CHAPTER III
EXPERIMENTAL

3.1 Materials

The oxide films characterized were formed on four different types of steels, A-106B, Qinshan, 2.5%Cr/1.0%Mo steel and type 304stainless steel. The chemical compositions of steels are shown in Table 3.1

Table 3.1 Chemical Compositions of studied steels

Steel	C	Mn	Si	P	S	Cr	Ni	Mo
A106B	0.30	0.29	0.10	0.035	0.035	0.03	-	-
Qinshan	0.30	0.29	0.10	0.035	0.035	0.33	-	-
2.5%Cr 1.0%Mo Steel	0.30	0.29	0.10	0.035	0035	0.25	-	1.0
304SS	0.07	1.02	0.75	0.022	0.012	19.1	10.0	-

Tube probes as shown in Table 3.1, were fabricated from these steels. The oxide films were formed inside the tube probes under the conditions of 20 m/s coolant velocity and a pH of 10.5 measured at room temperature. The schematic diagram of simulated high temperature test loop is shown in the Figure 3.1.

This loop was designed to simulate the operating conditions of the primary coolant of a CANDU reactor. In the test loop, light water (H_2O) rather than heavy water (D_2O) was used as the testing solution. The pH of the water solution was adjusted to 10.5 measured at room temperature by adding 0.1 M LiOH solution. The water solution was pumped from the reservoir to an exchanger to raise the fluid temperature to 225°C in SS preheater. After the preheater, the coolant flows through an autoclave, with contains turnings of carbon steel at 265°C. At this point, the coolant is saturated with dissolved iron at 265°C, which correspond to the condition of inlet feeder pipes. The coolant then flows through the inert section, composed of Zirconium and nickel alloys to assure no addition iron is added to the coolant, while

it is heated to 310°C and subsequently, passes to the test section. The test section corresponds to the outlet feeder condition.

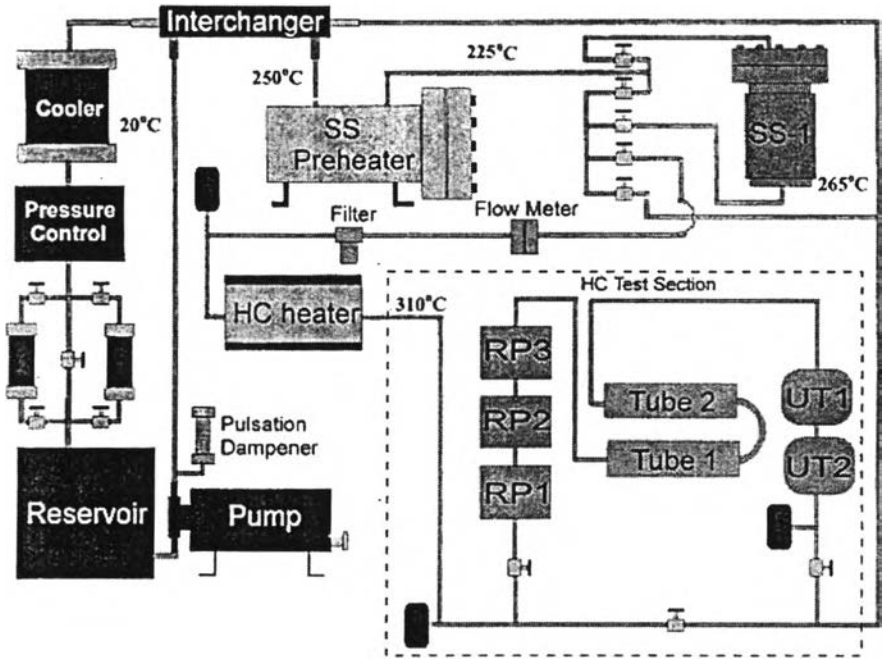

Figure 3.1 The schematic diagram of simulated primary coolant system of CANDU reactors (Supa-Amornkul, 2001).

In this work, the oxide films formed in the various tube probes were characterized by the surface analysis techniques and electrochemical techniques. All pre-filmed tube probes were cut into several pieces by using the saw method. The low speed cutting was applied to avoid the heat generation during cutting. The cut positions of each tube were marked to identify the places where the oxide films were probably destroyed. During surface characterization, the studied areas were not close to the marked positions.

For electrochemical measurements, all specimens were mechanically wrapped with two silver wires. The surrounding sides are coated with epoxy in order to expose a certain working area of oxide film to the water solution.

3.2 Equipment

Surface analysis was carried out in a JEOL-6400 SEM equipped with EDXA. The analyses were obtained with an EDXA Phoenix X-ray microanalyser with a Si (Li) detector and Genesis microanalysis software. The operating conditions for EDS X-ray analysis were 15kV and 1.5 nA with 50-60 s of spectral integration time. SEM images were collected with an accelerating voltage of 15 kV and beam current of approximately about 150 pA. The images were obtained with the dPict32 digital imaging from Geller Micro Analytical Lab. For cross-sectional characterization, TEM were carried out in JEOL 2010 STEM operated at 200 keV. The spectra were collected using an EDXA Genesis 4000 system. The specimens for TEM were prepared by the "Lift Out" technique, by polishing with ion-beam of gallium (Ga^+) until they reach the oxide film perforation (120-500 nm thick).

For electrochemical measurements, a typical electrochemical cell, containing coated specimens were the working electrodes. A Pt wire served as counter electrode and a Ag/AgCl electrode as a reference electrode. The electrochemical measurements were performed by using an EG&G Par 273A potentiostat. The potentiostat was controlled by CorrWare software. The IR drop, which resulted from the solution resistance, was compensated through the instrument. Electrochemical impedance spectra were obtained with Solartron 1255 Frequency Response Analyzer (FRA) system controlled by ZPlot software and fittings were formed with ZView software.

3.3 Methodology

For surface characterization, SEM and EDXA were used to study the morphology and composition of the outer oxide layer. SEM images were performed at × 50, 1,000 and 10,000 magnifications. The studied areas were randomly selected with several points for surface analysis to give statistical information on the oxide layer. EDXAs were carried out on the large particles and small particles as shown in the SEM images. In addition, the EDXA spectra were also conducted at the un-covered surfaces or metal surfaces. For TEM observations, the prepared specimens

allowed the investigation of the morphology of oxide films at different distances from interface. Moreover, electron diffraction pattern coupling with TEM were also conducted to reveal the microstructure of oxide films.

For the electrochemical measurements, the test solutions were prepared before conducting the electrochemical measurements. The pH level of the test solution was adjusted by adding 0.1M LiOH with distilled water until a 10.5 pH at room temperature was achieved. This simulates the water chemistry in the primary coolant of a CANDU reactor.

Polarization curve were measured with an EG&G Par 273A, which was connected to a separate counter, reference and working electrode. Potential was scanned in the positive or anodic direction at 0.5 mV s^{-1}. The impedance experiments were performed at a corrosion potential (E_{corr}) using Solartron 1255 FRA, applying ± 5 mV rms perturbation from 100,000 Hz down to 0.005 Hz. Experiment conditions were at room temperature (24° C) and normal pressure.