

CHAPTER III

EXPERIMENTAL

General Information

1. Instruments & Equipments

- Vacuum Emission Spectrometer; Shimadzu QC-6, Japan
- Scanning Electron Microscope; JEOL, JSM - 35CF, Japan
- Inductive Couple Plasma Emission Spectrometer; Varian, Liberty 220, Australia
- Oil bath; Memmert, 0-350, W-Germany
- Sater bath; Memert, W-350, W-Germany
- Microsyringe; size 10 ul, 100 ul; HAMILTION, Switzerland
- Refrigerator; Whirlpool, CN-293, U.S.A
- Cooling bath; Eyela CA-111, Japan
- Analytical Balance; Sartorius BA210S, W-Germany
- Grinding machine; Kent, U.S.A
- Cutting machine; Kent, W-Germany
- Drilling machine; Kira, Japan

2. Chemicals and Solvents

Petroleum ether (bp.80°C-100°C)	MERCK
Absolute methanol	J.T.Baker
Conc. hydrochloric acid	BDM
Dimethylmercury	FLUKA AG, PURISS
Conc. phosphoric acid	CARLO ERBA
Chromic acid	AJAX CHEMICALS

Stannous chloride	CARLO ERBA
Antimony trioxide	J.T. Baker
Ether	T.T. Baker
1,4 Dioxane	MERCK
Dimethyl sulfoxide (DMSO)	MERCK
Trichloroethylene	AJAX CHEMICALS
Isopropyl alcohol	AJAX CHEMICALS
Benzene	MERCK
Conc. sulphuric acid	BDH
Sodium sulfide	MERCK
Distilled water	

3. Materials for Specimens

- Commercial carbon steel bar for making of window obstacle
- Commercial aluminium bar for architectural works

Specimen Preparation

1. Initial Preparation

One 1-metre commercial carbon steel bar with 15 mm x 3 mm cross-section area was wet ground its surface coarsely by grinder machinery to eliminate a substantial layer of metal oxide until its cross-sectional area became about 11.2 mm x 2.75 mm and the surface was cleaned. It was then cut by cutting machine to make short strips with 25 mm long. These strip coupons were drilled for a hole for mounting with 3.5 mm in diameter near one end. Finally, the size of strip coupons was 11.2 mm x 25 mm x 2.75 mm and the holes were 3.5 mm. However, this was nominal size. Therefore, before immersing in corrosive solution, each of specimen was measured its dimensions precisely and recorded for calculation of corrosion rate.

For preparation of aluminium coupons, the long commercial aluminium bar with 25 mm x 3.2 mm cross-sectional area was sawn to split into half and cut into short strip with 25 mm long. These strip coupons were drilled for a mounting hole with 5 mm in diameter near one end and ground coarsely with abrasive paper No.50. The size of specimen became about 12.3 mm x 25 mm 3.0 mm and the holes were 5.0 mm. A few of these strip coupons were chosen to be samples for analysing compositions by the vacuum spectrometer shown in Figure 3.1. The compositions would support analysing the corrosion results in the later section..

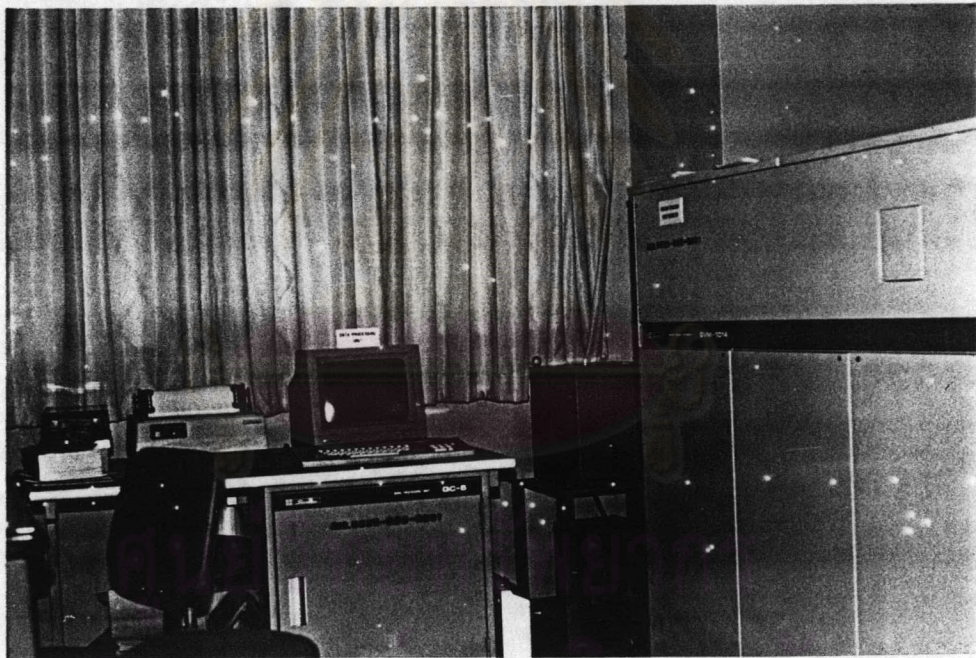


Figure 3.1 The vacuum spectrometer

2. Final Surface Treatment

Both kinds of strip coupons, carbon steel(CS) and aluminium, were wet rubbed by the No.120 abrasive paper until surface of coupons was cleaned and smooth from visual check. Up to this step, the size of CS coupons became

11.15 mm x 25 mm x 2.75 mm, and that of aluminium coupons became 12.0 mm x 24 mm x 2.9 mm. All of strip coupons were subsequently stamped figures on left hand side upper surface near the hole.

3. Measuring and Weighing

The stamped-figure coupons were measured dimensions and recorded together with corresponding figure stamped on coupon surface. After measuring, these strip coupons were degreased by scrubbing with the bleach-free scouring powder, followed by rinsing with distilled water and a mixture of 1 : 1 methanol : ether, and finally dried with air. However, for the aluminium coupons, they should be scrubbed by the powder softly.

The dried strip coupons were weighed on the analytical balance and recorded the certain weight of each one with an accuracy of 0.0001 g. Specimens were then kept inside dessicator at least 1 h before immersion in corrosive solution.

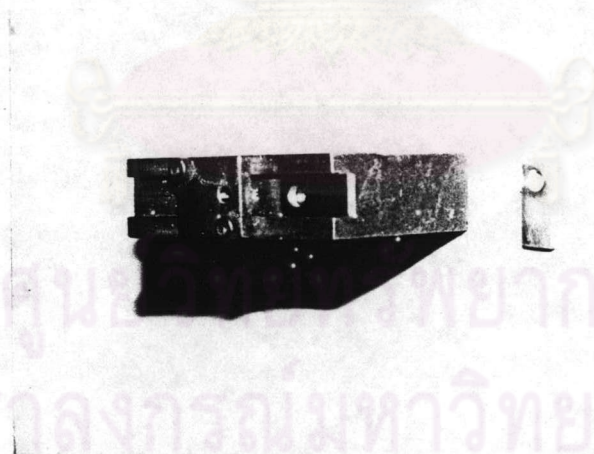


Figure 3.2 The finished test specimen

Preparation of Corrosive Solution

Solvents selected to dissolve corrosive media, DMM, are absolute methanol and petroleum ether with boiling point of 80°C-100°C. Both of solvents can dissolve DMM very well. The minimum solution volume-to-specimen area ratio was 20 ml/cm² of specimen surface, as recommended in

ASTM Standard A G31-72. In this test the used volume of corrosive solution must therefore be 150 ml for each of the exposure test.

1. Preparation of the CH₃OH-DMM and PE-DMM Solutions

An exact 150 ml of either CH₃OH or PE, which was used as solvent, was poured into the 150 ml volumetric flask, followed by 10- μ l microsyringe of the certain amount of DMM. Various concentrations of DMM and their corresponding amounts were as follows :

Table 3.1 Various concentration of DMM dissolved in either CH₃OH or PE

Concentration of DMM (ppm)	Certain amount (μ l)
50	2.5
100	5.1
150	7.6
200	10.1
250	12.7

The prepared solution in a volumetric flask was transferred to 250 ml Erlenmayer flask which was then closed by stopper to keep as a close system

2. Preparation of the CH₃OH/PE/H₂O+150 ppm HCl Solutions

Either H₂O or CH₃OH or PE in exact amount of 150 ml was poured into the 150 ml volumetric flask. Then 53.9 μ l(150 ppm) of conc. hydrochloric acid was discharged into the flask. In case of the PE+HCl 150 ppm solution, the volumetric flask must be shaken for a long period of time because HCl has low solubility in PE. The mixture was transferred to a 250 ml Erlenmayer

flasks which was closed by a stopper. These reaction flasks were ready to immerse in a temperature controlled bath.

3. Preparation of the CH₃OH/PE+150 ppm HCl+DMM Solutions

150 ml of CH₃OH or PE was added into a flask containing 53.9 ul (150 ppm) of conc. hydrochloric acid A certain amount of DMM, as listed in the table below, was discharged into the flask, and the mixture was shaken to obtained a homhogeneous solution.

Table 3.2 Various DMM solutions in the presence of 150 ppm HCl

Various 150 ml corrosive solutions	Amounts of each component		
	CH ₃ OH/PE	conc. HCl	DMM
The CH ₃ OH/PE+HCl 150 ppm+DMM 50 ppm solution	150 ml	53.9 ul	2.5 ul
The CH ₃ OH/PE+HCl 150 ppm+DMM 100 ppm solution	150 ml	53.9 ul	5.1 ul
The CH ₃ OH/PE+HCl 150 ppm+DMM 150 ppm solution	150 ml	53.9 ul	7.6 ul
The CH ₃ OH/PE+HCl 150 ppm+DMM 200 ppm solution	150 ml	53.9 ul	10.1 ul
The CH ₃ OH/PE+HCl 150 ppm+DMM 250 ppm solution	150 ml	53.9 ul	12.7 ul

The solution was transferred into a 250 ml Erlenmayer flask which was then closed by stopper.

In the preparation of the corrosive solution with concentration of DMM and HCl lower than 150 ppm, such as 0.015 ppm, 0.15 ppm, 1.5 ppm and 15 ppm, the amounts of conc. HCl and DMM were used as listed in the following table.

Table 3.3 Various DMM and HCl solutions with either CH₃OH or PE as solvents

Various 150 ml corrosive solutions	Amounts of each component		
	CH ₃ OH/PE	conc. HCl	DMM
CH ₃ OH/PE+HCl 15 ppm+DMM 15 ppm solution	150 ml	5.4 ul	0.76 ul
CH ₃ OH/PE+HCl 1.5 ppm+DMM 1.5 ppm solution	150 ml	0.54 ul	1.5 ml from CH ₃ OH/PE +DMM 150 ppm sol ⁿ
CH ₃ OH/PE+HCl 0.15 ppm+DMM 0.15 ppm solution	150 ml	150 ul from CH ₃ OH/PE + HCl 150 ppm sol ⁿ	150 ul from CH ₃ OH/PE +DMM 150 ppm sol ⁿ
CH ₃ OH/PE+HCl 0.015 ppm+DMM 0.015 ppm solution	150 ml	150 ul from CH ₃ OH/PE + HCl 15 ppm sol ⁿ	150 ul from CH ₃ OH/PE + DMM 15 ppm sol ⁿ

4. Preparation of the PE 100 ml+DMM 200 ppm+H₂O 50 ml+HCl 150 ppm Solution

10.1 ul of DMM was dissolved in 100 ml of PE and 53.9 ul of con. HCl was dissolved in 50 ml of distilled H₂O. After that, both solutions were mixed together in the 250-ml Erlenmeyer flask.

5. Preparation of the CH₃OH/PE/H₂O+saturated H₂S Solutions

150 ml of CH₃OH or H₂O or PE was poured into a 250 ml Erlenmeyer flask which was then equipped with the discharge pipe of the apparatus for H₂S-gas preparation shown in Fig 3.3. Concentrated H₂SO₄ was

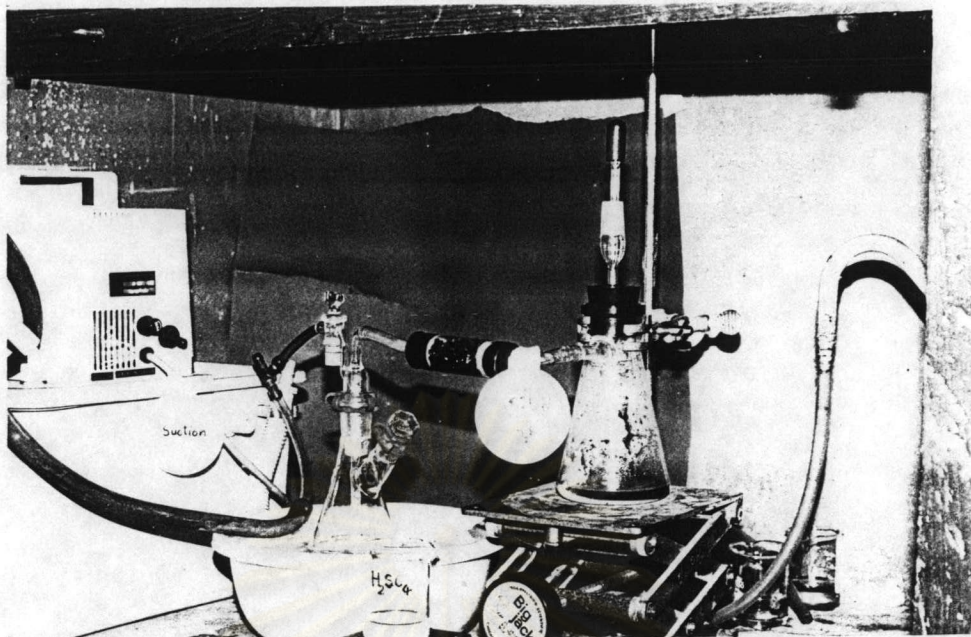


Figure 3.3 The apparatus for H₂S gas preparation

dropped on Na₂S powder contained in a conical flask. H₂S gas immediately evolved and flowed through pipe which its end was immersed under solvent in Erlenmeyer flask. The gas product was then left to dissolve in the solvent for a long period of time at a constant temperature, 20°C (more than 1 h). The H₂S mixture was added with desirable amount of DMM. Various corrosive solutions associated with H₂S are, as follow ;

- 1) 150 ml CH₃OH+saturated H₂S
- 2) 150 ml CH₃OH+saturated H₂S+200 ppm DMM
- 3) 150 ml PE+saturated H₂S+300 ppm H₂O+200 ppm DMM
- 4) 150 ml PE+saturated H₂S+H₂O 300 ppm
- 5) 150 ml PE+200 ppm DMM+100 ml H₂O saturated-with-H₂S

The above corrosive solution(No.5) was prepared by dissolving H₂S into 100 ml of distilled H₂O first, the H₂S saturated H₂O solution was then mixed with the 150 ml PE 150 ml+200 ppm DMM. At 20°C,413.2 mg of H₂S is soluble in 100 ml H₂O[21].

6) 140 ml PE+300 pmm H₂O+200 ppm DMM+Ether saturated with H₂S

The solution was also prepared first by dissolving H₂S into 10 ml of ether at 20°C until it was saturated, then the mixture was added into the 140 ml PE+300 ppm H₂O+200 ppm DMM solution.

- 7) 150 ml CH₃OH+200 ppm DMM+300 ppm H₂S solution

In this case, first the H₂S saturated CH₃OH was prepared by dissolving H₂S into certain amount of CH₃OH at 20°C until it was saturated. Solubility of H₂S in CH₃OH was calculated by use of solubility data in ref.[22], stating that one gram of H₂S can dissolve in 94.3 ml of alcohol at 20°C. 300 ppm of the H₂S/CH₃OH solution was finally added into the CH₃OH+200 ppm DMM solution

6. Preparation of the Hg-Saturated-in-Cyclohexane Solution

Since the solubility of Hg is about 3 ppm or 12.1×10^{-6} mole/l[23], solution of Hg in cyclohexane was thus prepared by weighing 5 mg. of Hg and adding into a 1-liter cyclohexane flask. The flask was shaken for 24 h. to obtained the desirable Hg-solution.

Procedure

Specimens were removed from a dessicator and fasten through the hole with short cotton staples. One pair of specimens, which were stamped the corresponding figure on surface, such as 1, 1⁻, 2, 2⁻, 3, 3⁻ and so on, were immersed in a small reaction flask. One reaction flask completely prepared was shown in Fig 3.4

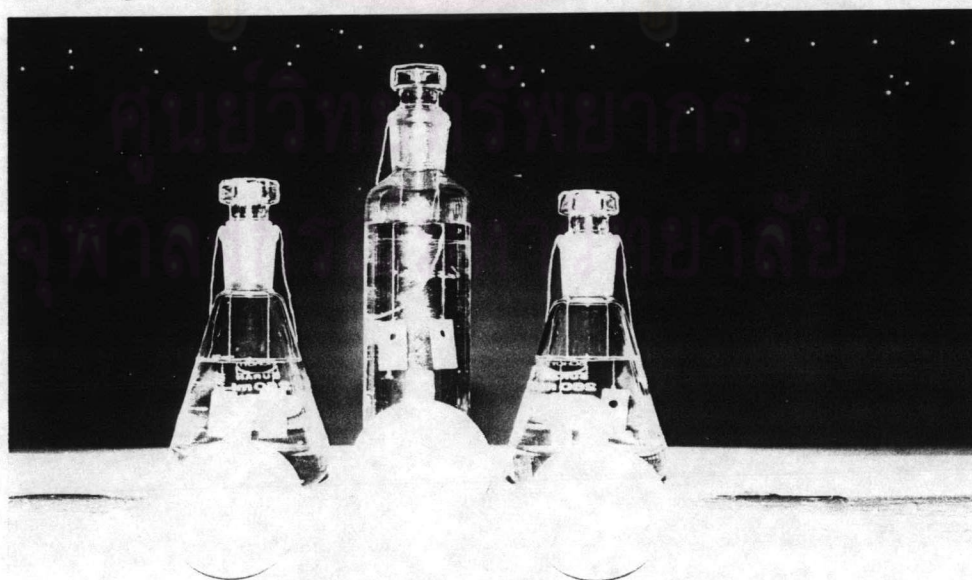


Figure 3.4 Small reaction flasks

These reaction flasks were closed by stopper slight loosely to release some of gas product evolved during the corrosion process and to prevent the reaction to be suppressed.

1. Control of the Reaction Flask Temperature

Various groups of reaction flasks, which each group composed of various concentrations and solvents, and was shown in appendix I, were controlled at various temperatures, -10°C , 0°C , 10°C , 20°C , ambient, 40°C , 50°C , 60°C and 70°C . At low temperatures, the flask were stored in the refrigerator, whereas the higher ones were studied using the temperature controlled bath.

2. Duration of Exposure

1) Corrosive solutions used PE or CH_3OH as solvent resulted in too low corrosion on both kinds of specimens, aluminium and carbon steel, then these must be immersed for a long period of time, that is during 700-1000 h. Each of small reaction flasks must be recorded its exposure time with precision of 0.01 h. However, at ambient and elevated temperature, some of corrosive solutions with CH_3OH as solvent resulted in severe corrosion on aluminium specimens. These tests must thus be observed all time and must be stopped in a short time.

2) Corrosion caused by other solutions, such as, pure H_2O , aqueous HCl solution and Hg in cyclohexane solution, was not severe. they were thus taken long period of time for exposure (700-1000 h).

Methods for Cleaning Specimen after Exposure

Specimen cleaning after exposure test in this research was done by the methods of ASTM G1-72 (Reapproved 1979). Mechanical cleaning was used together with chemical cleaning for cleaning both kinds of specimens, carbon

steel and aluminium. Since procedures of specimen cleaning were varied depending on the type of metal being cleaned, both kinds of specimens, carbon steel and aluminium were separately cleaned, as follows ;

1. Aluminium Specimen Cleaning

The following procedures was used for cleaning the aluminium specimens :

- 1) The coupons were cleaned as well as possible with a plastic knife
- 2) Oily or greasy deposits were removed by soaking in trichloroethylene
- 3) The coupons were then immersed in the cleaning solution with the following components ;

Chromic acid (CrO_3)	20 g
Phosphoric acid (H_3PO_4 , sp.gr. 1.69)	50 ml
Water to make	1 litre

at 80°C for 25 minutes.

- 4) The coupons were taken off the cleaning solution and rinsed with water, isopropyl alcohol, and finally, benzene.
- 5) The cleaned coupons were dried with paper towels, and placed in a dessicator for 1 h before weighing.

2. Carbon Steel Specimen Cleaning

The procedure was the same as above for No. 1 and 2. However , before immersed in a cleaning solution, remaining loose corrosion products(needed to be removed)by brushing with a bristle brush. Then the following procedure was followed ;

- 1) The specimens were immersed in the Clarke's solution which was composed of the following components;

Concentrated hydrochloric acid (sp gr. 1.19)	1 litre
Antimony trioxide (Sb_2O_3)	20 g
Stannous chloride (SnCl_2)	50 g

at room temperature for 25 minutes

2) The specimens were rinsed with water to remove all the above solution, followed by isopropyl alcohol.

3) They were then dried between paper towels, followed by warm air drying.

Investigation of Corrosion Appearances on Specimen Surface

1. Visual Investigation

Specimens were taken photograph at the interested positions on specimen surface.

2. Investigation of Surface Microstructure

The specimens were scanned by a scanning electron microscope (SEM) with magnification 60x, 600x or 1000x, depending on the desired details. The SEM used is made by JEOL, model JSM-T 100, as shown in Figure 3.5

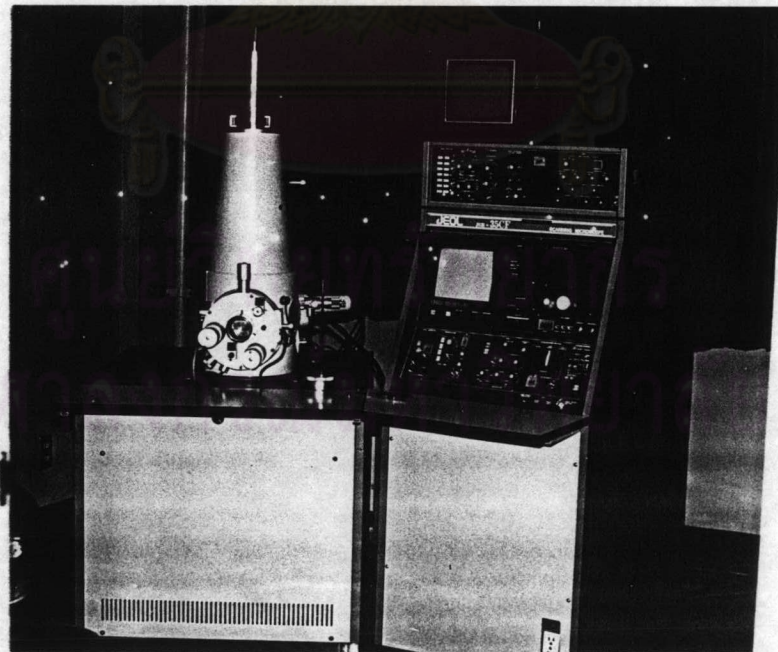


Figure 3.5 Scanning electron microscope