of anodic current was observed here, further 10 mV of the potential was lowered and the potentiostatic

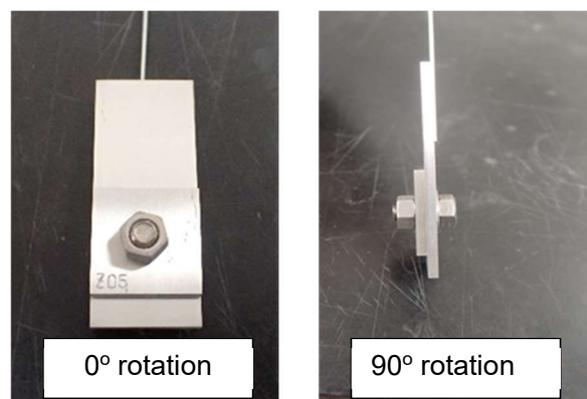


Fig.2. Appearance of assembled test electrode.

polarization of up to two hours was also performed. Step3 was performed repeatedly and the  $E_{R,CREV}$  was determined as the potential where the anodic current upward trend was no longer observed during potentiostatic polarization for two hours. After crevice corrosion test, the formation of corrosion products was investigated in order to evaluate the corrosion mode.

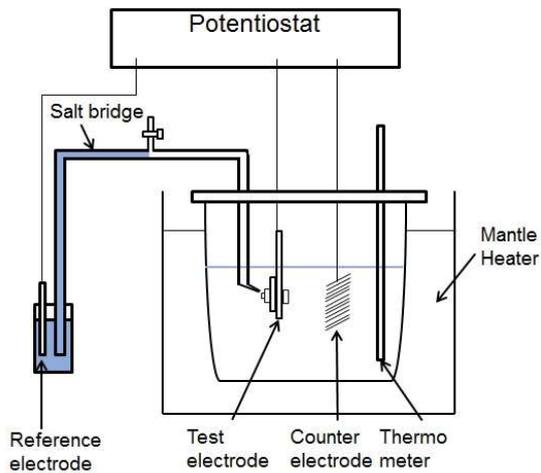


Fig.3. Test apparatus for the method of determining the  $E_{R,CREV}$ .

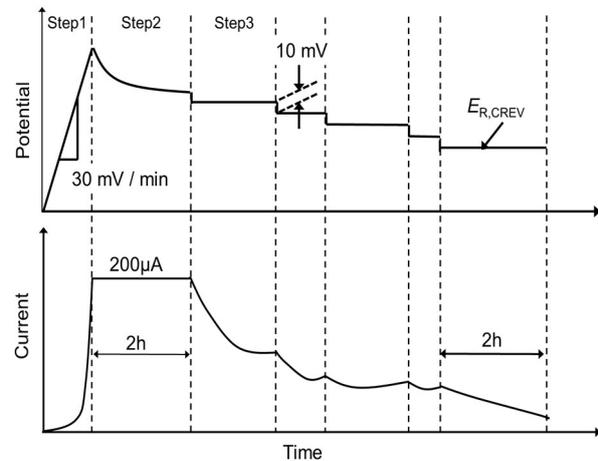
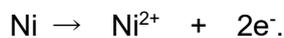
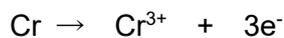
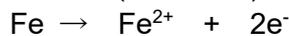


Fig.4. Test procedure of measuring the  $E_{R,CREV}$ .

### 3. Results and Discussion

At first, the typical observation images of the crevice test pieces after electrochemical corrosion tests are shown in Figure 5 and 6. Figure 5 shows the specimen surface after the crevice corrosion test at RT in 10 ppm chloride ions. Figure 6 shows the specimen surface after the crevice corrosion test at 80 °C in 100 ppm chloride ions. For both image, white parts were observed in contact surface. Further, brown films were observed along the edge of the large and small specimens in Fig.6. These products were typically observed in the case of corrosion for stainless steels [9]. Namely, it seems that the brown films correspond to Fe-rich oxides as indicated by below reaction formulas in the test electrode.

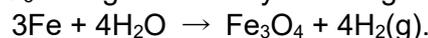
- Anode reaction (Oxidation):



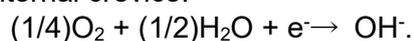
- Cathode reaction (Reduction):



Then, especially the ion of main component Fe in stainless steels,  $\text{Fe}_2\text{O}_3$  was generated by following reaction.



Moreover, the white part corresponds to the dissolved part of the specimens [9]. It is considered that following reaction occurred at internal crevice.



This hydroxide ion forms  $\text{CrOOH}$  film inside of the crevice structure and it is considered to be a white part of the

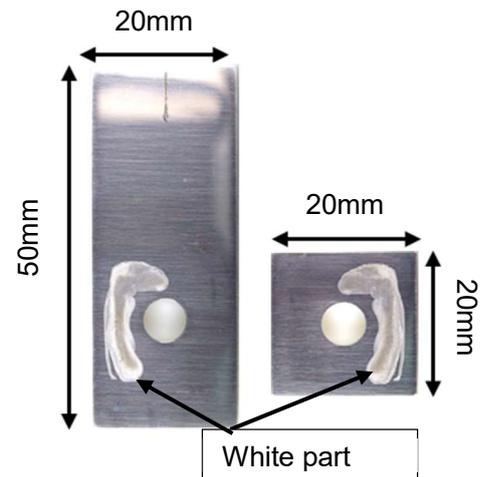


Fig.5. Appearance of the contact surface of specimen after crevice corrosion test at RT 10ppm.

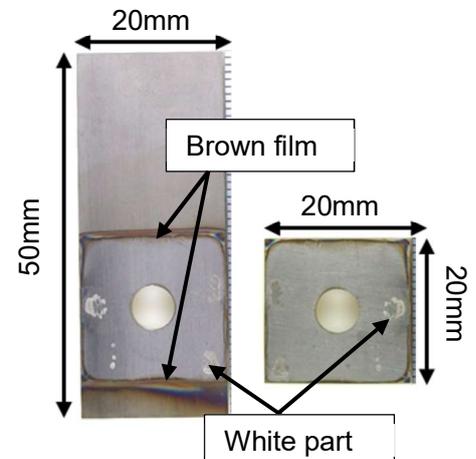


Fig.6. Appearance of the contact surface of specimen after crevice corrosion test at 80°C 100ppm.

specimen [5].

Of course, Cr and Ni oxides would be generated with small amounts. Therefore, now to be confirmed that the corrosion mode of 304L SS in this study was same as those of typical stainless steels.

Next, the obtained average  $E_{R,CREV}$  values of the 304L SS are shown in Figure 7. The blue symbol indicates the  $E_{R,CREV}$  of RT measurements. The green and red ones are the  $E_{R,CREV}$  of the 50 °C and 80 °C measurements, respectively. Here, the value of  $E_{SP}$  was described based on the following equation [10] which was reported by Nakayama et al.

$$E_{SP} = 0.733 - 0.059 \text{ pH (V vs SHE)}.$$

In this study, the value of pH of the solution was set at 8.2. Therefore, the value of  $E_{SP}$  indicated at 249 mV vs SHE. Comparing the obtained  $E_{R,CREV}$  with  $E_{SP}$  in Fig. 7, the  $E_{R,CREV}$  was lower than the  $E_{SP}$  when the chloride ion concentration was under 100 ppm and the temperature was 80 °C. Furthermore, when the temperature was 50 °C,  $E_{R,CREV}$  was lower than  $E_{SP}$  under 2500 ppm of chloride ion concentration. In the case of RT,  $E_{R,CREV}$  was lower than  $E_{SP}$  under 10000 ppm. In general, crevice corrosion will occur in the case that the  $E_{R,CREV}$  is lower than  $E_{SP}$ . On the other hand, when the  $E_{R,CREV}$  is higher than  $E_{SP}$ , no crevice corrosion will occur because of crevice specimens are repassivated. Therefore, in these conditions ( $\geq 100$  ppm at 80 °C,  $\geq 2500$  ppm at 50 °C,  $\geq 10000$  ppm at RT), it means that there is a possibility of crevice corrosion. For the tests of 10 ppm chloride ions, it was clear that crevice corrosion would not occur at three temperatures.

Focusing on the values of  $E_{R,CREV}$  over 100 ppm chloride ion concentrations, they were regularly independent of temperature and chloride ion concentration which were parameters for corrosion in stainless steels. As other corrosion parameters, the effect of dissolved oxygen concentration is considered. Amount of dissolved oxygen is decreased with increase of temperature in solution [11]. Dissolved oxygen also influences corrosion of stainless steels. However, the values of  $E_{R,CREV}$  were also independence of dissolved oxygen concentration. This implies that the effects of temperature, chloride ion concentration and dissolved oxygen concentration on the probability of crevice corrosion occurrence would be complexly competed in 304L SS.

Consequently, from these results, it was clear that there is a possibility that crevice corrosion of 304L SS will occur beyond 80 °C and 100 ppm chloride concentration. In addition, crevice corrosion may occur when the temperature is over 50 °C and chloride concentration is over 2500 ppm. Furthermore, crevice corrosion can occur when the temperature is RT, and chloride concentration is over 10000 ppm. According to the water quality environment change in the SFP of the 1F accident, the condition of RT and high chloride concentration and that of 80 °C and low chloride concentration need not to be considered. However, the condition of 2500 ppm chloride concentration at over 50 °C or that of 2500 ppm at over 80 °C are included in the SFP water quality conditions. Therefore, in the 304L SS parts of the 1F fuel assemblies that experienced seawater exposure, there is a possibility of crevice corrosion occurrence. However, the corrosion rate at each condition could not be accurately estimated. Additionally, not only the influence of the oxide film which is formed on the 304L SS surface during reactor operation but also the effect of dissolved oxygen concentration on the crevice corrosion behavior must be appropriately evaluated.

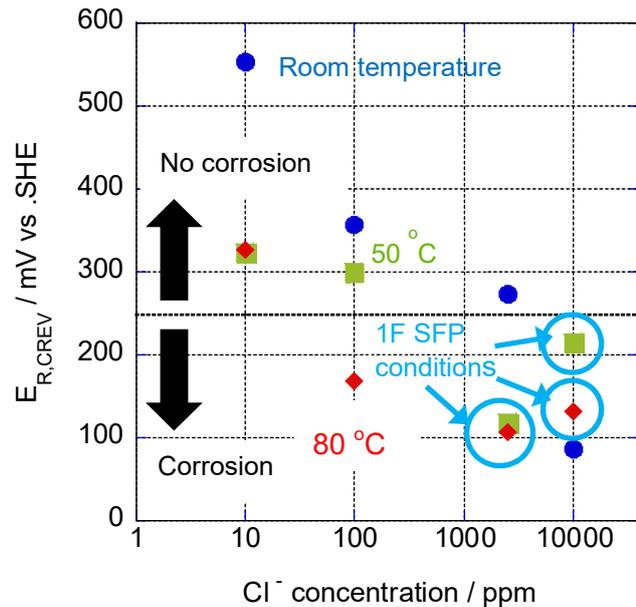


Fig.7. Relation between  $E_{R,CREV}$  and Cl<sup>-</sup> concentration.

#### 4. Conclusion

In this study, crevice corrosion behavior under salt water in a type 304L stainless was electrochemically investigated to evaluate the possibility of crevice corrosion occurrence for the fuel assemblies that experienced seawater exposure in the Fukushima Daiichi Nuclear Power Plant accident. The obtained knowledge is summarized below.

- Crevice corrosion mode of 304L SS is considered to be the typical mode obtained in stainless steels, in which the oxidation reaction of Fe, Cr and Ni occurred in anode side, and the reductive reaction of oxygen occurred in cathode side.
- The repassivation potential,  $E_{R,CREV}$ , was lower than a spontaneous potential ( $E_{SP}$ ) when the temperature was 50 °C and the chloride ion concentration was over 2500 ppm or these conditions were 80 °C and over 2500 ppm under the saturated concentration of dissolved oxygen. Under these conditions, there is a possibility that crevice corrosion will occur in the crevice structure composed by the 304L SS parts of the 1F fuel assemblies that experienced seawater exposure.

However, the possibility of crevice corrosion occurrence in 1F fuel assemblies should be discussed in detail after not only the corrosion rate but also the effect of the oxide film and dissolved oxygen concentration on the crevice corrosion behavior are evaluated.

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