Comparison of a Penetration in Different Sizes of Titanium Dioxides into a Tubesheet Crevice

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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 an IGA/SCC of alloy 600 tubes. Titanium dioxide is used as an inhibitor to mitigate a 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 a HT/HP (High Temperature/High Pressure) which has been developed to simulate a real tubesheet crevice of a steam generator.

A feed solution composed of titanium dioxide 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 $265 \,^{\circ}$ C, TiO₂ penetration into the crevice was observed by an Auger analysis.

2. Experimental

2.1 Titanium dioxide

Two types of titanium dioxide as a corrosion inhibitor were used for the penetration experiments. One is nano-TiO₂ powder from Aldrich #CAS-1317-70-0. It has an average size of 15 nano-meters and is an anatase type. Another one is Degussa P25 TiO₂ which has an average size of 857nm.

2.2 Heat transfer tube

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.

2.3 Loop for penetration tests

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.

A crevice section which has 0.15 mm gap and 40 mm depth is schematically described in Fig. 2. The CASS was instrumented with thermocouples and electrodes for a measurement of the Electro-Chemical Potential (ECP) in the crevice and bulk water.



Fig. 1. Schematic diagram of CASS.



Fig. 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 dioxide, 40 wppm NaOH, and 0.15 wppm H₂ 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.

3. Results and discussion

The primary water was maintained at a constant temperature of 285 °C. The secondary pressure was maintained at 5.08 MPa which corresponds to the saturation temperature of 265 °C 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 for a titanium penetration into a crevice was performed at $\Delta T = 20$ °C.

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.



Fig. 3. Number and orientation of specimens.

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 as nano-TiO₂ at $\Delta T = 25$ °C. 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. 4. Maximum titanium concentration in oxide layer with 1 wppm Ti feed as nano-Ti O_2 .

Fig. 5 illustrates the Ti concentration of the specimens after the penetration experiment with 0.1 wppm Ti feed as nano-TiO₂ 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 $2 \sim 5$ Ti percents of the specimens after a boiling were higher

than 0.29%, Ti percent of the base metal, Alloy 600/UNS N06600.



Fig. 5. Maximum titanium concentration in oxide layer with 0.1 wppm Ti feed as nano-TiO₂

Fig. 6 illustrates the Ti concentration of the specimens with a 1 wppm Ti feed as Degassa P25 TiO_2 .

Ti atomic percents of the specimens with P25 TiO_2 feed were much lower than those with a 1 ppm Ti feed as shown in Fig. 4.



Fig. 6. Maximum titanium concentration in oxide layer with 1 wppm Ti feed as Degussa P25 TiO₂.

4. Conclusions

Penetration experiments with different sizes of titanium dioxides into an open tubesheet crevice with a 0.15mm gap were carried in the CASS (Crevice Chemistry Analysis and Simulation System).

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

REFERENCES

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