

## Chapter 3

### Experimental procedure

The experimental procedure covering, sample preparations and the characterization is described in this chapter.

#### 3.1 Pellet specimens

##### 3.1.1 Raw materials and characterizations

Oxide and chemicals as shown in Table 3.1 were used as starting raw materials.

Table. 3.1 Alumina powder and chemicals used in this experiment.

Materials	Purity	Average particle size ( $\mu\text{m}$ )	Manufacturers
Aluminium oxide AKP-30	>99.99%	0.3	Sumitomo
Magnesium (II)nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\geq 99\%$	-	Fluka
Zirconium oxide TZ- 3Y, 3 mol% $\text{Y}_2\text{O}_3/\text{ZrO}_2$	$\text{ZrO}_2 + \text{HfO}_2$ : >94% $\text{Y}_2\text{O}_3$ : <5.65%, $\text{Al}_2\text{O}_3$ : <0.3%	-	TOSOH
Polyvinyl alcohol	9000-10000 MW	-	Fluka

Particle size distribution of AKP-30 was measured by sedimentation method using centrifugal particle size analyzer (Shimadzu SA-CP2). About 1 gram of alumina powder was mixed with 0.2wt% NaHMP solution before subjected into the centrifugal particle size analyzer. A solution with 0.2wt% NaHMP was used as a blank solution. Particle size distribution was reported in reference (1). The average particle size of AKP-30 was 0.3  $\mu\text{m}$ .

### 3.1.2 Composition and preparation of specimens

All compositions are shown in Table 3.2, which were prepared by conventional oxide mixing process. The flow chart of preparation is illustrated in Fig.3.1. MgO and ZrO<sub>2</sub> were used as the additives for preventing discontinuous grain growth and allowed the material to be sintered to theoretical or nearly theoretical density. The amount of MgO was selected at 0.5 wt% and the amounts of ZrO<sub>2</sub> were selected at 1.5 and 3.0 wt%. 200 grams of raw powders were wet mixed in polypropylene bottle (500 ml) for 4 hours, using alumina balls as grinding media and 350 ml of distilled water as solvent. Alumina balls were filled to a half volume of the bottle. The mixtures were filtrated and dried at 105 °C overnight in a dryer to remove the solvent. Before forming, the mixture was well mixed with 1.0 wt% of polyvinyl alcohol (PVA with 9000 - 10000 MW) - water solution, which acted as a binder and was sieved through a 100 mesh screen. One gram of the polyvinyl alcohol was dissolved in 99 ml of water. The specimens were pressed into pellets of 12 and 35 mm in diameter by biaxial hydraulic press with 20 MPa pressure and then repressed by cold isostatic pressing with 198 MPa. All specimens were heated to 540 °C for 2 hours with heating rate of 5 °C/min for binder removal. Further the temperature, was raised at a heating rate of 5 °C/min to 1500, 1550, 1600 and 1650 °C with a soaking period of 2 h for densification. The sintered samples were cooled to 35 °C in the furnace.

Table.3.2 Compositions of alumina specimens

Sample	Composition
1	AKP-30
2	AKP-30 + 0.5% MgO
3	AKP-30 + 1.5% ZrO <sub>2</sub>
4	AKP-30 + 3.0% ZrO <sub>2</sub>

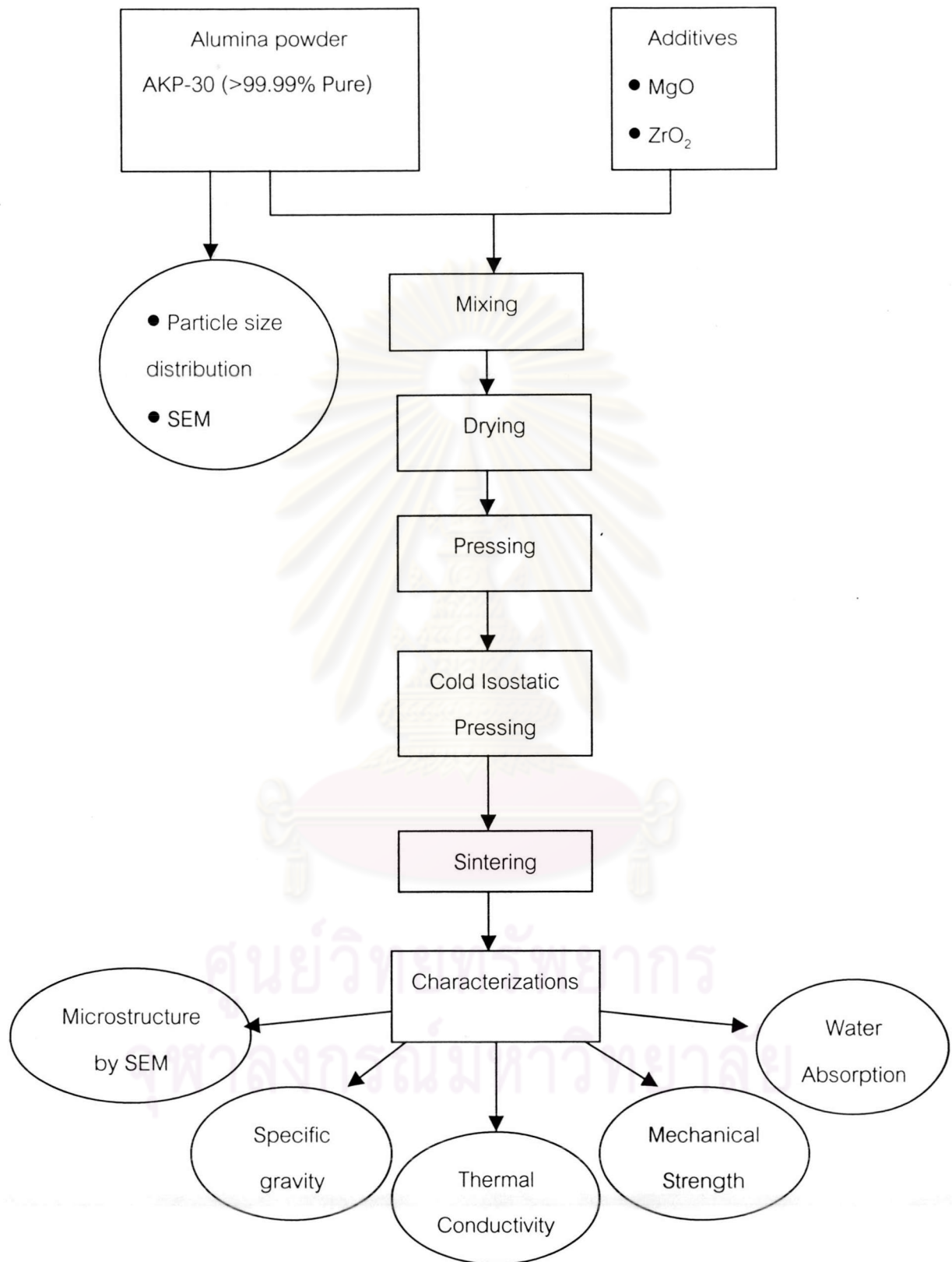


Fig. 3.1 Flow diagram of sample preparation of Alumina substrate by a conventional oxide mixing process.

### 3.1.3 Characterization of sintered specimens

#### 3.1.3.1 Density and water absorption

##### (a) Bulk density

The bulk density of specimens was measured by the Archimede's method. The air in open pores of specimen was removed in vacuum for 30 min and then water was poured onto specimens until all specimens submerged in water. Water was removed to the opened pores by vacuum for 1 h. The dry weight  $W_d$ , saturated weight  $W_{sat}$  and suspended weight  $W_{sus}$  were measured. The bulk density was calculated using equation (3.1) following ASTM standard (Designation : C830-93)

$$\text{Bulk density} = \frac{W_d}{W_{sat} - W_{sus}} \cdot \rho \quad (3.1)$$

Where  $\rho$  was water density at the measured temperature (0.99564 g/cm<sup>3</sup> at 27 °C).

##### (b) Theoretical density

The theoretical density of specimens was calculated from real density using the following equation.

$$\text{Theoretical density} = \frac{W_{total}}{W_a/\rho_a + W_b/\rho_b + \dots} \quad (3.2)$$

Where  $W_{total}$  is total weight of used components.

$W_a, W_b$  is weight of component a and b, respectively.

$\rho_a, \rho_b$  is real density of component a and b, respectively.

a, b,... is used component.



In this experiment, theoretical densities of pure  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{ZrO}_2$ ,  $3.97 \text{ g/cm}^3$ ,  $3.64 \text{ g/cm}^3$  and  $6.023 \text{ g/cm}^3$ , respectively, were used for the calculation. As a result, theoretical densities of all compositions are calculated as shown in Table 3.3.

Table 3.3 Calculated theoretical density of each composition.

Composition	Theoretical density ( $\text{cm}^3$ )
1	3.97
2	3.97
3	3.99
4	4.01

(c) Relative density (% of theoretical density)

The relative density is calculated from bulk density and theoretical density using the following equation.

$$\text{Relative density} = \frac{\text{Bulk density}}{\text{Theoretical density}} \quad (3.3)$$

(d) Water absorption

Water absorption of specimens was calculated from equation (3.4)

$$\text{Water absorption (\%)} = \frac{W_{\text{sat}} - W_{\text{d}}}{W_{\text{d}}} \cdot 100 \quad (3.4)$$

Where  $W_{\text{sat}}$  was saturated weight and  $W_{\text{d}}$  was dry weight of the specimens.

### 3.1.3.2 Microstructure

Microstructures of specimens were examined using a scanning electron microscope (JEOL : JSM-1670). The sintered specimens were ground by silicon carbide paper 400 mesh and then 1200 mesh, respectively, and then they were polished with various size of diamond paste and finally with 1  $\mu\text{m}$  diamond paste by Buehler machine at 250 rpm. And then thermally etched at 1500  $^{\circ}\text{C}$  for 30 min. The specimens were gold sputtered before subjected to the SEM observation. The average grain size was determined by a line intercepted method following ASTM standard (Designation E 112-96)

### 3.1.3.3 Mechanical strength

The compositions No. 1,2,3 and 4 in Table 3.2 were pressed into pellets of 35 mm in diameter by a hydraulic press with 20 MPa pressure and then repressed by cold isostatic press with 198 MPa. The surfaces of sintered samples were ground with 125 mesh of diamond wheel to make a parallel surface and then ground with 400 mesh and 1200 mesh silicon carbide papers to remove the scratches at which stress concentrate when load was applied. All specimens were annealed at 1500  $^{\circ}\text{C}$  for 30 min. Diameter and thickness of specimens were measured for the final calculation. The specimens were placed on three symmetrically spaced points near its periphery as shown in reference (1).

The load was applied to the center of specimen through a cylindrical ram. Scotch tape was attached to the compression side of each specimen to prevent the scatter of specimen after breaking. The force was applied to the ram at the rate of 0.05 mm/min using the machine (LLOYD Instrument LTD) with a load of cell 2500 N. The strength was calculated by equation (3.5), in conformity with the ASTM standard (Designation F 394-78).

$$S = -0.2387P(X-Y) / d^2 \quad (3.5)$$

Where  $S$  = maximum center tensile stress (MPa),  
 $P$  = total load causing fracture (N),  
 $X = (1+\nu) \ln(B/C)^2 + [(1-\nu)/2](B/C)^2$ ,  
 $Y = (1+\nu)[1 + \ln(A/C)^2] + (1-\nu)(A/C)^2$ ,  
 $A$  = radius of support circle (mm),  
 $B$  = radius of loaded area or ram tip (mm),  
 $C$  = radius of specimen (mm), and  
 $d$  = specimen thickness at fracture origin (mm)

In this experiment ;

$\mu$  = Poisson's ratio, 0.23,

$A$  = 12.5 mm

$B$  = 0.25 mm, it was measured from the contact area using optical microscope.

$C$  = 12-15 mm

$d$  = 1.3-2.7 mm

#### 3.1.3.4 Thermal conductivity

The powders were pressed in a die of 12 mm in diameter. The surfaces of sintered samples were ground using silicon carbide paper 400 and 1200 mesh and 24 pound load of Buehler machine for 60 minutes each. Thermal conductivity was measured by Laser Flash method at ULVAC – RIKO, Inc. Japan and Tokyo institute of Technology. The thickness and weight of test specimen were measured. It was subjected to a high-intensity short duration thermal pulse. The energy of the pulse was absorbed in the front surface of a specimen and conducted to rear face and, as a result, rear face temperature rised. The ambient temperature of specimens was controlled by a furnace or cryostat. Thermal diffusivity values were calculated from the specimen thickness and the time required for the rear face temperature rise to reach certain percentages of its maximum value following the ASTM standard (Designation : E 1461-92). The essential features of the apparatus are shown in page 27 in reference (1).

### 3.2 Thin tape specimens

#### 3.2.1 Raw materials

Raw materials as shown in Table 3.4 were used for the preparation of tape specimens by extrusion

Table 3.4 Raw materials for experimental of thin tape

Materials	Purity	Average particle size( $\mu\text{m}$ )	Manufacturers
Aluminium oxide AKP-30	>99.99%	0.3	Sumitomo
Yuken binder	*	-	Yuken
Miyazaki binder	*	-	Miyazaki

\* Materials and compositions are not disclosed. We suppose that the main material is methyl cellulose.

#### 3.2.2 Preparation of thin tape by extrusion

This process was operated by Miyazaki Company, Japan. The process flow chart is shown in Fig. 3.4 AKP-30 powder was mixed with Yuken binder and Miyazaki binder for each composition and distilled water as a solvent in Dalton mixer. The mixture ratios of powder, binder and water were not disclosed, however, it was supposed that the ratio was about 100: 12: 16 in wt. ratio. They were mixed by Kneader and followed by 3 roller mixer for 3 times and the mixed dough was kept in a refrigerator at temperature below 5 °C, because the solubility of methyl cellulose binder was high at low temperature.

Both mixtures were extruded by Extrusion machine (Miyazaki, FM30 -1) and dried by air at 60°C, and then by hot drum at 80°C. Photographs of the process are shown in Appendix 7.



All specimens were dried at 105°C in a dryer overnight to prevent cracking during sintering and heated to 300 °C for 1 h with a heating rate of 3 °C/min for binder removal. Further the temperature was raised with a heating rate of 3 °C/min up to 1500, 1550, 1600 and 1650 °C with a soaking period of 2 h for densification. The sintered samples were cooled to 35 °C in the furnace.



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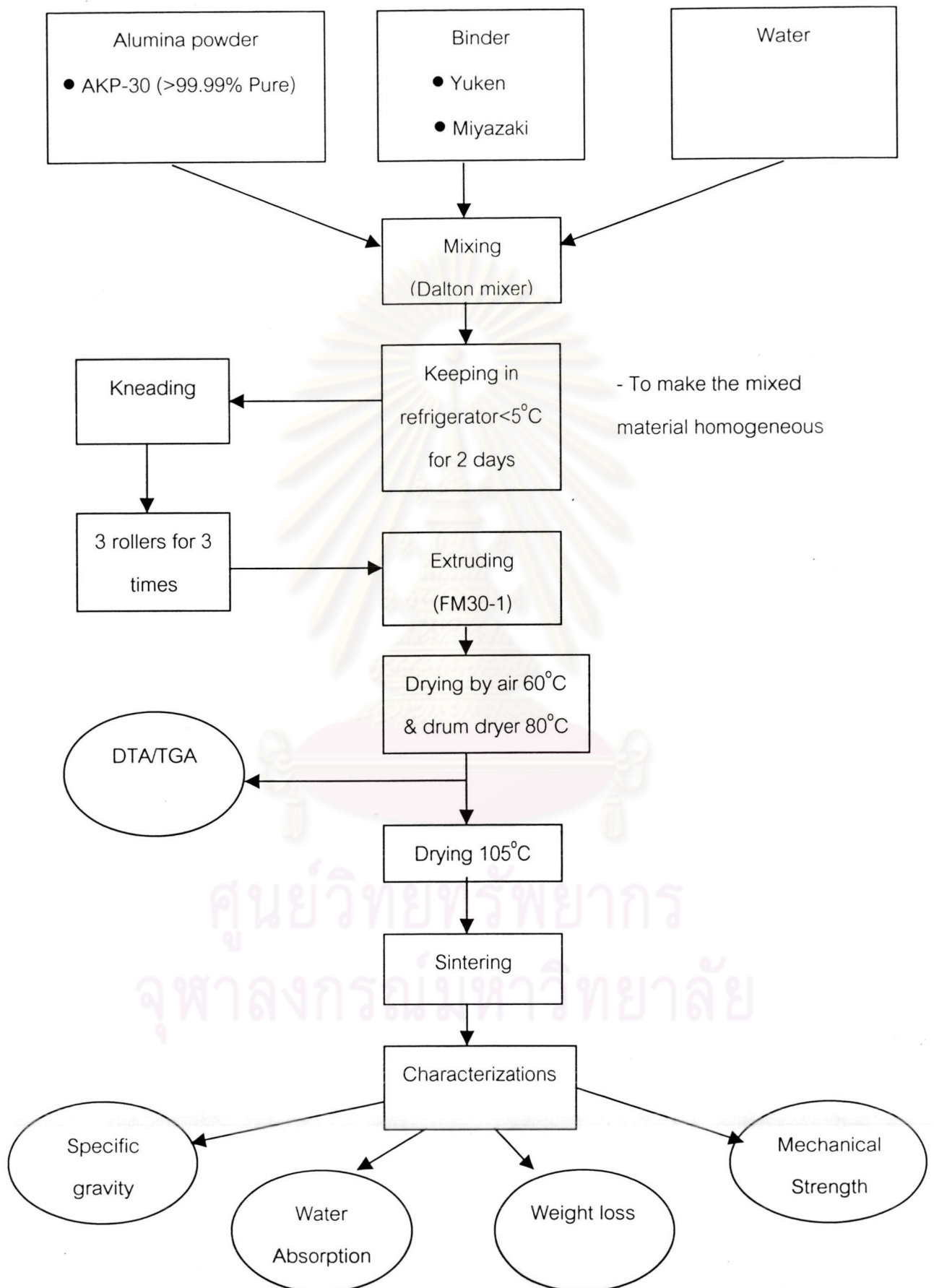


Fig. 3.2 Flow diagram of thin tape preparation by extrusion

### 3.2.3 Characterization of thin tape specimens

#### 3.2.3.1 Thermal analysis (DTA/TGA) and weight loss

Thermal decomposition of binders were examined using a Differential Thermal Analysis (DTA) (NETZSCH: STA 409 C). The as-received specimens were ground in a mortar and sieved through 100 mesh. The powder was analyzed by DTA at a heating rate of 5 °C.

Both types of tape specimens were heated at 300 °C, 500 °C, 700 °C and 900 °C for 1 h to measure the weight loss. Weight loss (%) was calculated by the equation (3.6)

$$\text{Weight loss}_{(\%)} = \frac{W_{\text{org}} - W_{\text{f}}}{W_{\text{org}}} \cdot 100 \quad (3.6)$$

Where  $W_{\text{org}}$  was initial weight and  $W_{\text{f}}$  was fired weight of the specimens

#### 3.2.3.2 Density and water absorption

The bulk density and water absorption of thin tapes were determined according to Archimede's method following ASTM standard (Designation : C373-72). The specimens were boiled in distilled water for 5 h and allowed for soaking 24 hours. Weighing and calculation had been mentioned in 3.1.3.1

#### 3.2.3.3 Mechanical strength of sintered specimen

The specimens were ground by hand using 400 mesh silicon carbide paper and the strength measured by the same method as mentioned in 3.1.3.3. Scotch tape was attached to the compression side of each specimen to prevent the scatter of specimen after breaking.