CHAPTER III

EXPERIMENTAL

This chapter describes the experimental set-up for hydrogen permeation through the bare and palladium-filmed carbon steel tube. Details of the steps required to assemble and operate an apparatus for hydrogen permeation testing are provided. The materials and chemicals, equipments and experimental procedure are also outlined.

The summarized procedure is shown in Figure 3.1. There are two main parts– hydrogen permeation experiments using as received metal tubes with surface and kinetic barriers to determine hydrogen mass transfer by oxide films on outside surface, using the coated metal tubes by palladium films to eliminate surface resistances. Characterization of the palladium filmed on the tube was also performed using an FESEM along with EDX technique.

3.1 Procedure for Hydrogen Permeation through Metal Tube Membrane

This procedure explains the steps to assemble and operate the apparatus while charging with hydrogen gas. Hydrogen is used to determine the membrane permeability at an initial pressure of 790 kPa (100 psig) at room temperature. The membrane will be coated with Palladium (Pd) to compare the diffusion rate with and without the presence of Pd on the membrane.

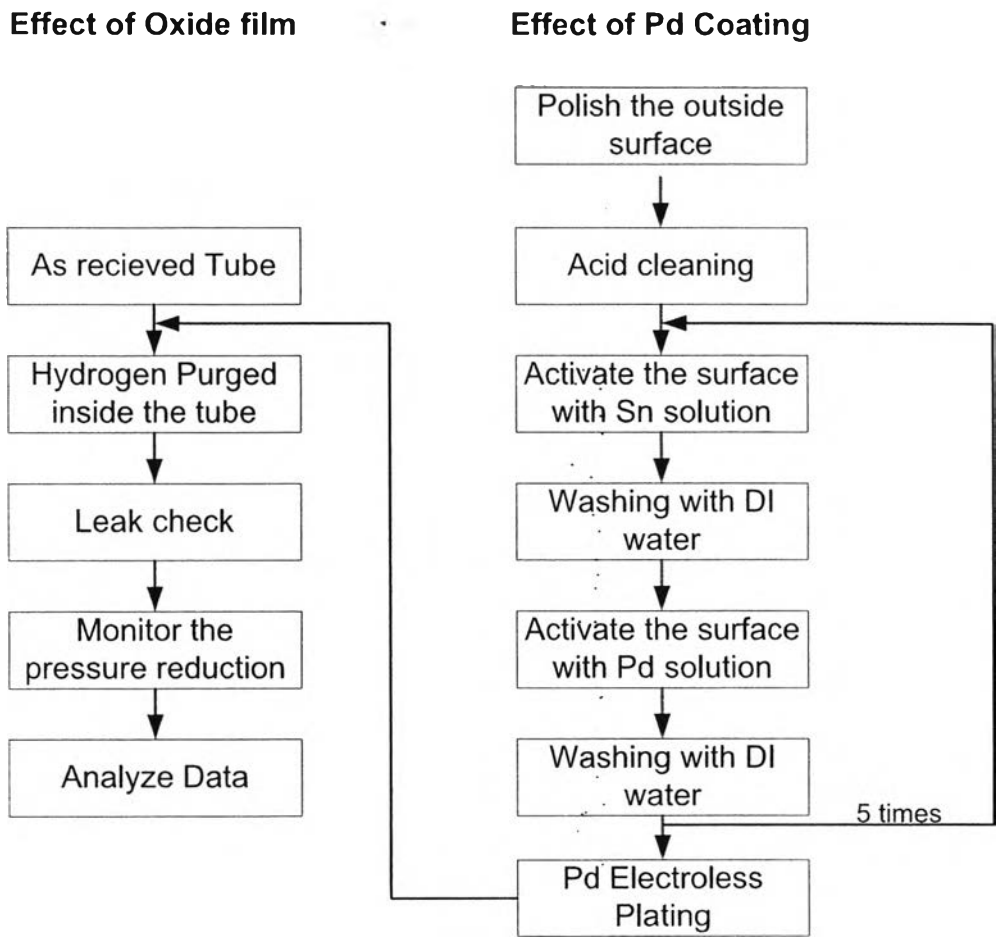

Figure 3.1 The summarized procedure for the experiments.

3.1.1 Material Required

1) Hydrogen gas cylinder (UHP Hydrogen) with regulator
2) Carbon steel tube ASTM A-179 and Hastelloy C-276
3) Furnace
4) Pressure transducer
5) Thermocouple

3.1.2 Test Specimen

The tube specimen which has 0.00635 m OD and 0.00089 m of wall thickness will be cut in 0.945 m of length. The tube was bent as illustrated schematically in Figure 3.2. Fittings are designed to be outside the heating zone to

prevent the hydrogen diffusion at fittings. The specimen was assembled in the test section containing the pressure transducer and valve as shown in Figure 3.3. The decrease in pressure inside the tube was monitored by using pressure transducer. Three thermocouples were installed on the tube surface at different positions as demonstrated in Figure 3.4. The specimen was installed in the oven. The diffusion area is the only the section in the furnace.

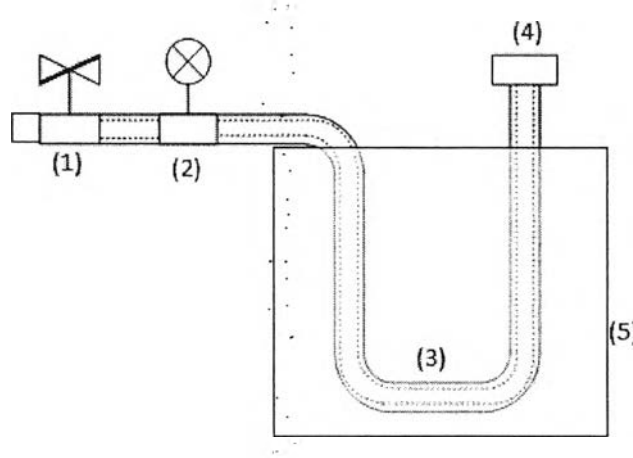

Figure 3.2 Experimental apparatus schematic: (1) System valve, (2) Pressure Transducer, (3) U Shape tube specimen, (4) End cap, and (5) Oven.

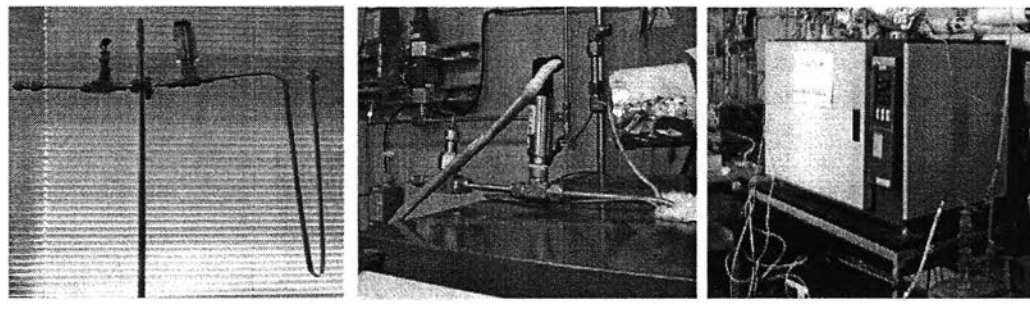

Figure 3.3 A test apparatus.

3.1.3 Steps for oxide film removal inside the tube

Before starting each run with the tube specimen, purging the system at 325°C should be done in order for an oxide film removal inside the tube. The testing apparatus was attached to hydrogen gas cylinder's regulator. Another end of the testing apparatus was connected to the flow meter. The hydrogen flow rate is 7.7

ml/min, which can be read from the rotameter scale at the scale of 20. These purging is done for 5 days. After 5 days, the system was cooled down to room temperature while hydrogen is flowing along the tube to prevent air entering into the system. The purging system is disconnected after five days.

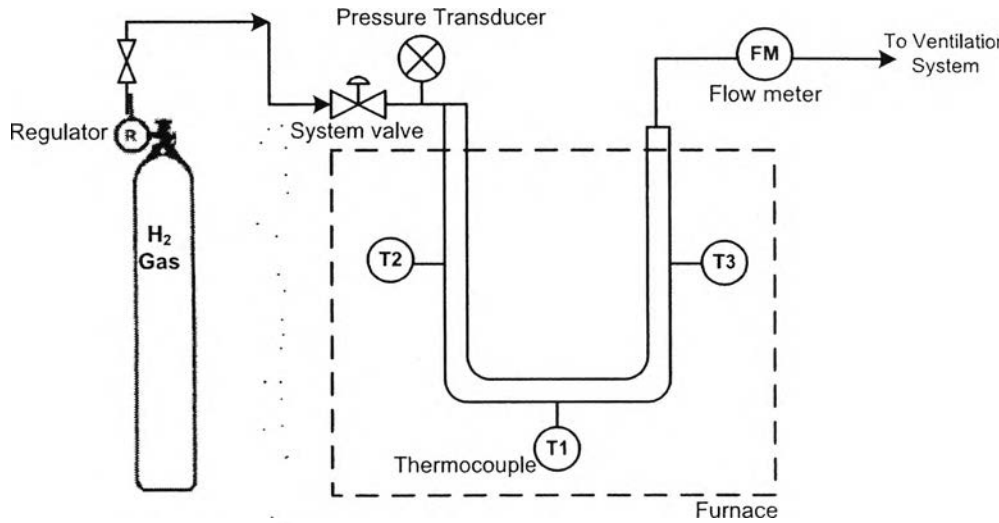

Figure 3.4 The schematic of the purging system.

3.1.4 Steps for measuring hydrogen permeation

After purging, hydrogen is charged into the system at the pressure of 790 kPa (100 psig) at room temperature. The entire system is leak checked by measuring the hydrogen pressure drop at room temperature. The apparatus is left for 2 days to determine if a pressure change occurs. The acceptable change in pressure is ±2 psig. The starting time, temperature and initial pressure are recorded.

3.2 Procedure for Electroless Palladium Plating on Steel Tube

Electroless plating is commonly used to deposit palladium films because of its coverage of surfaces, ease of implementation, and the ability to deposit on noncatalytic surfaces (Marcel Dekker, 2009). First, if the surface is nonconducting or noncatalytic for electroless deposition, it must be well activated to promote coverage

and good adhesion of the deposit. Electroless plating occurs through an auto catalytic reaction mechanism that is initiated by an activated surface. The substrate is activated prior to the plating operation by seeding the surface with metal crystallites (usually gold, silver, platinum or palladium). This is required to initiate plating and ensure adherence of the film. The metal nucleation sites initiate the electroless plating reaction by catalyzing the decomposition of a reducing agent in the plating bath. Electroless plating is performed by immersion in a plating bath containing the appropriate constituents at the optimum temperature and concentrations to produce the desired microstructure and plating rate. The plating rate and film morphology depend on many variables such as concentration of bath constituents and plating temperature.

Palladium film structure has been linked to limitation in high temperature stability, resistance to thermal cycling, and minimization of the defect-free film thickness. To obtain uniform deposition during electroless plating the solution should be mildly agitated to remove bubbles that form and obstruct deposition, creating pores.

This procedure is to illustrate the process of electroless palladium plating including preconditioning and activation of the noncatalytic specimen like carbon steels. The required steps to carry out electroless plating on the outside surface of the metal specimen are described.

3.2.1 Material and Reagents Required

1) Heating plate
2) Plating bath
3) Thermometer
4) Hydrochloric acid reagent grade 36.5-38%
5) Acetone reagent grade
6) Stannous Chloride reagent grade 98%
7) Palladium(II) Chloride reagent grade 99.9%
8) Ammonium Hydroxide reagent grade 28.0-30.0%
9) Ammonium Chloride
10) Sodium Hypophosphite hydrate

3.2.2 Solution preparation

The specimen of testing steel with a defined geometry was cleaned. Before depositing, the specimens were preseeded by dipping in two activation solutions of Sn^{2+} and Pd^{2+}, with the compositions reported in Table 3.1.

Table 3.1 Activation Solutions

Compositions of activation solutions		
Stannous Chloride solution		
$SnCl_2 \cdot 2H_2O$	10	g/L
HCl (37%)	40	ml/L
Palladium salt solution		
$PdCl_2$	1	g/L
HCl (37%)	10	ml/L

Electroless bath compositions are listed in Table 3.2, containing palladium salt, Ammonium Chloride, Sodium Hypophosphite as major components.

Table 3.2 Plating Solutions

Composition of electroless plating bath		
$PdCl_2$	2	g/L
HCl (37%)	4	ml/L
NH_4OH (28%)	160	ml/L
NH_4Cl	27	g/L
$NaH_2PO_2 \cdot H_2O$	10	g/L

3.2.3 Steps for Palladium Plating

The specimen has a U shape. The end caps should be ensured that they are all completely closed. The part of the specimen outside the oven is covered with Teflon tape so that only the specimen in the oven is plated.

The specimen should be cleaned before testing. These steps are to prepare the surface to ensure good adhesion of the electroless plating on the outside

surface. Firstly, the specimen is cleaned by polishing the outside surface of the specimen with 600 grit sandpaper followed by rinsing it with DI water. The specimen is then chemically cleaned by 10%HCl (v/v) at the temperature of 30°C for 5 minutes. It is then rinsed with DI water and immersed in organic solvent. Finally, it is blown dry with Argon.

Surface preconditioning and activation are regarded for a noncatalytic surface such as carbon steel. These steps are required for activation by generating catalytic nuclei on the tube surfaces. The specimen is immersed in Stannous Chloride solution in a 14''x 12'' glass dish for 5 minutes. Then, it is rinsed with DI water. The specimen is then exposed to Palladium Chloride solution in 14''x 12'' glass dish for 5 minutes. It is then rinsed with DI water. This immersion is repeated 5 times. The final step for activation is that the specimen is blown dry with Argon gas.

The electroless plating is carried out in 14''x 12'' glass dish with plating solution which has been prepared. The temperature of the plating bath is kept constant at 50°C. The immersion time of tube specimen is 30 minutes. After immersion, the specimen is removed and then rinsed with DI water. The last step is rinsing the specimen with acetone and drying with Argon gas.

The plating rate and film morphology depend on many variables such as concentration of bath constituents and plating temperature, understanding the fundamentals of electroless plating is the key to optimizing the conditions for producing usable palladium and palladium alloy films on various support.

3.3 Test Matrix

The tested materials and test conditions are presented in Table 3.3. Test no. 1 and 6 was initially performed to find the lowest temperature of hydrogen permeation through carbon steel and hastelloy respectively. The minimum temperature found from the initial test was selected to test as the low temperature of permeation. In case of high permeation temperature test, the temperature was increased in 100°C increment. A temperature of 250°C was chosen as a high temperature permeation test for carbon steel and 335°C for hastelloy. The 335°C was selected because the oven limitation.

Table 3.3 Test Matrix

Parameters	**Test no.**									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Temperature (°C)	MTL	150	250	150	250	MTL	250	335	250	335
Surface preparation	AR	AR	AR	Pd	Pd	AR	AR	AR	Pd	Pd
Steel	CS	CS	CS	CS	CS	HL	HL	HL	HL	HL

*MTL– Minimum Temperature Limit

**AR– As received material

***Pd– Palladium coated