

## CHAPTER 3

### EXPERIMENTAL PROCEDURE

This chapter describes about equipments and methods for all experiments in these studies. They are gas flow rate, specimen preparation, nitridation and carburization by direct metal-gas reaction, nitridation by direct metal-gas reaction, carburization by directly applying voltages, Rutherford backscattering spectrometer, x-ray diffractometer, energy dispersive x-ray, scanning electron microscopy, microhardness test and wear test.

#### 3.1 Gas Flow Rate

##### 3.1.1 Equipments

3.1.1.1 Gas flow rate controlling set with gas-flow-rate-measuring-tube, the components are shown in Figure 3.1.

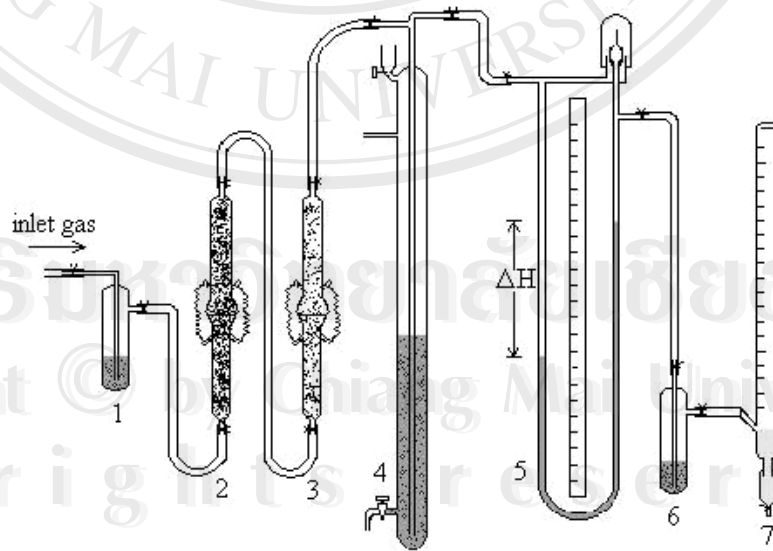


Figure 3.1 Gas flow rate measurement.

1) Inlet-gas-detected-tube with dibutyl phthalate solution. The incoming gas is detected by the appearance of air bubbles.

2) Gas-humidity-absorbent-tube with drierite.

3) C-containing-gas-absorbent-tube with ascarite. It does not use for C<sub>2</sub>H<sub>2</sub> gas flow rate controlling set.

4) Gas-pressure-controlled-tube, 3.0 cm diameter and 95.0 cm length, with dibutyl phthalate solution. Solution level in this tube correlates with the difference of solution level in U-shape tube.

5) Venturi meter, consisted of U-shape tube, 0.8 cm diameter and 88.0 cm length with dibutyl phthalate solution, and capillary tube with 3.0 cm diameter tubular cover. The difference of solution levels in U-shape tube reflects the gas flow rate.

6) Outlet-gas-detected-tube with dibutyl phthalate. The out gassing is detected by the appearance of air bubbles.

7) Gas-flow-rate-measuring-tube, 3.5 cm diameter and 51.0 cm length. There is the soap solution and rubber stopper at the bottom.

### 3.1.2 Method

3.1.2.1 The gas flowed into inlet-gas-detected-tube.

3.1.2.2 Solution level of gas-pressure-control-tube was adjusted to make the difference of solution level in U-shape tube ( $\Delta H$ , cm) attained the maximum value.

3.1.2.3 Rubber stopper was pressed to create soap film.

3.1.2.4 The time that the soap film spent for moving through the volumes of 50.0 cm<sup>3</sup> was determined.

3.1.2.5 Gas flow rate ( $F$ , cm<sup>3</sup>.s<sup>-1</sup>) was calculated.

3.1.2.6 The solution levels of gas-pressure-control-tube were adjusted to vary  $\Delta H$  values. Then, repeated from 3.1.3.2 to 3.1.3.5 for nine more times.

3.1.2.7 The relation between  $\log(F$ , cm<sup>3</sup>.s<sup>-1</sup>) and  $\log(\Delta H$ , cm) was plotted and found to be follow the equation

$$\log F = s \log \Delta H + c, \quad (3.1)$$

where  $F$  is the gas flow rate ( $\text{cm}^3 \cdot \text{s}^{-1}$ )

$\Delta H$  is the difference of solution level in U-shape tube (cm)

$s$  is slope of the curve

$c$  is constant.

3.1.2.8 The least-squares estimates of  $s$  and  $c$  for the prediction equation (3.1) were obtained from the sample data by the formulas

$$s = \frac{n \sum (\log \Delta H)(\log F) - (\sum \log \Delta H)(\sum \log F)}{n \sum (\log \Delta H)^2 - (\sum \log \Delta H)^2} \quad [27] \quad (3.2)$$

$$c = \frac{\sum \log F - s \sum \log \Delta H}{n}$$

3.1.2.9 The coefficient of determination  $r^2$  was determined from the correlation coefficient  $r$ , where

$$r = \frac{n \sum (\log \Delta H)(\log F) - (\sum \log \Delta H)(\sum \log F)}{\sqrt{[n \sum (\log \Delta H)^2 - (\sum \log \Delta H)^2][n \sum (\log F)^2 - (\sum \log F)^2]}} \quad [27] \quad (3.3)$$

## 3.2 Specimen Preparation

Two alloys, MJ12 and MJ47, were used in these studies. Their chemical compositions are given in Table 3.1.

Table 3.1 Chemical composition of MJ12 and MJ47 alloys.

Alloys	at %					
	Ti	Al	Nb	Cr	Mn	TiB <sub>2</sub>
MJ12	49	47	2	2	-	-
MJ47	48.2	47	2	-	2	0.8

### 3.2.1 Materials and Equipments

3.2.1.1 The 1.5 cm diameter rods of MJ12 and MJ47 alloys.

3.2.1.2 Low speed diamond saw.

3.2.1.3 Rotating disk for polishing.

3.2.1.4 Number 100, 400 and 1000 SiC papers.

3.2.1.5 1.0 and 0.3  $\mu\text{m}$  alumina powders.

3.2.1.6 Desicator.

3.2.1.7 Micrometer.

### 3.2.2 Method

3.2.2.1 MJ12 and MJ47 rods were cut into 1.0-2.0 mm thick disks, grinded with the number 100, 400 and 1000 SiC papers then polished with 1.0 and 0.3  $\mu\text{m}$  alumina powders.

3.2.2.2 The radius and thickness of the disks were measured to determine the total surface area calculated by the equation,

$$A = 2\pi r^2 + 2\pi rh, \quad (3.4)$$

where  $A$  is total surface area of the disk ( $\text{cm}^2$ )

$r$  is radius of the disk (cm)

$h$  is thickness the disk (cm).

3.2.2.3 The disks were kept in a desicator to prevent the alloys from contacting with moisture.

## 3.3 Nitridation and Carburization by Direct Metal-Gas Reaction

### 3.3.1 Materials and Equipments

3.3.1.1 Alcohol.

3.3.1.2 Commercial grade  $\text{C}_2\text{H}_2$ , Ar and  $\text{NH}_3$  gas.

3.3.1.3 Gas regulators.

3.3.1.4 Gas flow rate controlling sets. Each set was connected with a 3.0 cm diameter and 52.0 cm length gas mixed tube.

3.3.1.5 High temperature reaction chamber is shown in Figure 3.2.

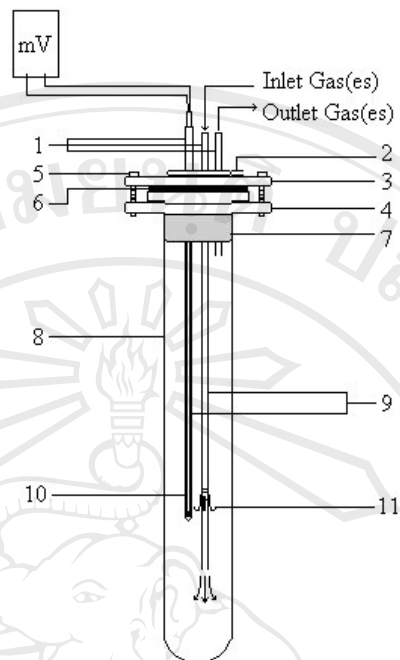


Figure 3.2 High temperature reaction chamber.

- 1) Copper tubes used for inserted thermocouple, the inlet gas and the outlet gas. Each tube has 1.0 cm diameter and was joined to a copper cap.
- 2) Copper tube of cooling system, 1.0 cm diameter, was curled and joined on the copper cap. One end for inlet water and the another end for outlet water.
- 3) Copper cap, 13.0 cm diameter and 5.5 cm thickness.
- 4) Cover clamp, 12.5 cm diameter and 0.6 cm. in thickness.
- 5) Screws.
- 6) Ring-shape-sealed-rubber, its inner diameter equals to inner diameter of chamber and its outer diameter equals to the edge of the chamber.
- 7) Brick of Asia Refractory Industry Co., Ltd., ARI C-2 model can tolerated temperature up to 1300°C. It was cut to cylindrical shape with 4.5 cm diameter and 6.0 cm height.
- 8) Chamber, made from high alumina porcelain. It has a cylindrical shape of 5.8 cm inner diameter, 6.5 cm outer diameter, 10.0 cm edge diameter, 0.8 cm edge thickness and 61.5 cm length.
- 9) Ceramic tubes closed at one end used to insert thermocouples, another one is open at both ends used for flowing the gases into the chamber.

10) Cromel-Almel Type K thermocouple connected with multimeter. It is sensitive at 727 - 1027 °C [28].

11) Heating element hook for hanging specimen. It was attached to the ceramic tube.

3.3.1.6 Rotary pump, 0523-U4-E21DX, Gast, MFG Crop.

3.3.1.7 Furnace. It can heat up to 1200°C, outer wall made from steel and has 48.0 cm width, 50.0 cm length and 70.0 cm height. The components are

1) Screw-thread-ceramic-tube made from high alumina porcelain and has 8.0 cm inner diameter, 12.0 cm outer diameter, 51.0 cm height, 1.0 cm thickness screw-thread and 2.5 cm interval length screw-thread. The tube wall is porous to enhance heat transfer. The tube was placed in the center of the furnace.

2) Heating element wire has 2.0 mm diameter and 29.5 m length. The coiled heating element wire has 2.5 cm diameter and has been winded round the screw-thread-ceramic-tube. Two ends are connected to a dimmer Switch.

3) Bricks of Asia Refractory Industry Co., Ltd., ARI C-1 and ARI C-2 model. ARI C-2 bricks (1300°C tolerant temperature) are placed next to the screw-thread-ceramic-tube while ARI C-1 bricks (1100°C tolerant temperature) are placed next to the furnace wall.

3.3.1.8 Temperature controlling unit. It consists of

1) Temperature controller of Shinko Electric Instrument Co., Ltd. Osaka, Japan, AF-720-R/F model.

2) Dimmer switch. It is a circuit which connected to the output of temperature controller. It controls the furnace temperature by adjusting voltages on heating element.

3.3.1.9 Multimeter.

3.3.1.10 Digital clock.

3.3.1.11 Precisa 240A digital balance which has 0.0001 g accuracy.

3.3.1.12 Specimen holder. It was the iron-chromium-aluminium alloys wire with a 1.0 mm diameter.

### 3.3.2 Method

3.3.2.1 The disks were degreased with alcohol.

3.3.2.2 The disks were held by the heating element as shown in Figure 3.3. They were hung on the heating element hooks in the chamber at position a.

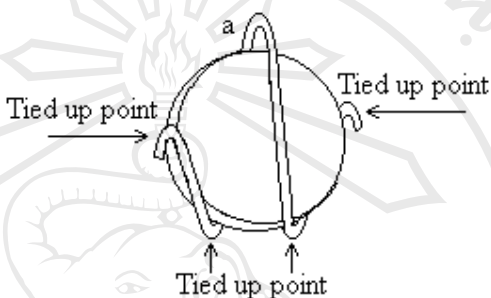


Figure 3.3 The disk with holder.

3.3.2.3 The cap was closed and the chamber was sealed.

3.3.2.4 The chamber was evacuated to 90 mmHg pressure and then filled with Ar.

3.3.2.5 Repeat 3.3.2.4 for 10 times to reduced the air in chamber.

3.3.2.6 Ar gas was fed into the chamber to prevent the alloys from oxidation during heating up period.

3.3.2.7 Let the cooling water flow and the chamber was put in the furnace.

3.3.2.8 The furnace was turned on and the thermocouple was connected to the multimeter.

3.3.2.9 When the temperature was attained, the  $\text{NH}_3$  gas with  $10.0 \text{ cm}^3 \cdot \text{s}^{-1}$  flow rate was fed into the chamber for 5.0 h. The nitridation was done at 1000 K (30.2 mV), 1100 K (34.4 mV), 1200 K (38.4 mV) and 1300 K (42.3 mV).

3.3.2.10 At the end of the nitridation process, the ammonia was replaced by a mixture of acetylene and argon. The flow rates of acetylene were 0.01, 0.03 and  $0.05 \text{ cm}^3 \cdot \text{s}^{-1}$  and the argon flow rates were set to balance the total flow rate of the gas mixture to be  $10.0 \text{ cm}^3 \cdot \text{s}^{-1}$ . The carburization proceeded for 5.0 h as well.

3.3.2.11 At the conclusion of the carburization process, the gas mixture was replaced by the argon and the disks were cooled down to room temperature.

3.3.2.12 Ar gas and cooling water were turned off. The specimens were brought for further analysis

### 3.4 Nitridation by Direct Metal-Gas Reaction

#### 3.4.1 Materials and Equipments

Use the same materials and equipments as that of the nitridation process listing in 3.3.1.

#### 3.4.2 Method

3.4.2.1 The disks were degreased with alcohol and the mass before nitridation ( $m_0$ ) were determined.

3.4.2.2 The experiment was done in the same way as 3.3.2.2 to 3.3.2.9.

3.4.2.3 At the conclusion of the nitridation process, the ammonia was replaced by the argon and the disks were left to cool down to room temperature.

3.4.2.4 Ar and cooling water were turned off. The specimens were brought for further analysis.

3.4.2.5 The disks were weighed to determined the mass after nitridation ( $m_t$ ).

3.4.2.6 The mass increase per unit surface area was determined using the equation

$$\Delta m = \frac{m_t - m_0}{A}, \quad (3.5)$$

where  $\Delta m$  is the mass increase per unit surface area ( $\text{g}\cdot\text{cm}^{-2}$ )

$m_0$  is mass before nitridation (g)

$m_t$  is mass after nitridation (g)

$A$  is total surface area of specimen ( $\text{cm}^2$ ).



3.4.2.7 The density increase was determined using the equation

$$\Delta\rho = \frac{\Delta m}{d}, \quad (3.6)$$

where  $\Delta\rho$  is the density increase ( $\text{g.cm}^{-3}$ )

$d$  is the film thickness (cm).

3.4.2.8 The values of  $D$  was calculated using equation

$$D = \frac{d^2}{4t}, \quad (3.7)$$

where  $t$  is nitridation time (s).

3.4.2.9  $\ln D$  was plotted against the inverse of the nitridation temperature ( $T^{-1}$ ).

The data points was fitted to the Arrhenius type equation,

$$\ln D = \ln D_0 - \frac{Q}{RT}, \quad (3.8)$$

where  $Q$  is the activation energy ( $\text{J.mol}^{-1}$ )

$R$  is the gas constant ( $8.3144 \text{ J.mol}^{-1}.\text{K}^{-1}$ ) [29].

3.4.2.10 The activation energies for diffusion was calculated.

### 3.5 Carburization by Directly Applying Voltages

#### 3.5.1 Materials and Equipments

3.5.1.1 Alcohol.

3.5.1.2 Polyvinyl alcohol-glue solution in 1:1 volume ratio.

3.5.1.3 Carbon powder.

3.5.1.4 Precisa 240A digital balance.

- 3.5.1.5 Agate mortar.
- 3.5.1.6 Dropper.
- 3.5.1.7 Stainless steel die, 1.745 cm inner-diameter, 5.070 cm outer-diameter and 6.160 cm height.
- 3.5.1.8 T.M.C. HP10 hydraulic pressing unit.
- 3.5.1.9 Ar.
- 3.5.1.10 Gas regulator.
- 3.5.1.11 Chamber apparatus, the components are given in Figure 3.4.
  - 1) Stainless steel caps, 15.245 cm diameter and 1.820 cm thick.
  - 2) Copper rods, 5.005 cm diameter and 3.000 cm thick.
  - 3) Cylindrical glass, 8.000 cm inner-diameter, 9.035 cm outer-diameter and 9.980 cm height.
- 3.5.1.12 Agilent 6572A DC power supply.
- 3.5.1.13 Digital clock.

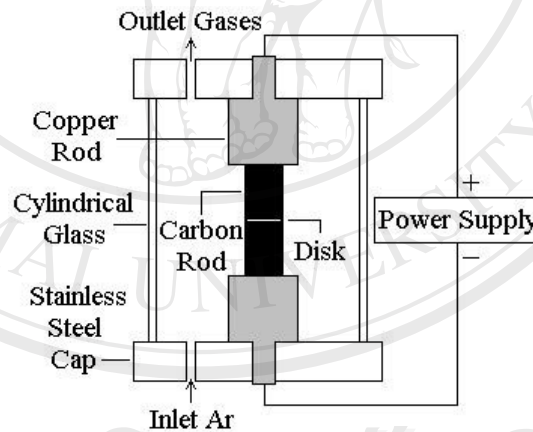


Figure 3.4 Carburation by directly applying voltages.

### 3.5.2 Method

3.5.2.1 The disks were degreased with alcohol and the mass before carburation ( $m_0$ ) were determined.

3.5.2.2 The disks were pressed in carbon powder at  $1.79 \text{ kg.mm}^{-2}$  to form rods of 18.9 mm diameter and 29.0 mm long.

3.5.2.3 The rod was placed between the copper rods in the cylindrical glass and the two stainless steel caps were closed on the top and the bottom as shown in Figure 3.4. Then, Ar was fed into the chamber.

3.5.2.4 The rods were carburized by directly applying electrical power at  $274.3 \pm 26.4$  W, 80 A across MJ12 disk and at  $293.4 \pm 16.8$  W, 80 A across MJ47 disk for 1 h. At fixed current, the applied voltages were naturally decreasing with prolonging in time and were constant afterwards.

3.5.2.5 The disks were left to cool down to room temperature and weighed to determine the mass after carburization ( $m_t$ ).

3.5.2.6 The mass change per unit surface area was determined using the equation (3.5).

3.5.2.7 The films density were determined using equation (3.6).

### **3.6 Rutherford Backscattering Spectrometer (RBS)**

#### **3.6.1 Equipments**

3.6.1.1 1.7 MV Tandem Accelerator

3.6.1.2 NUSDAN software [30]

#### **3.6.2 Method**

3.6.2.1 The disks were analysed using 1.7 MV Tandem Accelerator with 2.13 MeV  $^4\text{He}^{++}$  ions,  $170^\circ$  scattering angle and 2.196 keV/channel energy width.

3.6.2.2 The RBS spectra were analysed using NUSDAN software and the film thickness were determined.

### **3.7 X-Ray Diffractometer (XRD)**

#### **3.7.1 Equipments**

3.7.1.1 Bruker X-ray diffractometer

3.7.1.2 Holder

3.7.1.3 X'Pert Highscore software [31] with PDF-2 Data Base [32].

### 3.7.2 Method

3.7.2.1 The disks were held in the holder which were placed in the Bruker x-ray diffractometer.

3.7.2.2 The operation was done from 20° to 90° with 0.02° step scan and 1 s step time at 40 kV and 30 mA and using Cu-K<sub>α</sub> as the target.

3.7.2.3 The XRD spectra were analysed using the X'Pert Highscore software.

## 3.8 Energy Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM)

### 3.8.1 Materials and Equipments

3.8.1.1 JEOL JSM-5910LV SEM.

3.8.1.2 JEOL JSM-6335F SEM.

3.8.1.3 SPI module sputter coater of SPI Supplies, division of structure probe, Inc.

3.8.1.4 Stub and carbon tape.

3.8.1.5 Holder.

### 3.8.2 Method

3.8.2.1 The disks were contacted on the stubs by using the carbon tape.

3.8.2.2 The holder was placed in the JEOL JSM-5910LV SEM. Evacuation was done to reduced the pressure to 30 Pa.

3.8.2.3 The chemical composition of the specimens were analysed using the energy dispersive x-ray (EDX) operated at 15 kV accelerating voltage.

3.8.2.4 The holder was removed from the JEOL JSM-5910LV SEM. The specimens with the stubs were placed in the SPI module sputter coater. The gold coating process was operated at 18 mA, 4.7 cm apart for 20 s.

3.8.2.5 The disks with the stubs were held in the holder which was placed in the JEOL JSM-6335F SEM. Evacuation was done to reduce the pressure to  $9.63 \times 10^{-5}$  Pa.

3.8.2.6 The surface morphology of the disks was analysed using the SEI mode operated at 15 kV accelerating voltage.

### 3.9 Microhardness Test

#### 3.9.1 Equipment

3.9.1.1 MXT –  $\alpha$ 7 microhardness tester of Matsuzawa Seiki Co. Ltd..

#### 3.9.2 Method

3.9.2.1 Knoop hardness were done using 50 gf load.

3.9.2.2 The test were repeated for 10 times for the average value.

### 3.10 Wear Test

#### 3.10.1 Equipments

3.10.1.1 A pin-on-disk apparatus of Implant Science Corporation, ISC 200, with 3.175 mm WC ball using as a pin.

3.10.1.2 Microscope of MXT- $\alpha$ 7 Matsuzawa Seiki microhardness tester with 0.1  $\mu$ m accuracy was used for measuring distance.

#### 3.10.2 Method

3.10.2.1 Testing parameters are as follow;

Load : 250 gf load

Number of turns : 7100 rev.

Wear track radius : 4.5 mm

Speed : 4.71 cm.s<sup>-1</sup> or 100 rev.min<sup>-1</sup>.

3.10.2.2 Wear track width on the disk was measured using two bars and the distance between the bars is automatically shown. Wear track width is shown in Figure 3.5.

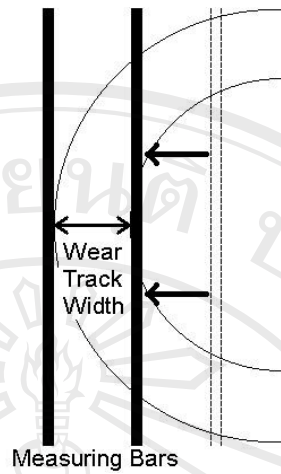


Figure 3.5 Wear track width.

3.10.2.3 The disk volume loss was calculated using equation

$$\text{Disk volume loss} = \frac{\pi r_t w_t^3}{6 r_p}, \quad [33] \quad (3.9)$$

where  $r_t$  is wear track radius (mm)

$w_t$  is wear track width (mm)

$r_p$  is pin radius (mm).

3.10.2.4 The disk wear rate was calculated using equation

$$\text{Disk wear rate} = \text{disk volume loss} / \text{total sliding distance}, \quad [33] \quad (3.10)$$

where total sliding distance is equal to  $2.0075 \times 10^5$  mm.

3.10.2.5 The steps 3.10.2.2 to 3.10.2.4 were repeated for 8 times for the average value.