



CHAPTER III EXPERIMENTAL

3.1 Materials

There were three materials used in this study; steam generator (SG) alloys, Zircaloy-4 and 304 stainless steel. The SG alloys were Alloy 600 (MA and CD), Alloy 690 (MA, CD and TT) and Alloy 800 (MA and SP) which were supplied by manufacturers as shown in Table 3.1.

Table 3.1 Supplied SG tubes

Material	Manufacturer	Heat Treatment	Size (inch OD)
Alloy 600	Westinghouse	MA, TT	3/4
Alloy 690	Valinox, Sandvik, Sumitomo	MA, TT, CD	3/4, 5/8, 7/8
Alloy 800	Sandvik	MA, SP	3/4, 5/8

The materials, SG alloys, Zircaloy-4 and 304 stainless steel, were cut from the supplied materials in different shapes depending on the test sections for providing the same surface ratio of three materials which are described as follows.

3.2 Equipment

The experimental setup was arranged to resemble PWR primary conditions. This required a water circulating loop, operating at typical secondary coolant temperatures, and a test section, static 1-L titanium autoclave and static 2-L stainless steel autoclave, which simulated PWR primary conditions.

3.2.1 Experimental Loop

A schematic diagram of the experimental loop is shown in Figure 3.1. The circulating water from the loop is used to remove heat from the test section in the titanium autoclave Ti-2. The circulating water leaving the reservoir is pressurized and pumped through an interchanger and preheater to raise its temperature. It then enters and leaves the test section to remove heat, and recirculates back to the reservoir via the interchanger and cooler.

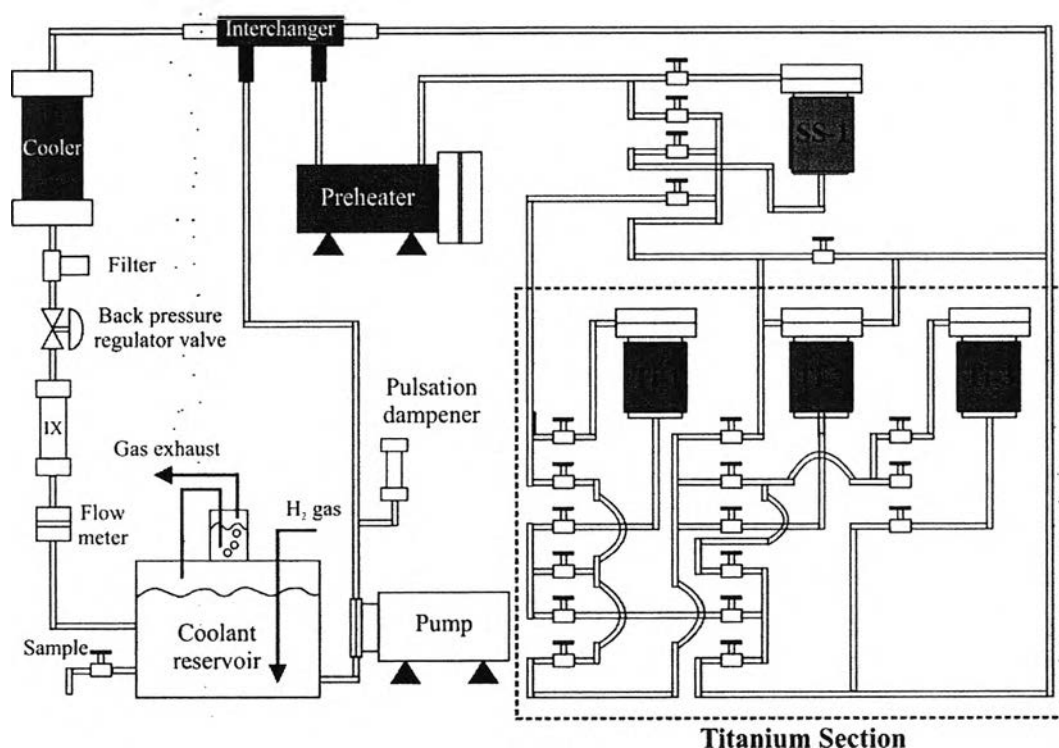


Figure 3.1 A schematic diagram of the experimental loop.

3.2.2 Test Sections and Specimens

The corrosion tests were carried out in two autoclaves simulating PWR primary conditions. The first autoclave was a static 1-L titanium autoclave (Ti-2 in Figure 3.1) which was operated with and without the circulating water. The second one was a static 2-L stainless steel autoclave (SS-1 in Figure 3.1) which was operated without the circulating water. Autoclave bulk temperature was set at 300°C. Due to safety reason, autoclave pressure could be set only as high as 1230 psig, i.e. at

saturation pressure. A heater jacket on each autoclave ensured that the bulk water was at the desired temperature.

3.2.2.1 Static Ti-2 Autoclave with Heat Transfer

The titanium autoclave, as a pressure vessel, was used to simulate PWR primary conditions because of its relative inertness. Three materials, Zircaloy-4, SG Ni-based alloy and 304 stainless steel, were exposed in the autoclave. For convenience in terms of surface analyses, SG tubing materials and Zircaloy were cut into 1-cm wide sample bands in the form of split cylinders and positioned as depicted in Figure 3.2. SS 304 was cut into 1-cm wide samples in the form of quarter-cylinders and also exposed in the autoclave. Numbers were assigned to SG sample bands as shown in Figure 3.3. The surface area proportions were 40% Zircaloy-4, 23% SG Ni-based alloy and 37% SS304. These surface area proportions were kept constant in all test sections and correspond to those in a typical PWR primary coolant system.

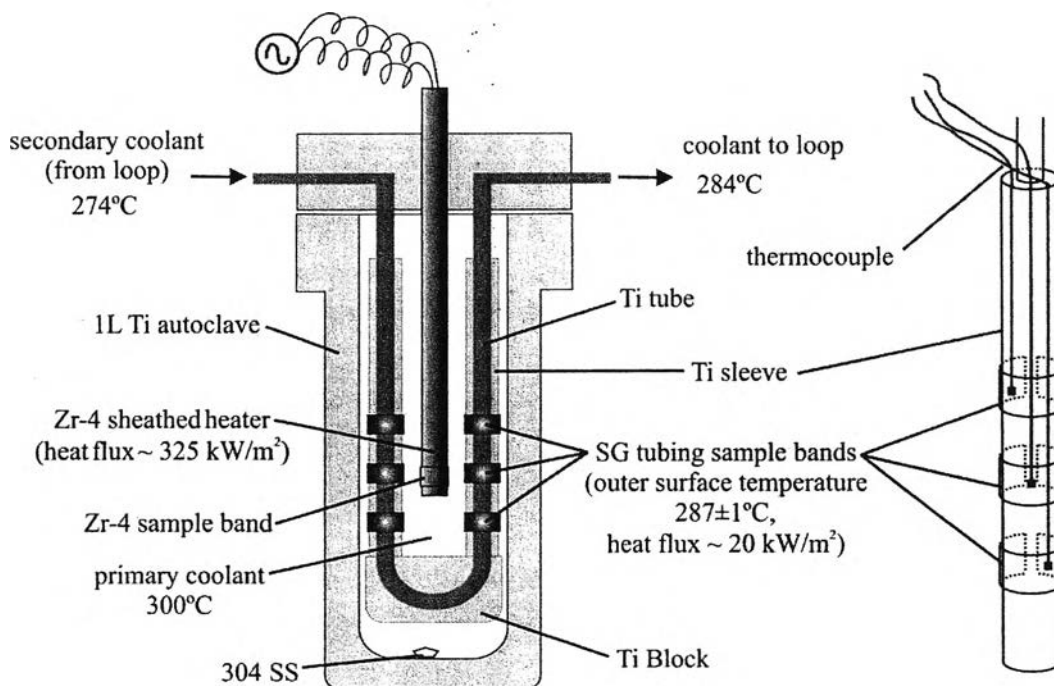


Figure 3.2 Configuration of Ti-2 autoclave with the circulating water.

Inside the autoclave, the electrically-heated Zircaloy tube, with an approximate heat flux of 325 kW/m², was installed in the middle of the

autoclave to simulate a fuel element. The heater cartridge temperature was measured with an internal thermocouple. A titanium u-tube cooled with circulating loop water was used to remove heat generated by the Zircaloy-sheathed heater and the autoclave jacket heater. The surface temperature of the cooling u-tube was monitored by adjusting the flow rate, temperature and pressure of the circulating loop water. Two titanium sleeves were slid over the titanium cooled u-tube on each side so that sample bands from the SG tubes could be fitted as illustrated in Figure 3.2. Surface temperatures of the SG sample bands were monitored via thermocouples installed underneath the sample bands in grooves machined in the titanium sleeves. It should be kept in mind that the SG surfaces of interest here are the outer surfaces, unlike actual reactor circuits where tube inner surfaces are exposed to primary coolant. A titanium block was installed at the bottom of the cooling u-tube to balance the heat transfer. A photograph of the autoclave lid assembled with titanium cooling u-tube, sleeves, block, thermocouples and sample bands is shown in Figure 3.3.

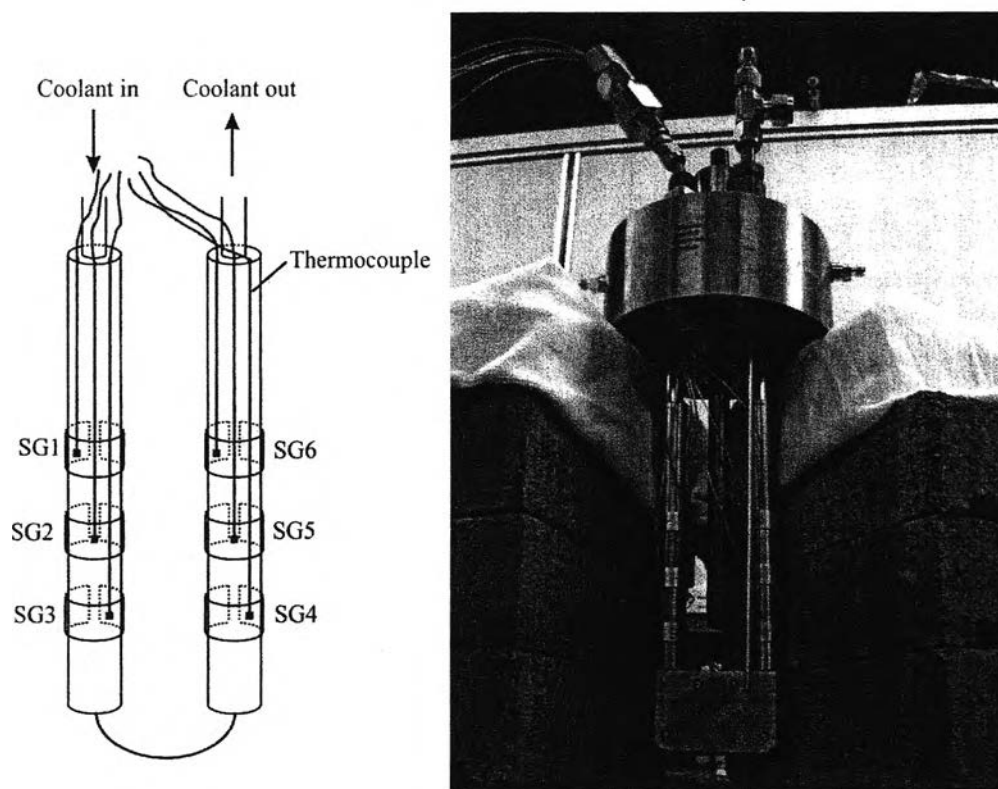


Figure 3.3 SG sample number assignment and autoclave lid assembly.

In this test section, the Zircaloy-sheathed heater and the autoclave jacket heater were used to heat the coolant inside the autoclave up to 300°C. With the heat flux from the Zircaloy-sheath heater at the temperature and pressure of the coolant, subcooled boiling was expected to occur and, thus, to provide significant turbulence. Heat transfer calculations showed that the heat flux through SG sample band surfaces was about 20 kW/m². The inlet and outlet temperature of the secondary coolant were approximately 274°C and 284°C, respectively. Comparison of the heat fluxes through the Zircaloy-sheathed heater and the SG specimens, and the calculated boiling rate on the Zircaloy surface between this experiment and PWRs is shown in Table 3.2.

Table 3.2 Comparison of heat fluxes and boiling rate in this experiment with plant data

Heat Flux	This experiment	Plant Conditions
Heat flux through the Zirc-sheathed heater, kW/m ²	325	600 (average)* 1400 (max.)*
Heat flux through the SG sample bands, kW/m ²	20	200*
Calculated boiling rate, kg/m ² .h	1045	2000-3000 (based on peak node)**

*(Chaplin, 2006)

** (EPRI and WECLLC, 2004)

3.2.2.2 Static Ti-2 Autoclave without Heat Transfer

In this test section, there was no circulating loop water to remove heat from the test section and the Zircaloy-sheathed heater was not used. Thus, the temperature of the coolant in the autoclave was raised to 300°C at saturation pressure using the autoclave jacket heater.

The surface area proportion of three materials exposed to the coolant was set to be as same as that in the static Ti-2 autoclave with heat transfer.

However, since the amount of SG alloys used in this test was more than that in the static Ti-2 autoclave with heat transfer, the SG tubing materials and 304 stainless steel were cut into 1 cm-long half cylinders. A small hole for hanging was made near the corner of each. The Zircaloy-4 surface was exposed in the form of a coil machined from rod because of the convenience in terms of exposure and surface analyses. The diameter of the coil was slightly less than that of the autoclave to avoid contact with the titanium surface. However, small sections of Zr-coil touched the titanium surface at the side and the bottom. A schematic of specimens used in this test section is shown in Figure 3.4.

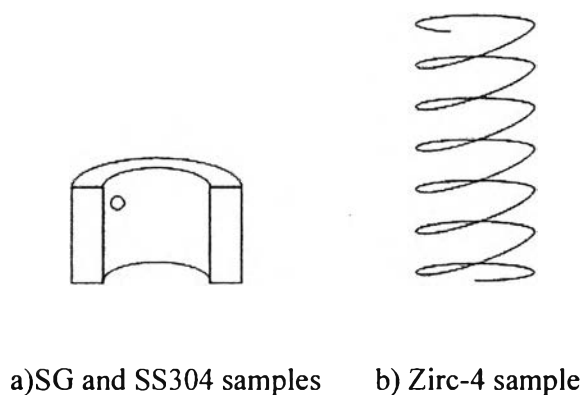


Figure 3.4 Schematic of specimens in autoclave without heat transfer.

For this test section, specimens of SG alloys and 304 stainless steel were hung from a previously-oxidized titanium sample tree using stainless steel wire. Then, they were placed in the Ti-2 autoclave. The Zircaloy-4 coil was placed surround the sample tree as shown in Figure 3.5.

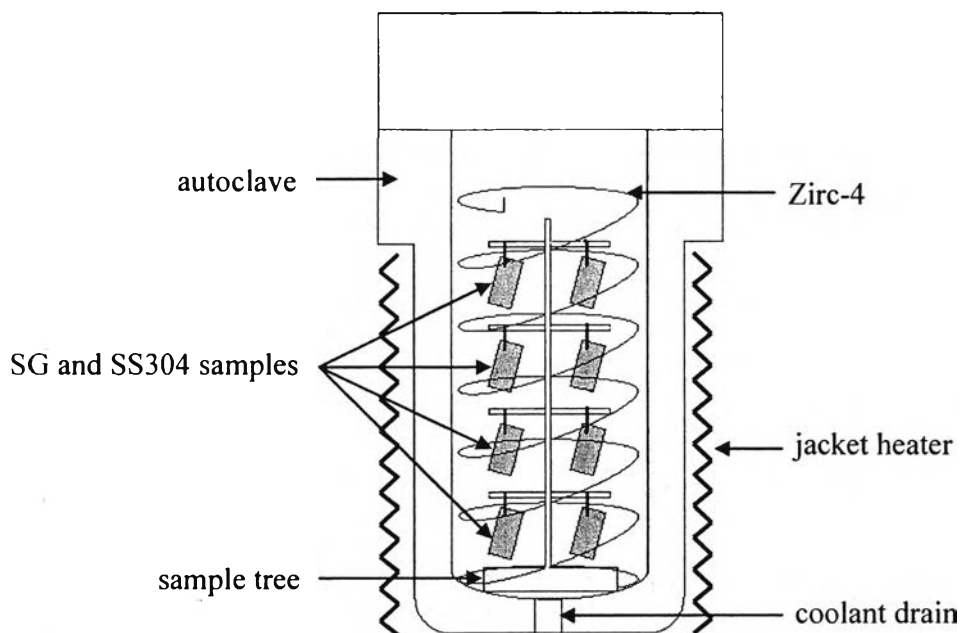


Figure 3.5 Configuration of static Ti-2 autoclave (without the circulating water).

3.2.2.3 Static Stainless Steel Autoclave without Heat Transfer

Three materials of interest were fabricated to have the same surface area proportion and volume/surface ratio (approximately 0.005 L/cm^2) as those in the static Ti-2 autoclave without heat transfer. Since the volume of the stainless steel autoclave is twice that of the Ti-2 autoclave, the surface of materials used in this autoclave was twice that in the Ti-2 autoclave. The SG tubing materials and 304 stainless steel were cut in the form of half cylinders, 2 cm and 2.2 cm long, respectively, and a small hole was drilled near the corner of each. The Zircaloy-4 surface was exposed in the form of a folded rod, approximately twice the length of that in the Ti-2 autoclave without heat transfer, because of the convenience in term of exposure.

The arrangement inside the stainless steel autoclave was similar to that in the Ti-2 autoclave without heat transfer as shown in Figure 3.6. The specimens of SG alloys and 304 stainless steel were mounted on a previously-oxidized stainless steel sample tree using stainless steel wire and placed in the stainless steel autoclave. The folded Zirc-4 was placed in the middle of the autoclave.

The coolant in the autoclave was heated to the desired temperature using the autoclave jacket heater.

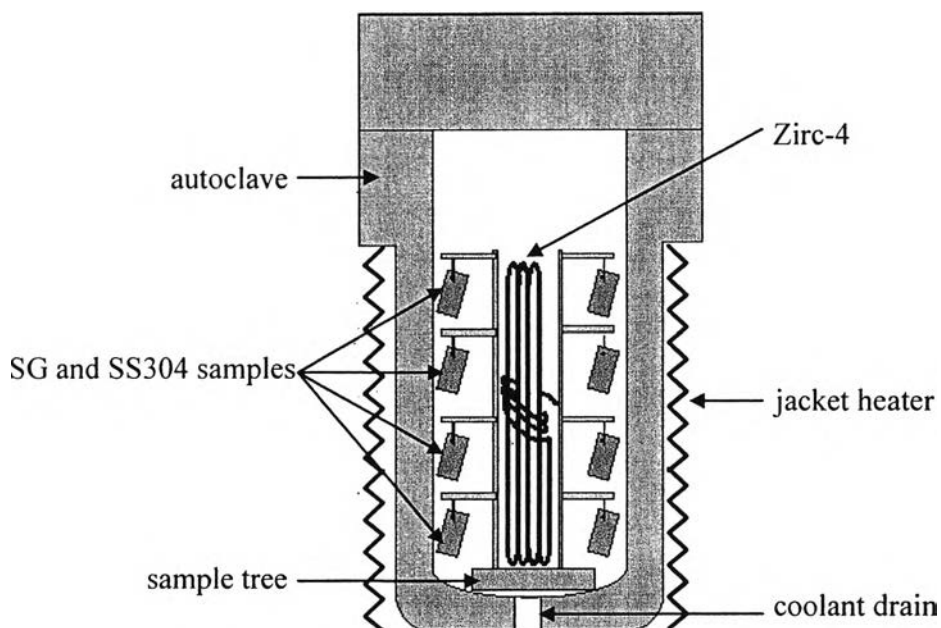


Figure 3.6 Configuration of static stainless steel autoclave (without the circulating water).

3.3 Methodology

3.3.1 Experimental Procedure

All samples were cleaned with acetone and de-ionized water and weighed before the experiment. Then they were mounted in their respective positions. After the materials were assembled in the autoclave, water with desired lithium and boron concentrations (and with desired zinc concentration for the tests to study the effect of zinc) was put into the autoclave - approximately 700 ml for the Ti-2 autoclave and 1400 ml for the stainless steel autoclave - and the autoclave lid was tightened to the body. The coolant was deaerated by purging hydrogen gas for at least 2 hours, after which the purge line was removed and the temperature was raised. Both autoclave temperature and coolant temperature from the loop were raised simultaneously until the desired autoclave temperature was reached. For the

test in the Ti-2 autoclave with the circulating water, during heating the Zircaloy-sheath heater was turned on by gradually increasing the percent heat flux. The final percentage of heat input applied to the Zircaloy-sheath heater was 80% and remained at that level until the end of run. During the run, surface temperatures of the SG sample bands were monitored.

At the end of each run, the autoclave jacket heater and/or the Zircaloy-sheath heater were turned off, the secondary coolant flow was diverted to the by-pass line, and the autoclave was allowed to cool down. The coolant was drained from the autoclave to determine pH, boron and ion concentrations; the last two were determined by titration and with ion chromatography, respectively. The autoclave lid was removed and the samples were then carefully taken out. All samples were weighed and prepared for analysis.

3.3.2 Coolant Chemistry

In this study, PWR Primary coolant chemistry conditions are followed as shown in Table 3.3.

Table 3.3 Coolant chemistry conditions

Condition	Value
pH _{300°C}	6.9-7.4
LiOH*	2-3.5 ppm as Li
H ₃ BO ₃	2,000-0 ppm as B
H ₂	18 cc/kg nominally

*adjusted accordingly

3.3.3 Oxide Characterization

Typical surface morphology of specimen and elemental composition of oxide were examined with SEM and EDX (Model JSM6400). Elemental depth profiles of oxide films were determined with SIMS and oxide phases were identified with XPS.

3.3.3.1 EDX and SEM analyses

The EDX and SEM analyses were performed on the convex surfaces and on the cross-sectional surfaces of the samples. It should be noted that all the EDX results were processed as elements without oxygen and the weight percentage was balanced with oxygen.

For Runs 1-3, the EDX analysis was performed on convex surfaces at different locations. These locations are on a circumferential line located in the middle of the samples as shown in Figure 3.7.

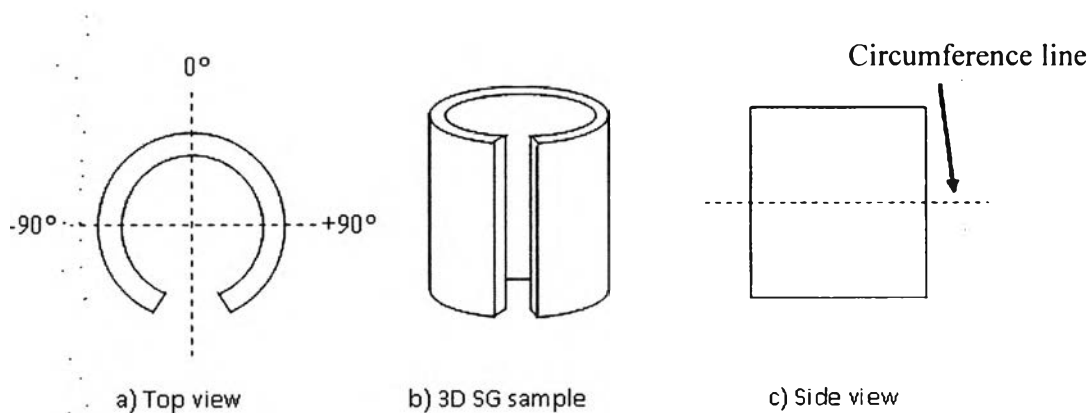


Figure 3.7 Schematic of SG sample and locations of analyses in Runs 1-3.

For Runs 4-9, the EDX analysis was performed on the convex surfaces of SG and SS304 samples at 0° and on the surface of Zirc-4 piece at half-length as shown in Figure 3.8.

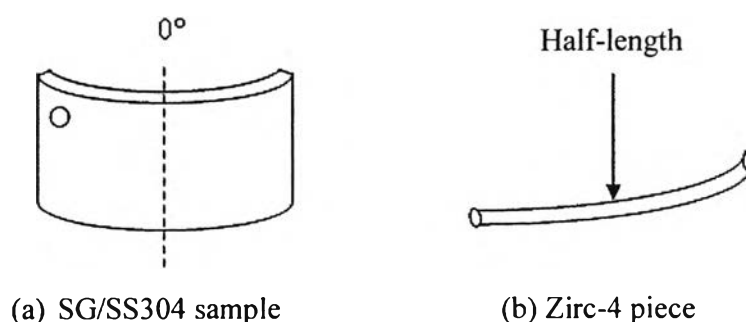


Figure 3.8 Schematic of samples and locations of analyses in Runs 4-9.

If EDX analysis was to be performed on a cross-sectional surface, the sample was molded in epoxy resin, sectioned at the circumferential line and polished. Three different locations along the radial lines were analysed as illustrated in Figure 3.9: A is at the metal/metal oxide interface and A, B and C are 10 μm apart.

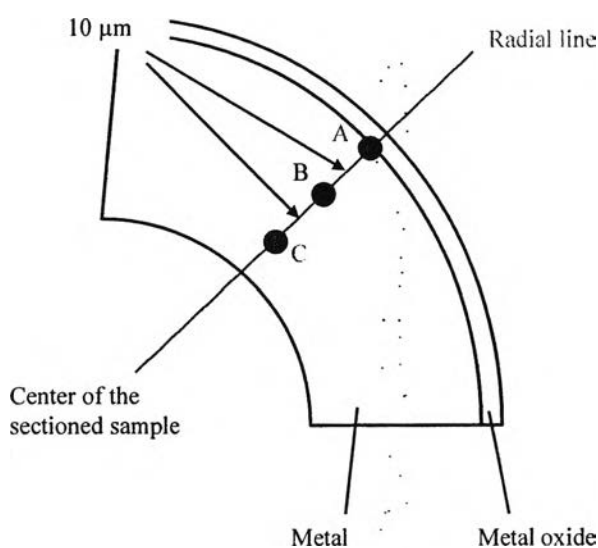


Figure 3.9 Magnified schematic of sectioned SG sample and locations of analyses.

3.3.3.2 SIMS Analysis

SIMS analysis was performed at Surface Science Western, University of Western Ontario. The SIMS analyses employed a Cameca IMS-3f ion microprobe using a Cs^+ beam and monitoring various negative secondary ions of interest, i.e. Fe, Ni, Cr, Ti, Zr, etc.

3.3.3.3 XPS Analysis

XPS analyses were also performed at Surface Science Western. The XPS depth profiles were done using a Kratos Axis Ultra X-ray photoelectron spectrometer. XPS can detect all elements except hydrogen and helium, probes the surface of the sample to a depth of 7-10 nanometers and has detection limits ranging from 0.1 to 0.5 atomic percent, depending on the element. XPS survey spectra were obtained from an area of approximately $300 \times 700 \mu\text{m}$ using a pass energy of 160 eV. A 4 kV argon ion beam (15 mA filament current,

sputter rate calculated at 1.2 nm/min based on an Al₂O₃/Al standard) was used for depth profiling. The depth profiles were allowed to run until the oxide layer was sputtered through and it appeared that the metal had been reached. To obtain chemical state information, high-resolution XPS analysis was employed. XPS high-resolution spectra were obtained from using a pass energy of 20 eV. The survey spectra and analysis area were the same as in the XPS depth profile analysis.

3.3.4 Test Matrix

The test matrix and simulated PWR primary coolant conditions are presented in Table 3.4. Run 0 was a commissioning run to see if the experimental setup was viable. It was found that with the coolant entering the cooling u-tube and passing through the autoclave, the heat from the heat sources (the Zircaloy-sheath heater and the jacket heater) was insufficient to maintain bulk temperature at 300°C as initially desired. A temperature of 295°C was achievable, however, and specified as bulk temperature in Run 1 and Run 2. Exposure time was 10 days for Runs 1 and 3 and 5 days for Run 2. As mentioned earlier, operating pressure must not exceed saturation pressure due to safety reasons. After Run 1, it was found that the oxides formed on samples were too thin for detailed analyses, so the exposure time was increased to 30 days for later runs to confirm that the oxide film was thick enough to analyse.

Table 3.4 Test matrix

Parameters	Run							
	Ti-2 Autoclave							
	With Heat Removal				Without Heat Removal			
	0	1	2	3	4	5	6	7
Supplied SG tubes								
- Alloy 600 ¹	-	MA	MA	TT	MA, TT	MA, TT	MA	MA
- Alloy 690 ²	-	-	-	-	MA, TT, CD	MA, TT, CD	-	-
- Alloy 800 ³	-	-	-	-	MA, SP	MA, SP	-	-
Coolant chemistry								
- pH _T	6.9	6.94	6.94	7.01	7.4	7.4	7.01	7.01
- [B] (ppm)	2000	2022	0	1989	1990	1993	1990	0
- [Li] (ppm)	4.89	4.89	0.27	4.89	12.92	12.92	4.89	0.28
- [Zn] (ppb)	0	0	0	0	0	20	0	0
- [H ₂] (cc/kg) nominal	18	18	18	18	18	18	18	18
Exposure time (days)	9	10	5	10	30	30	5	5
Measured Pressure (psi)	1030	1140	1140	1200	1200	1200	1200	1200
Bulk temperature (°C)	291	295	295	300	300	300	300	300

¹ Manufactured by Westinghouse, ² Manufactured by Valinox, ³ Unknown the manufacturer for MA and Manufactured by Sandvik for

SP

Table 3.4 Test matrix (Cont.)

Parameters	Run	
	SS Autoclave	
	Without Heat Removal	
	8	9
Supplied SG tubes		
- Alloy 600 ¹	MA, TT	MA, TT
- Alloy 690 ²	MA, TT, CD	MA, TT, CD
- Alloy 800 ³	MA, SP	MA, SP
Coolant chemistry		
- pH _T	7.4	7.39
- [B] (ppm)	1996	2008
- [Li] (ppm)	12.92	12.92
- [Zn] (ppb)	0	20
- [H ₂] (cc/kg) nominal	18	18
Exposure time (days)	30	30
Measured Pressure (psi)	1200	1200
Bulk temperature (°C)	300	300

¹ Manufactured by Westinghouse, ² Manufactured by Valinox, ³ Unknown the manufacturer for MA and Manufactured by Sandvik for SP