

## Effect of Surface Precipitate on the Crevice Corrosion in HYBRID and Oxalic Acid Solution

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### 1. Introduction

Commercialized reductive decontamination reagents, represented by CORD, CITROX, CANDECON, etc., have mostly adopted oxalic acid (OA) as a base decontamination solution. However, it is known that OA has a critical drawback of a corrosion effect of the base metal[1-3]. Bradbury [2] reported that the intergranular attack (IGA) initiated during the decontamination might propagate during subsequent power plant operation, and residual chemicals afterward left in crevices might affect the integrity of the base metal.

In this study, we investigated the characteristics of the crevice corrosion for Inconel-600 and 304SS in OA solution according to the change in pH. The evaluation of the crevice corrosion with the chemical thermodynamic analysis identified the effect of the residual chemicals such as iron-oxalate and nickel-oxalate to the crevice corrosion behavior. Test results were compared with those of HYBRID (HYdrizine Base Reductive metal Ion Decontamination)[4].

### 2. Experimental Procedure

304SS and Inconel-600, which are mainly used in a PWR reactor coolant system, were selected for corrosion tests in HYBRID and 2000 ppm oxalic acid solution. Specimens were prepared with dimensions of 20×20×2mm after polishing with silicon carbide polishing paper of #2000 grit. All specimens were sensitized at 600°C for 24 hours. Crevice corrosion coupons were setup as described in a reference [5]. A corrosion test was carried out for 20 hours at 95°C, and the reduced weight of the specimens was measured after the corrosion test. Localized corrosions on the surface of the specimens were observed through a scanning electron microscope (SEM). The corrosion solution contains 15.84mM (2000 ppm) of OA, and the pH was adjusted using HNO<sub>3</sub>.

### 3. Results

The corrosion rate of Alloy 600 and 304SS against a change in pH is shown in Fig. 1. The crevice corrosion in the OA solution was measured based on the weight loss after the dissolution test with the removal of the surface precipitate by ultrasonic cleaning. As a result,

Alloy 600 had a corrosion rate equal to 50mg/dm<sup>2</sup> or less for all experimental pH regions. The corrosion rate of 304SS, on the other hand, was drastically changed at around pH 2. It was 6- to 20-fold higher at pH 1.8 compared to a pH of greater than 2. It was reported that the corrosion of iron is general accelerated by hydrogen generation under a pH of 3[6]. In the case of alloy 304SS, iron accounts for about 70% and nickel and chrome account for 28%. Therefore, it is considered that the corrosion behavior in the OA solution is similar to that of iron. For the case of Alloy 600, the same principle is applied to explain that there is no accelerated corrosion at pH 1.8 since the alloy has an iron component of less than 10%.

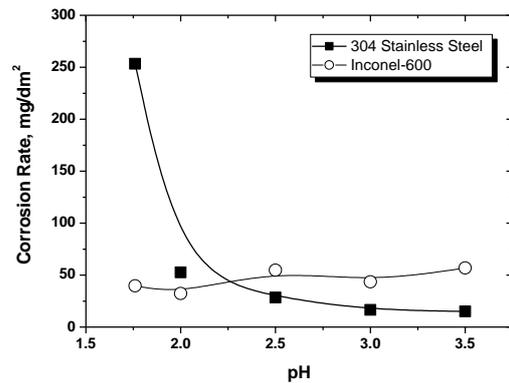


Fig. 1 Effect of pH on corrosion rate of Alloy 600 and 304 SS

The corrosion rates of 304SS and Alloy 600 in the OA solution were similar when the pH was 2 or greater, but at a pH condition of lower than 2, the corrosion rate of 304SS was significantly increased, as we described in the previous section. It is thought that the NiC<sub>2</sub>O<sub>4</sub> formed on the surface of Alloy 600, which is difficult to remove, even using ultrasonic cleaning, might prevent such corrosion. Giacomelli et al. [7] studied the effect of insoluble salts on the corrosion. In a study on the corrosion of carbon steel in an OA solution, they expected the formation of insoluble salt depending on the pH and the concentration of OA component, and reported the effect of these on the corrosion of the base metal. However, the study did not provide the exact concentrations of insoluble salt formed at different pH levels, and Ni-oxalate was not their concern.

Fig.2 shows the iron-based chemical composition in OA/Fe-containing solution and nickel-based chemical composition in OA/Ni-containing solution. Fe and Ni metal ion concentrations that may exist in the crud on the surface of the specimen are shown against the pH and total concentrations of nickel or iron respectively. In both cases,  $\text{NiC}_2\text{O}_4$  and  $\text{FeC}_2\text{O}_4$ , there are two important differences. First,  $\text{NiC}_2\text{O}_4$  is formed no matter how low the concentration of total nickel ions, but  $\text{FeC}_2\text{O}_4$  can be formed if the Fe concentration is above the threshold level, that is  $[\text{Fe}^{2+}] = 0.2 \text{ mM}$ . Second, the pH region where  $\text{NiC}_2\text{O}_4$  is formed is mainly between pH 1 and 3, but the formation of  $\text{FeC}_2\text{O}_4$  occurs in a pH region between 2 and 4. Owing to these differences, nickel oxalates can be formed earlier than iron oxalate in a low pH region.

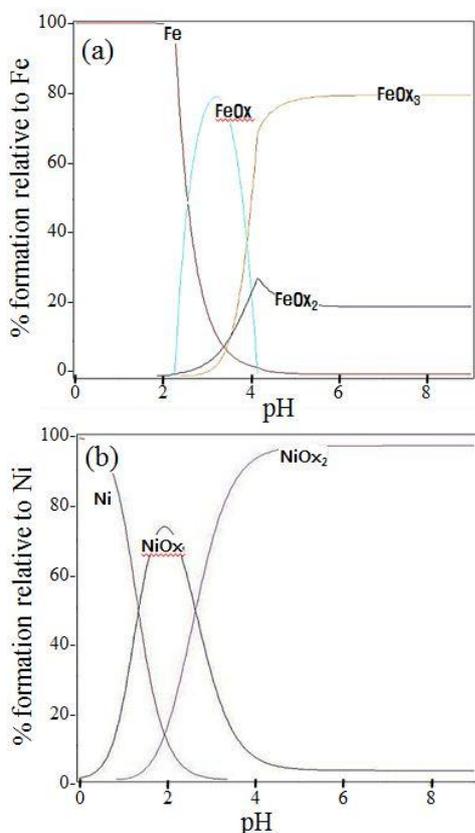


Fig. 2 Iron base (a) and nickel base (b) chemical composition of OA /Fe and OA/Ni-containing solutions as a function of pH

For these reasons, as supported by the chemical thermodynamic analyses, it can be explained that  $\text{NiC}_2\text{O}_4$  is formed on the inner surface and  $\text{FeC}_2\text{O}_4$  is precipitated on the outer layer, as shown in Figs. 4 and 5. In other words, the experimental condition of pH 1.8 has a higher possibility to have nickel oxalates other than iron oxalates. The lesser the concentration of Fe or Ni ions in the solution at such a lower pH, the higher the formation of  $\text{NiC}_2\text{O}_4$  alone. It can be seen that  $\text{FeC}_2\text{O}_4$

was formed after the formation of  $\text{NiC}_2\text{O}_4$  on the inner surface owing to the increase of Fe concentration. For the case of 304SS, on the other hand, the increased concentration of Fe resulted in the formation of  $\text{FeC}_2\text{O}_4$  when the crevice corrosion was progressing, and was dramatically increased during the corrosion. This is the reason why only yellow precipitates were observed on the surface of the 304SS specimen.

### 3. Conclusions

The crevice corrosion properties of 304 SS and Inconel-600 in HYBRID and oxalic acid solution were evaluated. In case of oxalic acid solution, the corrosion rate on 304SS was rapidly increased with a pH decrease of around 2, but there was no increase in the corrosion rate on Inconel-600. These observations were explained through the formation and distribution of  $\text{NiC}_2\text{O}_4$  and  $\text{FeC}_2\text{O}_4$  depending on the pH and concentration of metal ions in the solution, as well as the interactions of both oxalates with corrosion. In case of HYBRID solution, however, there are no corrosion problems of the materials in the low pH region. From this study, it was suggested that the contamination of Inconel-600, such as the insoluble salt formed inside a crevice, requires an effective method of removal or dissolving.

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