

## CHAPTER III EXPERIMENTS

### 3.1 Materials

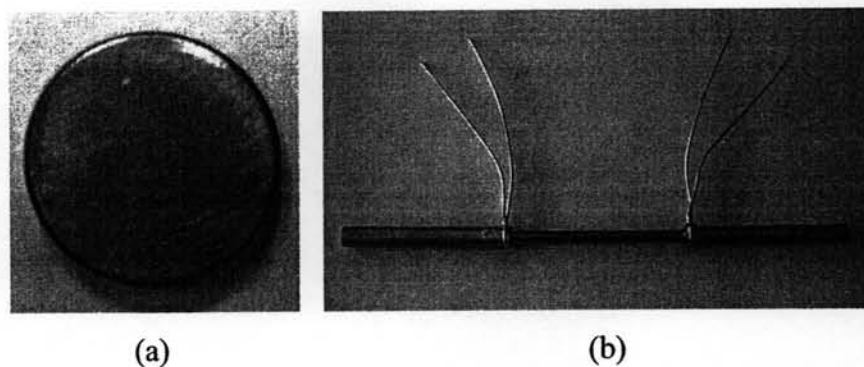
The oxide films were formed on carbon steel ASME SA106 Grade B under different coolant velocities and exposure times. The chemical composition of carbon steel ASME SA106 Grade B is shown in Table 3.1.

**Table 3.1** Chemical composition of carbon steel ASME SA106 Grade B

Element	Mass fraction (%)
Fe	99.20
C	0.30
Mn	0.29
Si	0.10
P	0.04
S	0.04
Cr	0.03
Total	100.00

There were two sets of experiments conducted. One is referred to as the static experiment (no flow or 0 m/s coolant velocity) and the other is referred to as the flow experiment (5 m/s coolant velocity). Each set of experiments was conducted with different exposure times.

Two shapes of carbon steel samples were used for this work – coupons and tube probes as shown in Figure 3.1. The coupons (Figure 3.1a) – 10 mm diameter x 1 mm thick and 16 mm diameter x 5 mm thick – were used as the samples for static experiment while the tube probes (Figure 3.1b), 2 mm inside diameter, were used as the samples for flow experiment.

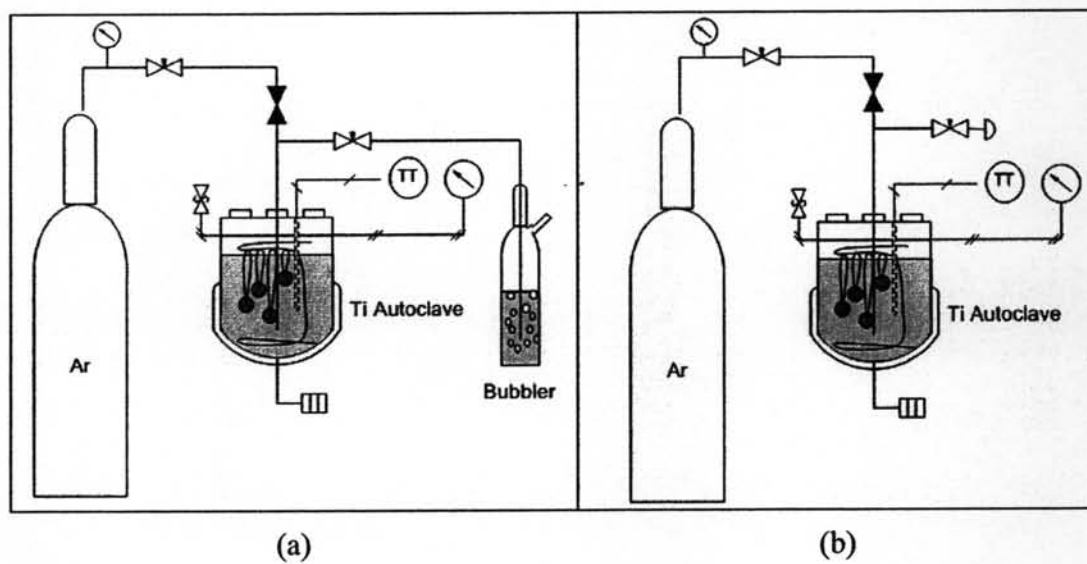


**Figure 3.1** Carbon steel samples used in the experiment (a) coupon sample for static experiment (b) tube probe sample for flow experiment.

## 3.2 Equipment

### 3.2.1 Sample Filming

#### 3.2.1.1 Static Experiments

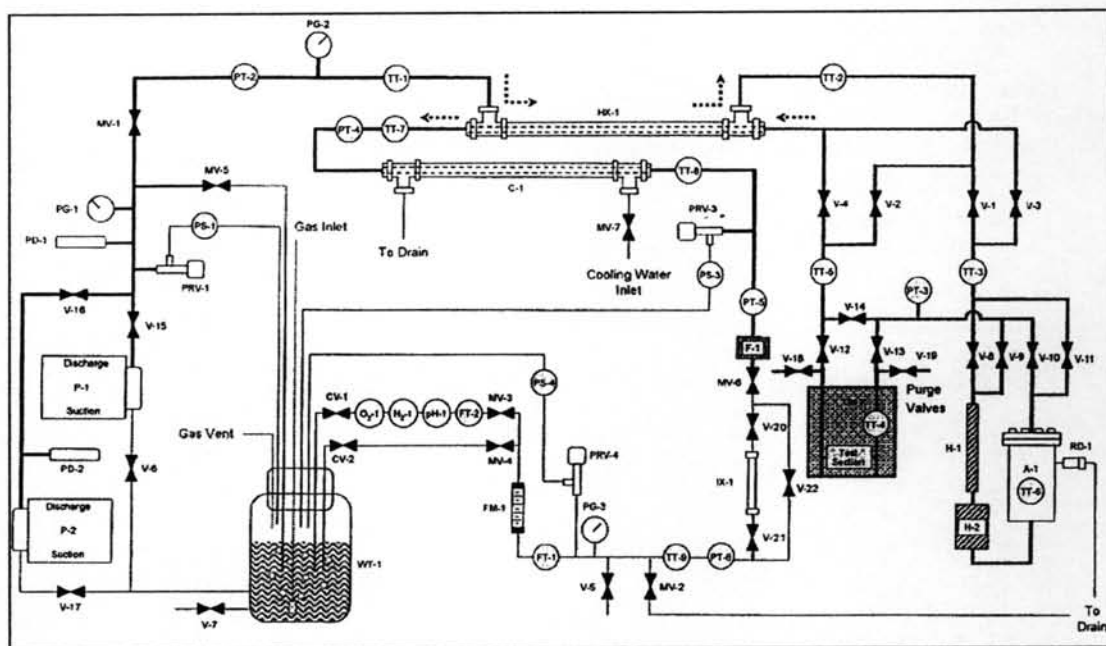


**Figure 3.2** Schematic diagram for static experiments (a) purging Ar mode and (b) filming mode.

The static experiment were performed in a titanium autoclave under the conditions of 0 m/s coolant velocity at 305 °C and 9.9 pH of solution (measured at room temperature). Figure 3.2 shows the schematic diagram of the static experiment. In order to minimize the concentration of oxygen in both the solution and the atmosphere, the purgr Ar mode (Figure 3.2a) was set before switching to the run mode (Figure 3.2b).

### 3.2.1.2 Flow Experiments

The CNER Test Loop 1, Figure 3.3, was used to conduct the flow experiments. Under the conditions of 5 m/s coolant velocity at 300 °C and 9.9 pH of solution (measured at room temperature) the samples were placed in the test section of the loop. The loop was purged with Ar before starting to film the probes, in order to minimize the concentration of oxygen in both the solution and the atmosphere.



**Figure 3.3** Schematic diagram of the CNER Test Loop 1 for flow experiments.

### 3.2.2 Sample Characterization

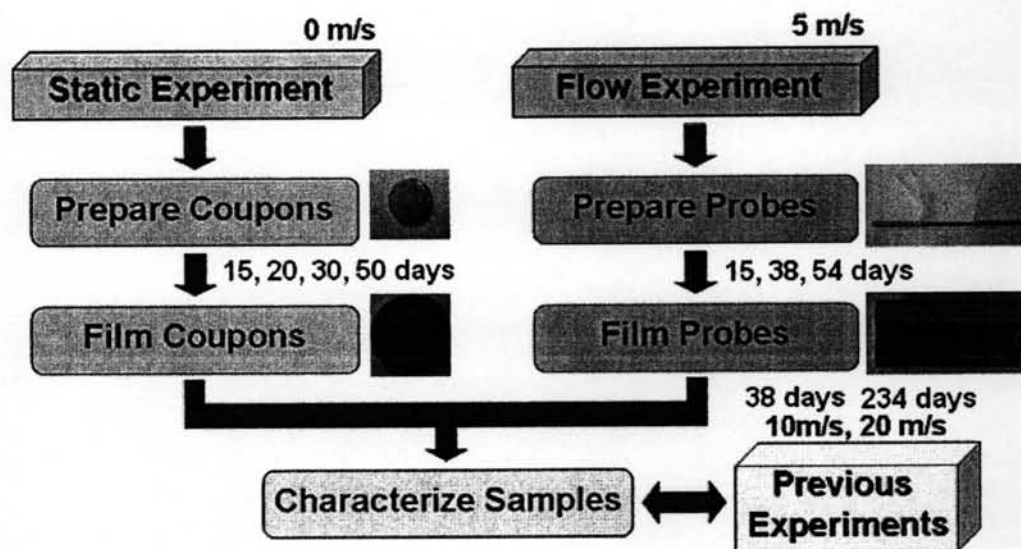
For the characterization of samples, there were two equipments. Firstly, a Scanning Electron Microscope was used for investigating the surface morphology, the cross-sectional morphology and the coupled with EDXA microanalyzer for determining the chemical composition of surface. Secondly, a Raman Microscope was used for identifying the chemical structure of oxide films.

SEM analysis was carried out in a JEOL-6400 SEM equipped with EDAX. The analyses were obtained with an EDAX 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 the beam current was approximately about 150 pA. The images were obtained with the dPict32 digital imaging from Geller Micro Analytical Lab.

Raman Spectroscopy was conducted in a Renishaw's inVia Raman Microscopes (Model inVia). The operating conditons were 100 – 240 volts(AC) or 50/60 hertz and power 150 watts.

### 3.3 Methodology

The summarized methodology is shown in Figure 3.4. There were three main parts – static experiments, flow experiments and characterization of samples.



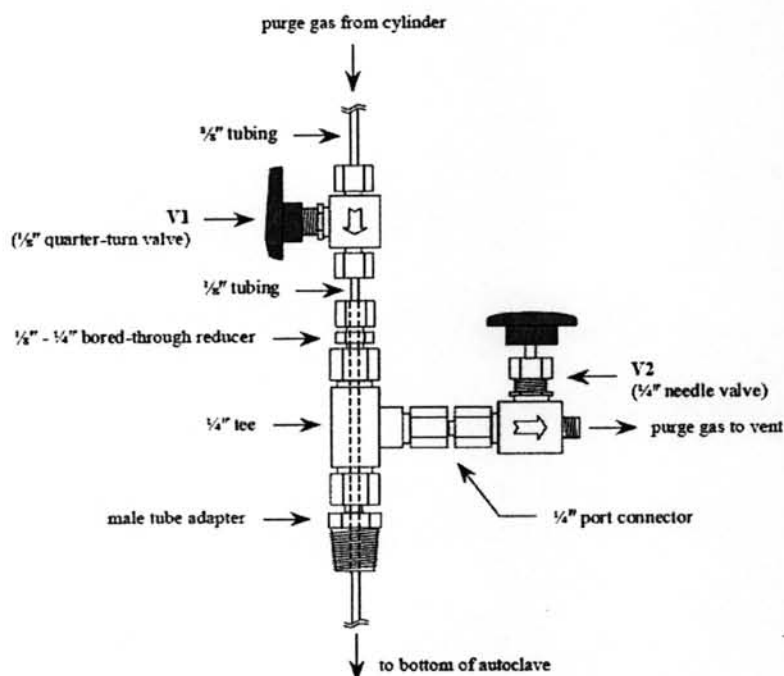
**Figure 3.4** The summarized methodology for experiments.

#### 3.3.1 Static Experiment

Before filming a coupon, all coupons and instruments should be prepared. First, all instruments used in this experiment was verified that they have a valid calibration. For coupons, first they were identified by using a metal punch and a hammer , mark on one side of each coupon with a unique pattern of dots. All identified coupons were degreased with acetone and wet ground by using 240 grit SiC paper followed by 600 grit SiC paper. Then the coupons were cleaned with distilled water and dried immediately with hot dry air. Finally, coupons were stored in an inert gas desiccator before filming.

The pH of the solution was adjusted to 9.9 by using LiOH solution. The 0.1 M LiOH was prepared and slowly added to deionized water to obtain the desired pH.

For an autoclave, all bolts used to seal the autoclave were clean by an ultrasonic cleaner to remove old lubricant dirt. After cleaning the argon purge/vent assembly (Figure 3.5) was installed in the autoclave head. The remaining ports of the autoclave were plugged. After the autoclave was prepared, the coupons were loaded to the holder (coupons should not touch other coupons, the holder, or the side of the autoclave). The holder was finally placed inside an autoclave.

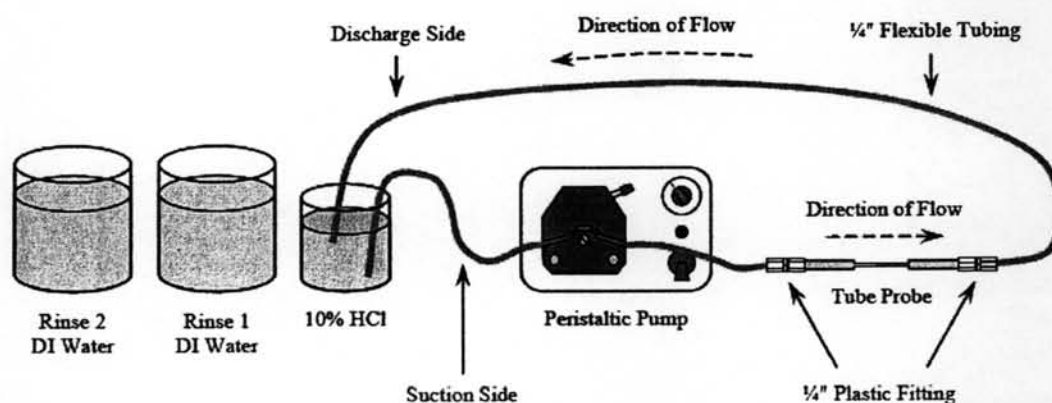


**Figure 3.5** Detail of purge/vent assembly.

The autoclave was filled with 600 ml prepared solution and sealed by using a torque wrench. A K-type thermocouple was inserted into the thermocouple well of the autoclave head. The coupons were purged with Ar for at least 48 hours. Finally, the system was heated to 305 °C and all coupons were filmed for the desired exposure time.

### 3.3.2 Flow Experiment

The tube probes were prepared by acid cleaning inside of the probes. The equipment was set as shown in Figure 3.6. The solution used was 10% HCl (v/v) solution. Acid was circulated through the probe for 5 minutes. Then deionized water (first rinse) was circulated through the probe for at least 5 minutes following by the second rinse of deionized water for at least 5 minutes. The probe was flushed with methanol, then acetone and was blown dry with argon. Finally, all probes were stored in an inert gas desiccator before filming.



**Figure 3.6** Schematic of the experimental setup for acid cleaning.

In order to put the probes in the test section of the loop, the probes were assembled as shown in Figure 3.7. Two probes were filmed at the same time, so they were connected to each other following the probe configuration as shown in Figure 3.8. The probes configuration consisted of two assembled probes, with isolation valves at the outlet ends of the probes, and a reference electrode. Finally the probes were filmed in the loop for the desired exposure time. The loop filming parameters are shown in Table 3.2.

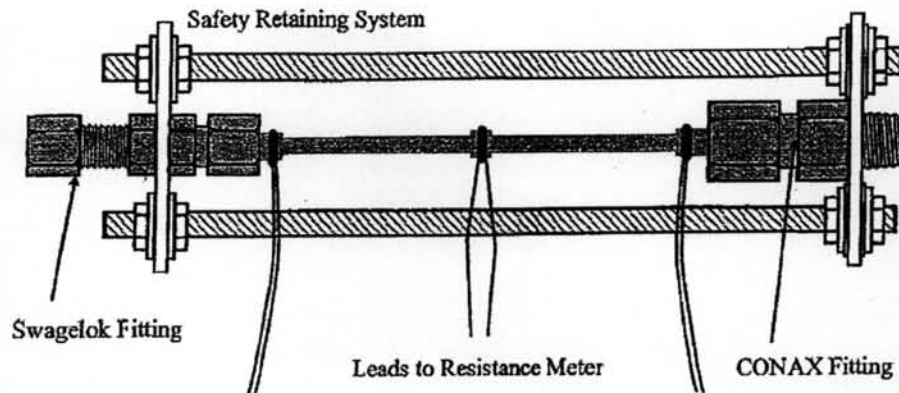


Figure 3.7 Schematic of the assembled probe.

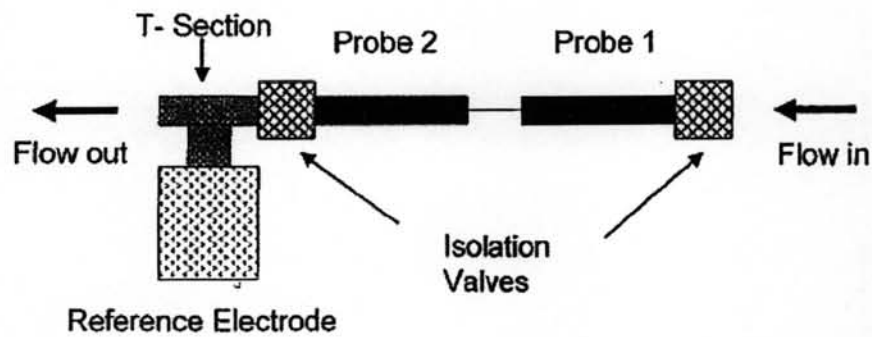


Figure 3.8 Probe configuration.

Table 3.2 Loop filming parameters

Parameter	Value	Allowable Deviation
Oxygen	< 1 ppb	+1 ppb
Hydrogen	3 – 10 cm <sup>3</sup> /kg	6.5 +/- 3.5 cm <sup>3</sup> /kg
pH	9.9	+/-0.15
Chlorides	< detectable	-
Flow Rate	840 ml/min	+/- 100 ml/min
Temperature	300 °c	+/- 3 °c
Pressure	1500 psi*	+/- 50 psi

\* Note: Loop pressure must be maintained at a level that prevents flashing



### 3.2.3 Sample Characterization

The filmed coupons can be directly analyzed whereas the filmed probes need to cut before characterization of the oxide films formed inside the tube probes. After the cut probes were prepared, visual inspection was used to obtain the visual image and color of all samples.

For the SEM technique, the SEM surface micrograph and EDX analysis were performed on the filmed coupons and the cut filmed probes. However, the SEM cross-sectional microscopy required a thin sample. Hence, all samples were prepared by thin-sectioning (Appendix A). The thinned samples were used to characterize their cross-sectional micrograph by using the SEM technique.

Raman Spectroscopy is a non-destructive technique, so all samples can be analyzed by this technique without any sample preparation requirement. However, this technique can change the phase of samples because of the laser beam focused on surface. Therefore, the samples were characterized by this technique after other characterization techniques were completed.