Development of SCC Mitigation Method in BWR Plant by TiO_2 Technique

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1. INTRODUCTION

TiO_2 addition into boiling water reactor (BWR) primary system is being developed as a method to mitigate stress corrosion cracking (SCC) of the BWR structural materials. This technique aims for electrochemical corrosion potential (ECP) decrease of reactor materials by photo-excitation reaction under Cherenkov irradiation.

In this study, tests have been conducted in the test loop in both BWR and OECD Halden reactor to estimate the feasibility of the SCC mitigation method with TiO_2 .

2. EXPERIMENTAL

2.1 ECP measurement in BWR plant

The test loop was settled in a 1100MWe class BWR unit and the reactor water from the recirculation line was introduced to the test loop through the reactor water clean up system inlet piping.

The prepared specimens were exposed to the reactor water at the exposure section under NWC environment and then the specimens were set into the ECP measurement section and ECP was measured under UV light irradiation on the surface of the specimens.

2.2 TiO_2 injection demonstration and ECP measurement in the Halden BWR simulation loop

The experiment consisted of an in-core test rig and an external test loop system in the Halden reactor. TiO_2 solution was added into the loop water (0.7m/sec flow rate) to deposit on the inner surface of test rig and test loop materials during nuclear heating (190 C) at the beginning of the reactor cycle. After the TiO_2 deposition, TiO_2 was removed from the loop water by the loop purification system. Then, reactor started operating at full power.

The loop water flowed through the test rig and the test loop autoclave by $\sim 0.7\text{m/sec}$ flow rate and $\sim 288\text{ C}$ at full power operation. ECP measurement was conducted under simulated BWR environment, controlling hydrogen oxygen molar ratio (about 10^0 to 10^3) in the loop water.

3. RESULTS AND DISCUSSION

3.1 ECP measurement in BWR plant

Fig. 1 showed the ECP measurement of TiO_2 deposited Ni based alloy. Before the ECP measurement, the specimen was exposed to the reactor water for 2900 hours at the exposure section. The ECP of the TiO_2 deposited specimen (C1 $193\mu\text{g/cm}^2$ TiO_2) decreased to -0.31 V (vs.SHE) when the UV irradiation started.

3.2 TiO_2 injection demonstration and ECP measurement in the Halden BWR simulation loop

$77\mu\text{g/cm}^2$ TiO_2 was deposited on the surface of the specimen in the out-of-core monitor (autoclave) for 28 hours. After TiO_2 injection demonstration, the ECP of in-core pressure flask indicated $< -0.43\text{ V (vs.SHE)}$ under high intensity radiation near in-core fuel rods in simulated BWR environment. It is supposed that the in-core Cherenkov irradiation generated significant ECP decrease with photo-excitation reaction.

4. CONCLUSIONS

The test results showed that the ECP of TiO_2 deposited materials was decreased to $< -0.3\text{ V (vs.SHE)}$ in both tests. This TiO_2 technique was confirmed to be feasible as a SCC mitigation method for BWR structural materials.

Fig. 1 ECP measurement results of Ni alloy 600 in a BWR NWC environment

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ABSTRACT

TiO₂ addition into boiling water reactor (BWR) primary system is being developed as a method to mitigate stress corrosion cracking (SCC) of the BWR structural materials. This technique aims for electrochemical corrosion potential (ECP) decrease of reactor materials by photo-excitation reaction under Cherenkov irradiation. Tests have been conducted in the test loop in both BWR and OECD Halden reactor to investigate the feasibility of the SCC mitigation method with TiO₂. The test results showed that the ECP of TiO₂ deposited materials was decreased to <-0.3V(vs.SHE) under both UV light irradiation in the BWR reactor water normal water chemistry (NWC) environment and in-core Cherenkov irradiation in the Halden BWR simulation loop under higher dissolved oxygen condition. This TiO₂ technique was confirmed to be feasible as a SCC mitigation method for BWR structural materials.

1. INTRODUCTION

SCC sensitivity of BWR materials is mitigated by reduction of ECP. At low ECP condition, the SCC sensitivity is mitigated in high temperature water (Andresen, 2002). Current SCC mitigation methods, such as hydrogen water chemistry (HWC) and noble metal chemical addition (NMCA), are applied in many BWRs to reduce the ECP (Hettiarachichi, 1995). However, it is well known that higher hydrogen injection causes an increase in dose rate at the turbine system due to the radiolysis and N-16 carry over from the reactor water to main steam.

TiO₂ is an n-type semiconductor and it oxidizes H₂O and generates anodic current due to photo-excitation reaction under the ultraviolet light irradiation with <400nm in the water,

The polarization curve indicates the possibility of ECP decrease by the TiO₂ photo-excitation reaction in high temperature water (Akashi, 2001). As the Cherenkov radiation has continuous spectrum including <400nm in the reactor, ECP of TiO₂ treated

material is expected to be lower than that of untreated material in the reactor without sufficient hydrogen addition.

In the previous studies, laboratory tests have been performed and the possibility of the SCC mitigation using TiO_2 method was estimated under UV light irradiation that was simulated as in-core Cherenkov irradiation (Okamura, 2005 and Takamori, 2005).

In this study, tests have been conducted in BWR and Halden reactor to estimate the feasibility of the SCC mitigation method with TiO_2 . TiO_2 was deposited by chemical injection on the stainless steel and Ni based alloy specimens. TiO_2 injection demonstration was also performed in the Halden BWR simulation loop. The test results showed that the ECP of TiO_2 deposited materials was decreased to $<-0.3\text{V}(\text{vs.SHE})$ under both UV light irradiation in the BWR NWC environment and in-core Cherenkov irradiation in the Halden simulated BWR environment under higher dissolved oxygen condition. And also, TiO_2 injection demonstration was performed in the Halden BWR simulation loop and the TiO_2 deposition on the surface of the test loop materials was observed.

This TiO_2 technique was confirmed to be feasible as a SCC mitigation method for BWR structural materials.

2. EXPERIMENTAL

2.1 ECP measurement in BWR plant

The specimens were made of Type 316L stainless steel and Ni alloy 600 ($\phi 20\text{mm} \times 3\text{mm}$ thickness) and exposed in the 288 C pure water for 500 hours for the prefilming. The prefilming condition was a simulating NWC (250ppb dissolved oxygen, 10ppb dissolved hydrogen and 200ppb hydrogen peroxide). After the prefilming, the specimens were coated with TiO_2 by chemical injection method. Specimens were exposed in flowing high temperature pure water in the test loop autoclave and TiO_2 solution was added into the high temperature water in the test loop. Then TiO_2 was deposited on the surface of the specimen. Amount of deposited TiO_2 was measured by a X-ray fluorescence Analyzer (XRF). The surface of the specimens was observed by scanning electron microscopy (SEM).

Figs.1 and 2 show the schematic of the test loop. The test loop was settled in a 1100MWe class BWR unit and the reactor water from the recirculation line was introduced to the test loop through the reactor water clean up system inlet piping by 12 L/min (1.2m/sec) at specimen exposure section and 25 L/min (1.0m/sec)

at ECP measurement section. The BWR was operated in NWC environment. The test section temperature was 275 C when the reactor water flowed through the loop during the test. The prepared specimens were exposed to the reactor water for 2900 hours at the exposure section. After the exposure, the amount of deposited TiO_2 was measured to confirm the durability of the deposition.

And then, the specimens were set into the ECP measurement section and ECP was measured. UV light was introduced to the specimen through optical fiber glass and sapphire glass. Two specimens were set in the ECP measurement section at once. The measured ECP with internal reference electrode (Ag/AgCl, 0.1N KCl) was converted to SHE scale. The intensity of UV light was estimated as 2 to 6 mW/cm^2 at 254 nm on the surface of the specimen.

2.2 TiO_2 injection demonstration and ECP measurement in the Halden BWR simulation loop

TiO_2 injection demonstration was conducted at the test loop through in-core vessel settled in the Halden reactor, and after this demonstration, in-core ECP measurements of TiO_2 treated materials were performed during reactor operation.

The experiment consisted of an in-core test rig and an external test loop system. Fig.3 shows a schematic of the test rig. Test rig included two fuel rods in pressure flask with four ECP reference electrodes (two $\text{Fe}/\text{Fe}_3\text{O}_4$ and the others Pt), with one electrode of each type located at two axial levels below the fuel rods. Pressure flask was made of AISI Type 316Ti stainless steel. Test rig was prefilled at 288 C with 10 ppm dissolved oxygen for 10 days.

The test loop system consisted of the main loop system, purification system, water analysis system and TiO_2 injection system. Fig.4 shows a schematic of the test loop system. Main loop system contained two autoclaves to monitor the amount of deposited TiO_2 on the surface of specimens and to measure ECP of TiO_2 deposited union tees into which the reference electrodes were installed. The analysis system was used to obtain water samples from the loop to monitor conductivity, dissolved oxygen and dissolved hydrogen concentrations and to provide a facility for the controlled TiO_2 injection into the loop. Fig.5 shows a schematic of the test loop autoclave union tees with three reference electrodes (two $\text{Fe}/\text{Fe}_3\text{O}_4$ and the other Pt). The test loop

including union tees was made of Type 316L stainless steel. The union tees were prefilmed at 288 C with 200 ppb dissolved oxygen for 200 hours and then 300ppb dissolved hydrogen for 500 hours. The test loop without union tees and test rig was prefilmed with 10 ppm dissolved oxygen for 7 days, 2 ppm dissolved oxygen for 7 days, 400 ppb dissolved oxygen for 6 days and then 300 ppb dissolved oxygen for 1 day.

TiO₂ solution was added into the loop water (0.7m/sec flow rate) to deposit on the inner surface of test rig and test loop materials during nuclear heating (190 C) at the beginning of the reactor cycle. The TiO₂ concentration in the loop water was measured as less than 16ppm. The loop water concentrations of both O₂ and H₂ were specified to be <100 ppb. The purification flow rate was specified in the range from 15 to 25 L/h.

Measurement of the amount of TiO₂ deposition was performed after Type 316L stainless steel specimens were removed from autoclave while reactor was under subcritical condition. Amount of deposited TiO₂ was estimated by a X-ray fluorescence Analyzer (XRF). After the TiO₂ deposition, TiO₂ was removed from the loop water using the loop purification system. Then, reactor started operating at full power.

The fuel rods were irradiated for approximately 200 full power days. The average linear heat rate of the fuel rods was specified as 400 W/cm. The fast neutron flux ($E > 1\text{MeV}$) specified was $\sim 3 \times 10^{13} \text{ n/cm}^2$.

The loop water flowed through the test rig and the test loop autoclave by $\sim 0.7\text{m/sec}$ flow rate and $\sim 288\text{ C}$ temperature at full power operation. Water chemistry of the test loop was simulated BWR NWC environment (200 to 300 ppb dissolved oxygen and 10 to 50 ppb dissolved hydrogen) for the almost all period of fuel irradiation. ECP measurement was conducted, controlling hydrogen/oxygen molar ratio (about 10^0 to 10^3) in the loop water. The ratio was determined from the measurements of H₂ and O₂ concentrations in the loop sampling system. Dissolved oxygen concentration was controlled between about 10^0 to 10^3 ppb. Of seven ECP reference electrodes installed in the test system, four settled in the test rig when the test system was fabricated. The union tee without TiO₂ deposition was installed as the reference after TiO₂ injection was completed, and three electrodes were installed in the autoclave union tees before reactor started. The measured ECPs with these electrodes were converted to SHE scale.

3. RESULTS AND DISCUSSION

3.1 ECP measurement in BWR plant

Fig.6 showed SEM observation results of the surface of the specimens. These specimens were prefilmed in simulated HWC condition for 500hours before TiO₂ coating.

(a) TiO₂ untreated specimen

Large size particles (about 2 μm) and small size ones (<1 μm) were observed. By the EDX analysis, it was determined that the large size particles were Fe rich oxides with Ni and small size particles were Cr rich oxides with Fe.

(b) TiO₂ deposited specimen by chemical injection

33 $\mu\text{g/cm}^2$ TiO₂ was deposited on the specimen. The fine TiO₂ particles were uniformly deposited on the surface. TiO₂ deposition seemed to be thinner but the fine particles were distributed on and among the oxides.

Table 1 shows the specimens for which ECP was measured in the test loop in a BWR. The amount of the TiO₂ deposition after 2900 hours exposure was shown in this table. The 0 $\mu\text{g/cm}^2$ TiO₂ specimens without reactor water exposure were prepared as the reference in case of Ni based alloy. The plant was operated at full power during the ECP measurement tests. The water chemistry was NWC, the reactor water conductivity was less than 0.1 $\mu\text{S/cm}$ and the dissolved oxygen concentration was about 260ppb. Figs.7-1, 7-2 and 7-3 show the ECP measurement results for stainless steel and Ni based alloy. TiO₂ deposition and UV irradiation worked well to reduce the stainless steel and Ni alloy ECP in the BWR water.

(a) TiO₂ deposited specimens without reactor water exposure before ECP measurement (Fig.7-1)

The ECP of the TiO₂ deposited 316 SS decreased from -0.13V(vs.SHE) to -0.30V(vs.SHE) when the UV irradiation started. When the irradiation stopped, the ECP returned back to -0.13V(vs.SHE).

The ECP of the TiO₂ deposited Ni based alloy also decreased to -0.39V(vs.SHE) during UV irradiation. The ECP of both specimens responded to the UV irradiation on/off dramatically.

(b) TiO₂ deposited stainless steel (Fig.7-2)

Before the ECP measurement, the specimen was exposed to the reactor water for 2900 hours at the exposure section.

The ECP of the TiO₂ deposited specimen decreased to

−0.33V(vs.SHE). The residual ratio of the TiO_2 deposition was 86% after the 2900 hours exposure.

(c) TiO_2 deposited Ni based alloy (Fig.7-3)

The ECP of the TiO_2 deposited specimen decreased to −0.31V(vs.SHE). The TiO_2 residual ratio after 2900 hours exposure was 91%. Thus the durability of the TiO_2 treatment for stainless steel and Ni alloy after exposure of 120 days in the reactor water was confirmed.

ECP of all the TiO_2 deposited specimen were about −0.3V(vs.SHE) in BWR NWC environment under UV light irradiation after the long-term reactor water exposure. It is proved that the TiO_2 technique for the SCC mitigation depends on the TiO_2 photo-excitation reaction rather than bulk water chemistry.

3.2 TiO_2 injection demonstration and ECP measurement in the Halden BWR simulation loop

Fig.8 showed the TiO_2 injection demonstration result. TiO_2 injection demonstration was performed under 190 C. The amount of TiO_2 deposition on the surface of the specimen in the out-of-core autoclave was estimated as $77\mu\text{g}/\text{cm}^2$ for 28 hours. The maximum conductivity of loop water increased to about $1.0\mu\text{S}/\text{cm}$ due to dispersing agent in the solution during TiO_2 injection and the increase of purification system led to water conductivity decrease to less than $0.1\mu\text{S}/\text{cm}$ after TiO_2 addition was finished.

Fig.9 showed the pictures of the surface of the specimens (30mm×12mm) in the autoclave and the internal of the union tee after TiO_2 injection demonstration.

(a) The surface of the plane specimen

$77\mu\text{g}/\text{cm}^2$ TiO_2 was deposited on the left specimen and the right one was prepared as the reference ($0\mu\text{g}/\text{cm}^2$). The slightly white deposition was observed on the surface of specimen. It was estimated that the fine TiO_2 particles were uniformly deposited.

(b) The internal of the union tee

The amount of TiO_2 deposited on the inner surface of the union tee was estimated as $156\mu\text{g}/\text{cm}^2$ due to identical flow rate on the surface of the plane specimen in the autoclave. TiO_2 particles were uniformly deposited on the inner surface of the pipe.

The different properties of TiO_2 deposition between plane specimen and pipe were not observed significantly.

Table 2 shows the specimens for which ECP was measured in the test loop autoclave. In the test loop autoclave, the $0\mu\text{g}/\text{cm}^2$ TiO_2 union tees were installed as the reference. Although the amount of TiO_2 deposited on the inner surface of pressure flask was not measured, it was considered that it was almost the same as the amount of TiO_2 deposition on the surface of the specimen in the out-of-core autoclave. The reactor was operated at full power (15MW) during the ECP measurement tests. The water chemistry was cyclic NWC and HWC, changing the hydrogen/oxygen molar ratio (H_2/O_2) with $10^0\sim 10^3$. The loop water conductivity was almost less than $0.1\mu\text{S}/\text{cm}$ during the test period. Fig.10 shows the ECP measurement results of in-core and out-of-core materials.

(a) In-core pressure flask

The ECP of TiO_2 deposited pressure flask indicated less than −0.53V(SHE) under lower dissolved oxygen environment (dissolved oxygen concentration (DO) <100 ppb).

The ECP also indicated between −0.50 ~ −0.43V(vs.SHE) under high dissolved oxygen environment (DO>200ppb).

(b) Out-of-core union tee

The ECP of the TiO_2 deposited union tee changed between −0.21 ~ 0V(vs.SHE) in the oxygen-rich condition (DO>200ppb) and also decreased to −0.6V(vs.SHE) at 2ppb.

The TiO_2 deposited ECP was lower than that without TiO_2 deposition with the difference of −0.02 ~ −0.1V(vs.SHE).

The ECP of in-core pressure flask indicated <−0.43V(vs.SHE) in spite of DO>200ppb. As the in-core ECP was always lower than that with TiO_2 deposition in the out-of-core autoclave, it is supposed that the in-core Cherenkov irradiation generated significant ECP decrease with photo-excitation reaction.

The ECP of TiO_2 deposited union tees was lower than that without TiO_2 in the out-of-core autoclave. The mechanism of this ECP decrease should be studied in detail.

The demonstration results showed that in-core material ECP decreased to <−0.43V(vs.SHE) by TiO_2 deposition under high intensity radiation near in-core fuel rods in simulated BWR environment, and this technique was considered to be feasible as a SCC mitigation method for BWR structural materials.

According to these results, when the TiO_2 injection is performed in the actual BWR primary loop water, reasonable TiO_2 deposition on the surface of the reactor structural materials (for

example, in-core shroud and primary loop recirc piping) will be expected. The period of TiO_2 injection to BWR reactor water to attain $40 \mu\text{g}/\text{cm}^2$ under this condition was estimated to be about 15 hours. After TiO_2 injection, TiO_2 generates anodic current by in-reactor Cherenkov irradiation to decrease the ECP of the reactor components. Thus, SCC mitigation of BWR structural materials will be achieved.

According to Fig.10, it is suggested that the ECP of TiO_2 deposited inner surface of the recirc piping will be lower than that of untreated piping. It was shown by Okamura (2006) that ECP decrease was observed by TiO_2 deposition on the FeO-rich oxide films prefilled under HWC condition, controlling dissolved hydrogen. Thus, the ECP decrease without Cherenkov irradiation will be achieved by controlling reactor water chemistry.

4. CONCLUSIONS

- 1) The ECP of stainless steel and Ni based alloy in the BWR reactor water was decreased by fine particle TiO_2 deposition on the materials under UV light irradiation. The ECP of TiO_2 deposited stainless steel and Ni alloy decreased to $-0.3\text{V}(\text{vs.SHE})$ under UV light irradiation in a BWR NWC environment. The durability of the TiO_2 deposition was confirmed after the 2900 hours exposure to the reactor water.
- 2) TiO_2 injection demonstration was performed in the Halden BWR simulation loop. The TiO_2 deposition on the surface of the test loop materials was observed.
- 3) The ECP of in-core pressure flask in the Halden BWR simulation loop coolant was also decreased under in-core condition after TiO_2 injection demonstration. The ECP of in-core TiO_2 deposited materials was lower than $-0.43\text{V}(\text{vs.SHE})$ in spite of higher dissolved oxygen condition. The ECP decrease of out-of-core TiO_2 deposited material was also lower than that of untreated material. The TiO_2 technique was confirmed to be feasible as a SCC mitigation method for BWR structural materials.

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Fig. 1 Schematic diagram of test loop in BWR plant

Fig. 2 Schematic diagram of ECP measurement section

Fig. 3 Schematic diagram of test rig

Fig. 4 Schematic diagram of the test loop system in the Halden reactor

Fig. 5 Schematic diagram of test loop autoclave union tees

(a) TiO₂ untreated specimen

(b) TiO₂ deposited specimen by chemical injection

Fig. 6 SEM observation results of the surface of the specimen

Fig.7-1 ECP measurement results of Type 316L stainless steel and Ni based alloy in a BWR NWC environment

Fig.8 TiO₂ injection demonstration result in the Halden BWR simulation loop

Fig.7-2 ECP measurement results of Type 316L stainless steel in a BWR NWC environment

Fig.7-3 ECP measurement results of Ni alloy 600 in a BWR NWC environment

(a) TiO₂ deposited plane specimen (left)

(b) TiO₂ deposited union tee

Fig. 9 Pictures of the surface and the internal of the specimen

Fig. 10 ECP measurement results of in-core and out-of-core materials in the simulated BWR environment

Table 1 Specimens for the ECP measurements in BWR

Specimen ID	Material	TiO ₂ deposition (μg/cm ²)	Exposure in reactor water before the ECP measurement (hours)
A1	316L SS	52	0
A2	Ni alloy 600	65	0
B1	316L SS	147	2900
C1	Ni alloy 600	193	2900
C2	Ni alloy 600	0	0

Table 2 Out-of-core union tees for the ECP measurements in the

Halden test loop

Union tee ID	TiO ₂ deposition (μg/cm ²)	Reference electrode
1	77	Fe/Fe ₃ O ₄
2	0	Fe/Fe ₃ O ₄
3	156	Pt

The amounts of TiO₂ deposition were estimated as 77μg/cm² and 156μg/cm² due to identical flow rate on the surface of the plane specimen in the autoclave. These values were different due to loop water exposure time.