Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 18-19, 2017

Effect of Cu ion on the Corrosion of PWR Materials in HyBRID Decontamination Solution

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1. Introduction

The inside of the piping of the primary system of a nuclear power plant is corroded with radioactivity by forming a corroded oxide film by long time operation. In order to repair or decommissioning the power plant, it is necessary to decontaminate to remove the contaminated oxide film. However, there is a problem that corrosion of the material of the primary system occurs due to a commercial decontamination agent containing oxalic acid used in the decontamination process.[1] KAERI has been developing a new decontamination process that does not contain any organic chemicals in the decontamination solution and minimizes the use of ion exchange resin in the solution purifying step.[2] The process is hydrazine base reductive metal ion decontamination for decommissioning (HyBRID) and consists of N_2H_4, H_2SO_4 and Cu^+ ions. $CuCl_2$ or $CuSO_4$ may be used to add copper ions to HyBRID. However, it is known that the addition of copper can cause corrosion problems for Inconel-600, the main material of the steam generator.[3] Therefore, in order to apply a HyBRID to an actual process, additional corrosion evaluation related to copper is necessary.

In this study, we investigated the effect of copper ion on pitting corrosion of PWR materials in HyBRID decontamination solution. Experiments were performed in the presence of $CuCl_2$ or $CuSO_4$ and in the absence of copper ion in HyBRID. Assuming a problem that may appear during actual process operation, it was also performed under conditions that were lower than the original pH of HyBRID.

2. Experimental Methods

Inconel-690(I-690), Inconel-600(I-600) and 304 stainless steel(304 SS) specimens were prepared with the dimension of 20×20×2mm after polishing with silicon carbide polishing paper of #800 grit. To make harsh environments, the heat treatment of specimens was conducted at 600℃ for 1 hours before polishing of specimens.

The compositions of reductive decontamination solutions used for corrosion test are shown in Table I. The experiment was carried out at pH 3, which is the HyBRID decontamination condition, and lower range of pH 1.5 and 2.0. pH of decontamination solutions was adjusted with sulfuric acid. Specimens were corroded in decontamination solutions for 20 hours at 95℃. Specimens were corroded in decontamination solutions for 20 hours at 95℃. The weight of the specimen was measured before and after the experiment to determine the weight loss. Surface corrosion was analyzed by SEM.

Table I. Condition of reductive decontamination

Decontamination solution	Chemical composition
HyBRID without Cu ion	0.05M N_2H_4 + H_2SO_4 (pH=1.5, 2.0, 3.0)
HyBRID with $CuCl_2$	0.05M N_2H_4 + 0.5mM $CuCl_2$ + H_2SO_4 (pH=1.5, 2.0, 3.0)
HyBRID with $CuSO_4$	0.05M N_2H_4 + 0.5mM $CuSO_4$ + H_2SO_4 (pH=1.5, 2.0, 3.0)

3. Results

Fig. 1 shows the corrosion test results for Inconel-600. In HyBRID without copper, corrosion occurred at all pH conditions. Similar results were obtained at pH 1.5 and 2.0. In both cases, it was found that the IGA (intergranular attack) and the pitting of 10 ~ 20μm size were formed sparsely. At pH 3, relatively shallow pitting corrosion was found. When $CuSO_4$ was added in HyBRID, only shallow corrosion occurred at pH 1.5.

Inconel-690 showed severe corrosion only at pH 1.5 in HyBRID without copper.

Corrosion occurred in all cases at pH 1.5 on 304 stainless steel. In particular, there was severe corrosion when copper ion was absent or $CuCl_2$ was present. And small pitting corrosion was found in HyBRID with $CuSO_4$. At pH 2, corrosion occurred only in the absence of copper ion and many shallow pittings were found. Corrosion was not observed in other cases.

Fig. 2 shows the weight loss of the specimen in the corrosion test. In the case of Inconel-690, there was a large amount of weight loss only at pH 1.5 without copper ion. In the results of Inconel-600, weight loss was observed at pH 1.5 and 2.0 only in the absence of copper ion, and weight loss decreased with increasing pH. The results of 304 stainless steel showed much corrosion at pH 1.5 only when copper ion was absent or $CuCl_2$ was present.

These results show that addition of copper ions to HyBRID can inhibit corrosion of metals such as Inconel-690, Inconel-600 and 304 stainless steel. In addition, when $CuCl_2$ was added to HyBRID, it was found that 304 stainless steel was weak at pH 1.5 or less. HyBRID with

$CuSO_4$ showed shallow surface corrosion on Inconel-600 and 304 stainless steel at pH 1.5, but there was little weight loss. Thus, HyBRID with $CuSO_4$ is more stable with respect to the material corrosion in decontamination process for PWR than $CuCl_2$ contained HyBRID.

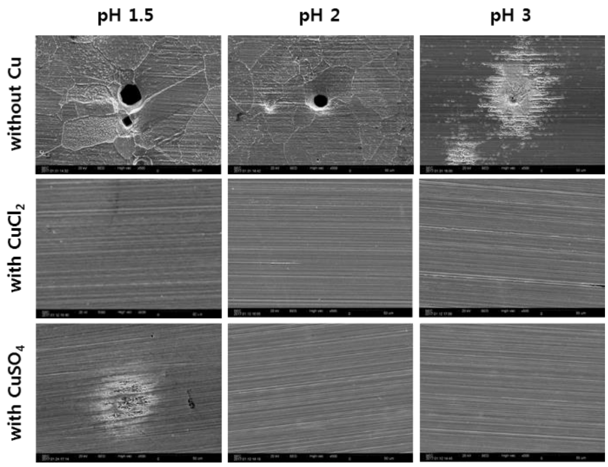

Fig.1. Surface morphology of corroded I-600 under various HyBRID conditions at 95℃ for 20h (×500).

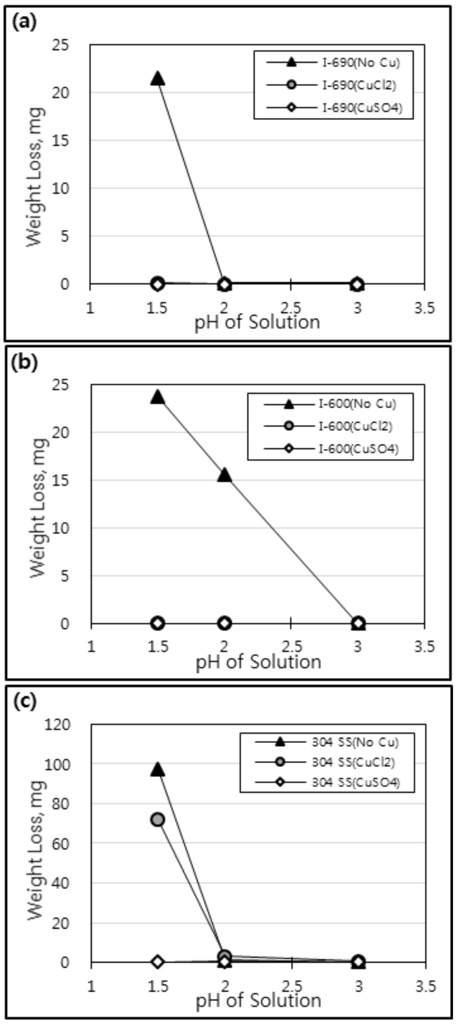

Fig. 2. Weight loss of specimens corroded in the HyBRID (a) I-690 (b) I-600 (c) 304 SS.

4. Conclusion

According to the results of corrosion tests, it was confirmed that copper ions added to the HyBRID not only improve the decontamination performance but also improve the stability for corrosion of the materials in PWR. In order to prevent corrosion of the material in the HyBRID decontamination step, it is required that the pH should not be lowered below 2.0. Additional electrochemical studies will be needed to interpret these results. These results are expected to be used as a useful resource to study the process conditions and performance improvement of HyBRID decontamination.

ACKNOWLEDGE

The authors would like to express their appreciation to the National Research Foundation of Korea (NRF) for the award of a grant funded by the Ministry of Science. ICT and Future Planning (MSIP) of the Republic of Korea, in support of the authors' work through the Nuclear Research and Development Program (NRF-2012M2A8A5025655).

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