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# Nano-$TiO_2$ Penetration into a Tubesheet Crevice of a Steam Generator

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## 1. Introduction

In flow restricted regions of a steam generator, impurities such as sodium in the bulk water can be concentrated by a boiling to an extreme pH that may then accelerate IGA/SCC of alloy 600 tubes. Titanium dioxide is used as an inhibitor to mitigate the tube corrosion under a caustic condition[1]. $TiO_2$ penetration into a crevice was investigated in a CASS(Crevice Chemistry Analysis and Simulation System) with HT/HP (High Temperature/High Pressure) which has been developed to simulate a real tubesheet crevice of a steam generator.

In the CASS, primary water is circulated with a high flow rate through the 3/4" tube and a crevice section which has 0.15 mm gap and 40 mm depth. The CASS was instrumented with thermocouples and electrodes for a measurement of the Electro-Chemical Potential (ECP) in the crevice and bulk water. A secondary solution composed of titanium (as anatase nano-$TiO_2$) with 40 wppm NaOH was supplied with a flow rate of about 2 L/hr. After the boiling concentration for about 24 hours at a saturation temperature of 265℃, Nano-$TiO_2$ penetration into the crevice was observed by an Auger analysis.

## 2. Experimental

A HT/HP crevice simulation system was designed and constructed by Seoul National University [2]. The CASS which was based on the above HT/HP system has been modified by KAERI (Korea Atomic Energy Research Institute) including a crevice vessel, pressure dampers, heat exchangers, deaerators and a water purification system.

Fig. 1 is a schematic of the CASS which was composed of two main loops: a primary water loop and a secondary water loop with a crevice. The primary water was circulated at a high flow rate of about 2,300 L/hr by a centrifugal pump into a 3/4 inch OD Alloy 600 tube. A 3.8 L autoclave was used as the primary water heater with a maximum power of 4.8 kW.

The SG simulation vessel of the secondary side is schematically described in Fig. 2. To form a bottom-closed crevice a tube support ring was machined to have a crevice section which has a 0.15 mm gap and 40 mm depth for the A600 tube.

The crevice simulation vessel was instrumented with small size sensors including thermocouples and reference electrodes for a measurement of the temperature and ECP distributions.

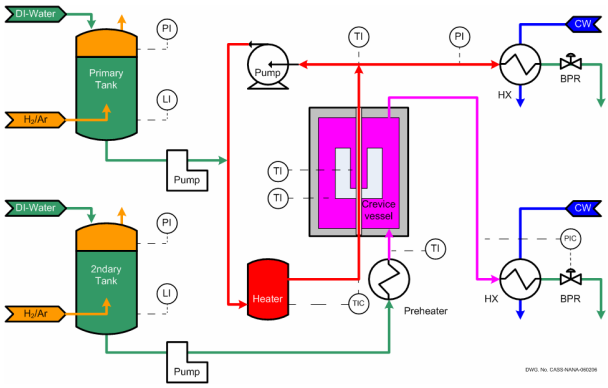


Figure 1. Schematic diagram of CASS.

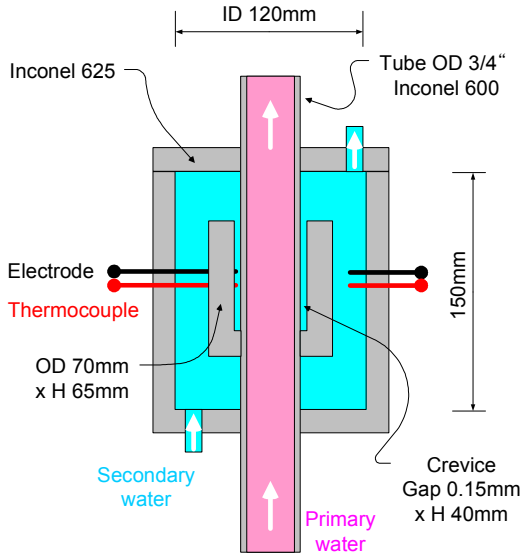


Figure 2. Schematic diagram of SG tubesheet crevice simulation vessel.

The secondary water storage tank, made of titanium, was deaerated with 4% hydrogen gas (argon balanced). The secondary water containing titanium (as anatase nano-$TiO_2$), 40 wppm NaOH, and 0.15 wppm $H_2$ was pumped by a diaphragm pump and drained through a back pressure regulator as shown in Fig. 1. Flow rate of the secondary system was maintained at 2 L/hr.

Nano-$TiO_2$ powder from Aldrich #CAS-1317-70-0 was used. It has an average size of 15 nano-meters and is an anatase type.

## 3. Results and discussion

The primary water was maintained at a constant temperature of 290℃. The secondary pressure was maintained at 5.08 MPa which corresponds to the saturation temperature of 265℃ so that a boiling could occur. In this work, the difference between the primary water temperature and the secondary saturation temperature represents the available superheat, ΔT. The experiment of a titanium penetration into a crevice was performed at $\Delta T = 20$℃.

In order to investigate the penetration of $TiO_2$ into the crevice, the tube was pulled up from the vessel after the boiling concentration and divided into eight specimens with an 8mm length as shown in Fig. 3. Each specimen was washed for an Auger electron spectroscopy.

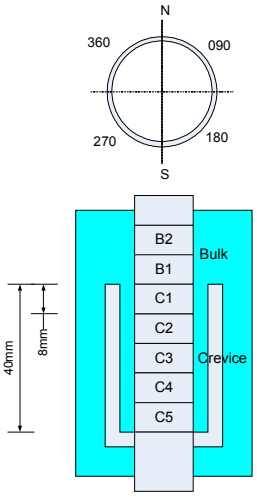


Figure 3. Number and orientation of Specimens.

The tube was Alloy 600/UNS N06600, Heat #770177, supplied by Sandvik steel, having the following composition (in weight percent): Ni 74.19, Cr 15.52, Fe 9.30, Ti 0.29.

Fig. 4 shows the maximum titanium concentration of the specimens at different positions after about a 24 hours boiling with a 1 wppm Ti concentration at $\Delta T = 25$℃. Ti concentrations at positions C1, C2, and C3 were higher than those at the others. It means that a Ti penetration occurs at a wet/dry region of the crevice.

Fig. 5 illustrates the Ti concentration of the specimens after the penetration experiment with 0.1 wppm Ti feed under the same condition as in Fig. 4. Ti Atomic percents of the specimens with a 0.1 ppm Ti feed were much lower than those with a 1 ppm Ti feed as shown in Fig. 4. But the 2 ~ 5 Ti percents of the specimens after a boiling were higher than 0.29%, Ti percent of the base metal, Alloy 600/UNS N06600.

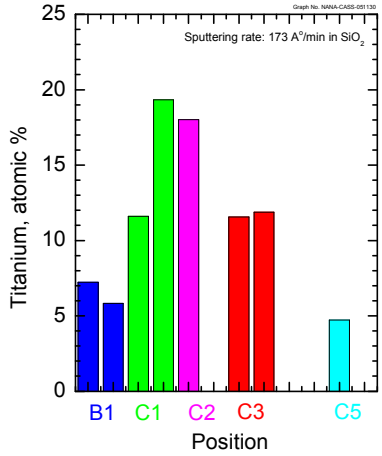


Figure 4. Maximum titanium concentration in oxide layer with 1 wppm Ti feed.

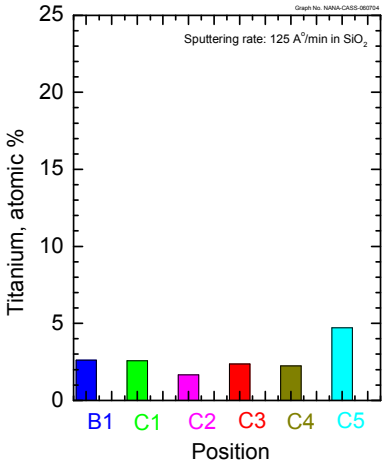


Figure 5. Maximum titanium concentration in oxide layer with 0.1 wppm Ti feed.

## 4. Conclusion

Nano-titanium penetration into an open tubesheet crevice with a 0.15mm gap was confirmed in the CASS (Crevice Chemistry Analysis and Simulation System).

After about 24 hours of a boiling at a superheat of 20℃, Maximum titanium concentrations in the oxide layers of Alloy 600 specimens were much higher than 0.29%, Ti concentration of the base metal of the tube.

## REFERENCES

[1] J. Daret, J. P. Paine, and M. Partridge, "Model Boiler Testing to Evaluate Inhibitors for Caustic Induced Stress Corrosion Cracking of Alloy 600 Tubes", Proc. 7th Int. Symp. Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Breckenridge, CO, p. 177, 1995.

[2] C. B. Bahn, I. S. Hwang, I. H. Rhee, U. C. Kim, J. W. Na, "Experimental Simulation of Boiling Crevice Chemistry," Proc. 9th Int. Symp. Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Newport Beach, CA, p. 537, 1999.