

Possibility of Localized Corrosion of PWR primary side materials in oxidative decontamination condition

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1. Introduction

The primary circuit of a PWR (Pressurized Water Reactor) cannot avoid the contamination of radioactive isotopes during the operation [1]. It is well known that corrosion and contamination in the primary cooling circuit of nuclear reactors are essentially interrelated: the contaminant isotopes are mostly corrosion products activated in the reactor core, and the contamination takes place on the outer core surface throughout the primary circuit. Accordingly, radionuclides uptake in the inner oxide layer and oxide/metal interface occurred inevitably. Therefore, it is necessary to remove the inner oxide layer as well as the outer oxide layer to achieve excellent decontamination effects. It is known that the outer oxide layers are typically composed of Fe_3O_4 and $NiFe_2O_4$. On the other hand, the inner oxide layers are composed of Cr_2O_3 , $(Ni_{1-x}Ni_x)(Cr_{1-y}Fe_y)_2O_4$, and $FeCr_2O_4$ [2]. Because of chromium in the trivalent oxidation state which is difficult to dissolve, the oxide layer has an excellent protectiveness and is hard to decontaminate. For the dissolution of chromium-rich oxide, there have been developed an alkaline permanganate (AP) or nitric permanganate (NP) [3, 4]. A disadvantage of the AP process is the generation of a large volume of secondary waste. On the other hand, NP process is highly incompatible to the corrosion of the structure materials.

In this study as a part of developing decontamination process, we investigated the corrosion behavior of the structure materials such as Inconel-600 and type 304 stainless steel in NP and AP oxidative decontamination conditions for the safe use of an oxidative phase in PWR system decontamination. The corrosion behavior was analyzed through the potential-pH equilibrium for the system of Cr-H₂O / Mn-H₂O at 90°C and potentiodynamic polarization in a typical AP and NP solution were evaluated. The AP or NP treated specimen surface was observed using an optical microscope and scanning electron microscopy (SEM) for an evaluation of the localized corrosion.

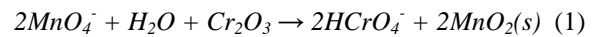
2. Experimental Methods

Test specimens were prepared in the form of coupons with the dimension of 20×20×2mm. The specimens were polished using 600-grit emery paper, degreased with acetone and ethanol, and then rinsed with deionized water before AP or NP treatment.

The test solutions were made up of 0.3 - 2.0 g/L of potassium permanganate with a small quantity of sodium hydroxide or nitric acid at 90°C. PGSTAT30 and GPES software (AUTOLAB) were used to measure the potentiodynamic polarization curves. A three-electrode corrosion cell kit with a platinum counter electrode and Ag/AgCl reference electrode was used. The reference electrode was connected with a cooled salt bridge to high temperature corrosion cell. Weight loss during the decontamination treatment was measured and the surface morphology of the tested specimen after NP treatment was examined by OM and SEM.

3. Results

Permanganate ion has a role of oxidative decontamination of Cr^{3+} to soluble bichromate ion and itself reduced to manganese dioxide in an NP solution. As the main feature of this dissolution reaction is that there is no pH change due to the self-buffering action and MnO_2 precipitate is generated from permanganate ion as follow;



On the other hand, the reaction in an AP solution differently generates hydrogen ion and pH accordingly increases during the dissolution of Cr_2O_3 .

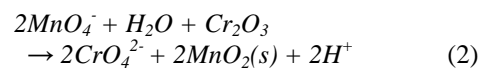


Fig. 1 shows a potential-pH equilibrium diagram of Cr-H₂O and Mn-H₂O at 90°C [5]. Referring to this figure and equations (1) and (2), MnO_4^- ion in NP or AP solution increases the potential and dissolves Cr^{3+} from the Cr_2O_3 to bichromate or chromate ion.

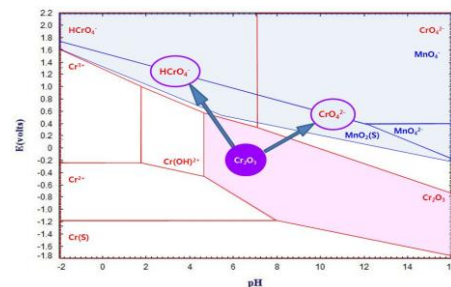


Fig. 1. Potential-pH equilibrium diagram for the system Cr-H₂O and Mn-H₂O system at 90°C showing the dissolution path of Cr_2O_3 in NP and AP solution.

Fig.2 shows potentiodynamic polarization curves of Inconel-600 under typical NP and AP conditions at 90°C. The corrosion current of the NP condition at an open circuit potential (OCP) is similar to that of the AP condition, however, the OCP of an NP condition is 500 mV higher than that of an AP condition. A passive state is more unstable and a passive range of the NP is shorter than those of the AP condition.

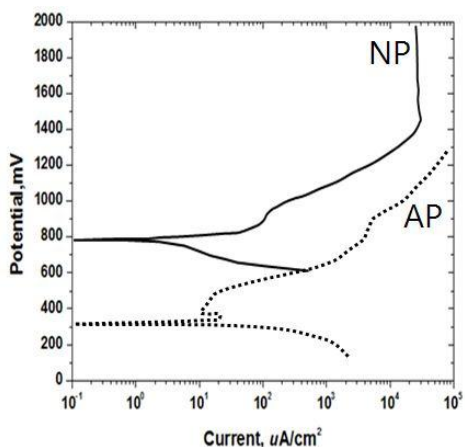


Fig. 2. Potentiodynamic polarization curves of Inconel-600 in typical NP and AP condition at 90°C.

A potential-pH equilibrium diagram and potentiodynamic polarization curve at around pH 3 for an NP and 11 for the AP processes are shown in Fig. 3. In the case of NP oxidization, the trans-passive region of Inconel-600 lies in the region of MnO₂. In the trans-passive region, the local corrosions such as pitting and IGA tend to occur (Fig. 3(a)). Therefore, Inconel-600 has a higher local corrosion rate in the NP process. On the contrary, the passive region of the anodic polarization curve of AP process lies in the MnO₂ region, as shown in Fig. 3(b). This explains why Inconel-600 in the AP process has a lower corrosion rate during Cr₂O₃ dissolution.

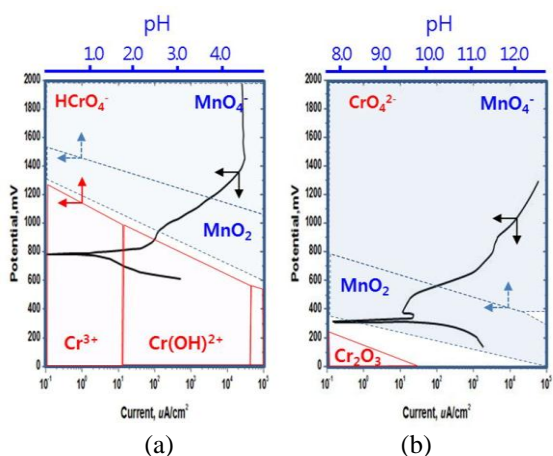


Fig. 3. Potentiodynamic polarization curve of Inconel-600 in a typical NP(a) and AP(b) solution overlapped with a potential-pH equilibrium diagram for the Cr-H₂O and Mn-H₂O system at 90°C.

After the corrosion tests for 20 hours in an AP and NP solutions, the surface of the specimens was looked over through an optical microscope. Specimens tested in the AP condition show no localized corrosion, but some localized corrosions on Inconel-600 specimens were observed in the NP condition at a pH of 3.4 or lower. The degree of corrosion of Inconel-600 at a pH of 2.1 was very severe, and pitting and intergranular attacks (IGA) were particularly observed. Since a typical NP solution is operated at a pH of 3, these corrosion results shown in Fig 4 indicate that Inconel-600 is highly expected to have corrosion problems during decontamination. Thus, the NP decontamination condition needs an improvement to suppress such corrosion problems.

Along this line, we investigated the effect of metal ions of Fe³⁺, Ni²⁺, Cr⁶⁺, or Cu²⁺ in the range of 0 - 2 mM as a corrosion inhibitor. It was shown that Cr⁶⁺ ion inhibited the corrosion when it added at less than 0.1 mM but the corrosion rapidly increased when the concentration of Cr⁶⁺ ions was greater than 0.1 mM. In the case of Fe³⁺, its addition was not helpful to inhibit the corrosion. Among the metal ions tested in these experiments, the addition of Ni²⁺ and Cu²⁺ effectively suppressed the corrosion below 0.0004 mil/h and we found that Cu²⁺ ion is the best candidate to minimize the corrosion rate. Except the addition of Cu²⁺, there were observed localized corrosions on the surface of Inconel-600.

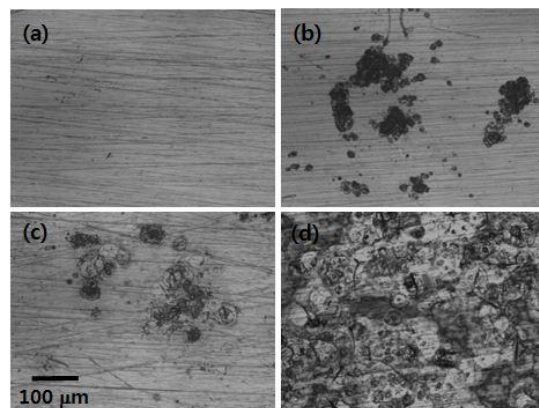


Fig.4. Localized corrosion morphology of Inconel-600 corroded in a pH of 4.5(a), 3.4(b), 2.7(c) and 2.1(d) NP solution at 95°C for 20 h.

4. Conclusions

The possibility of localized corrosion of PWR primary side materials under oxidative decontamination condition was evaluated using a potentiodynamic polarization technique, observation of localized corrosion morphology, and consideration of potential-pH diagrams at 90°C. From the results of these tests, we can conclude the following.

1) The corrosion characteristics of a classical NP process rely highly on the acidity of the

decontamination solution, and the typical process performed around a pH of 3 needs to be improved since it is vulnerable to corrosion.

2) A small amount of copper (II) ion works as a corrosion inhibitor in the oxidative process and by the addition of 0.5mM copper (II) ion the general corrosion dropped to a level of 25% and local corrosion was completely inhibited. This modified nitric acid permanganate process was named MONAP.

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