CHAPTER III

EXPERIMENTAL PROCEDURES

3.1 Plaster Mold Preparation

The specimens required for characterizations in section 3.3 onwards are mostly in shape of rectangular bars of around 3 x 4 x 40 mm^3.To prepare a mold for forming rectangular bars, rigid rectangular models are employed. The surfaces of the model bars are necessary coated with soap or oil to facilitate demolding. The model bars were placed in an array on the flat surface surrounded by rigid side walls as in Figure 3.1(a) one may simply use a flat bottom container. Plaster is mixed with water by 4:3 weight ratio, gently stirred for a few minutes to get rid of bubbles and poured onto the arranged model bars, then allow to set.

On setting, the plaster becomes warm to touch. After about 15-20 minutes or once the setting process is complete, the surrounding walls and the bars are gently removed from the set plaster. The prepared mold is left dry in air for a few days before using. It is recommended that the plaster mold should contain 20-30% water to prevent strong water absorption on the first cast.

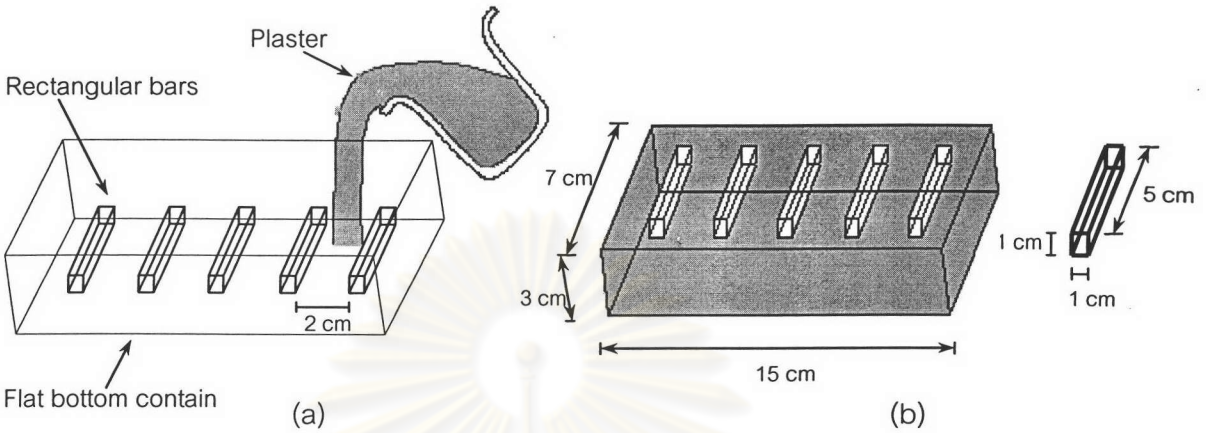
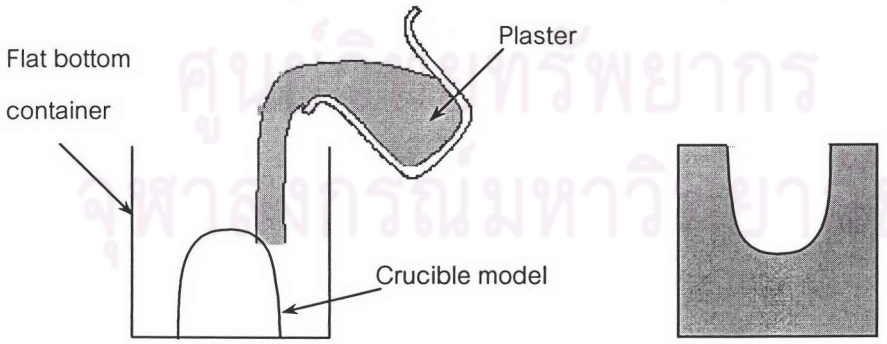


Figure 3.1 (a) The plaster slurry is being poured onto the arranged bars,
(b) The plaster mold after complete setting and removing
the rectangular bars and flat bottom container.

To make plaster mold for forming crucible sample, a crucible model is used instead of the bars. The preparation is carried out in the same manner as for the mold for making bars (Figure 3.2).



(a) crucible mold making (b) completely set plaster mold for crucible making.

Figure 3.2 The crucible plaster mold.

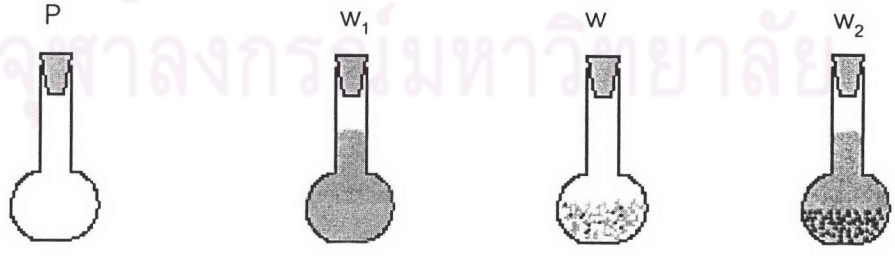
3.2 Characterizations of Raw Materials

Raw materials are rice husk ash (RHA) from power plants, waste sediment from aluminum industry (WS) and SRM30 grade alumina powder from Loxley public company limited. RHA is ball milled for two hours with tungsten carbide balls filled up to one-third of the pot. Milled RHA is dried at 100 °C for 30 minutes and sieved to under 120 Mesh (125 μm).

3.2.1 Density, Particle Size and Size Distribution

Liquid pycnometry is used to measure densities of the powders: RHA, and WS. The steps of measurement are as following:

50 ml pycnometer and stopper are weighed; take a reading p, filled up with deionized water (DI water); measure the weight w_1, and then dried. After pycnometer is completely dried, 10-15 g of the powder to measure is added in and weighed with the stopper; take a reading w. DI water is then filled upto 1/4-1/2 of the volume of the pycnometer. The pycnometer is evacuated for 60-90 minutes to remove entrapped air. After that, fill up the pycnometer with DI water, put the stopper in place, wipe out water drops outside the pycnometer and then take a weight reading w_2. According to C329 ASTM standard, the powder density is calculated by



$$\text{Density} = \frac{w - p}{(w_1 - p) - (w_2 - w)} \qquad (3.1)$$

Particle size and size distribution are determined by laser light scattering technique using Malvern Mastersizer S Ver. 2.19.

3.2.2 Phase, Composition and Thermal Behavior

The powders under 120 Mesh (125 μm) are packed in sample holders then phase analyzed using a X-Ray diffractometer (JEOL) Model JDX-3530 at MTEC with conditions stated in Table 3.1.

Table 3.1 XRD Condition.

Start angle (degree)	15.000
Stop angle (degree)	80.000
Step angle (degree)	0.040
Count time (second)	1.000
Tube voltage (kV)	30.000
Tube current (mA)	40.000

For the composition analysis, RHA-S is fused and casted into beads while WS is pressed into a pellet of 3 cm in diameter. The prepared samples are analyzed using XRF (Philips spectrometer Model PW 2404).

Weight loss of the powders are measured in NETZSCH Simultaneous Thermal Analysis (STA), Model 449C Jupiter®. The unit consists of Differential Thermal Analysis (DTA) and Thermogravitic Analysis (TGA). The powders are individually filled in alumina crucibles and heated from 25-1000 °C with a heating rate of 300 °C/hr.

3.2.3 Microstructure

The raw material powders is attached to aluminum stubs with a sticky carbon tape and gold sputtered with 15 mA for 60 seconds to examine in JEOL Scanning Electron Microsope model JSM5410.

3.3 Influence of Al_2O_3 sources to mullite formation

Two different sources of Al_2O_3, WS from the aluminum anodizing and SRM30 from Loxley public company limited were studied. These two powders are mixed with RHA~~S~~ in proportions indicated in Table 3.2. Each mixture is prepared in 100 g batch and wet milled overnight (24 hours) using a 250 g propylene bottle with Al_2O_3 grinding media of half a volume of the bottle. In wet milling, the water is added by 60 wt% of the solid's. Small amount of the deflocculant is also added by 0.2 wt% of the solid's.

Table 3.2 Slip compositions with two different Al_2O_3 sources

composition	RHA (g)	Al_2O_3 (g)	
		SRM30	WS
80:20A	80	20	-
60:40A	60	40	-
40:60A	40	60	-
20:80A	20	80	-
80:20W	80	-	20
60:40W	60	-	40
40:60W	40	-	60
20:80W	20	-	80

Particle size and size distribution of the solid in the slip are inspected using a Malvern Mastersizer S Ver. 2.19.

The slip of each composition is casted in the plaster molds earlier prepared to make rectangular bars. The after cast bodies normally shrink away from the plaster mold, readily to be removed. Otherwise little air pressure is applied to aid the removal. The cast bodies, usually called green, are then fired at 1300, 1400 and 1500 °C for 2 hours with the heating profiles given in Figure 3.3.

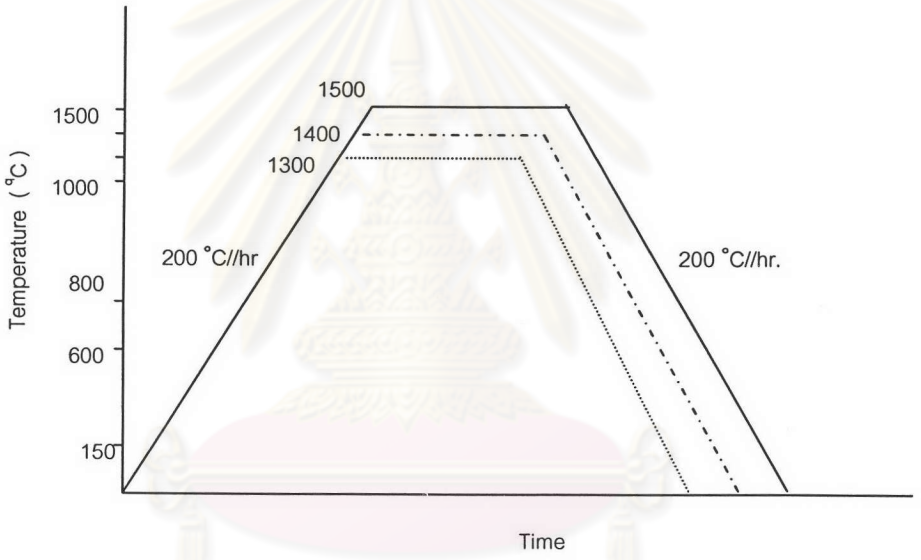


Figure 3.3 Profile I for firing the cast bodies with different Al_2O_3 sources

After firing, all the samples are XRD analyzed to compare the effect of alumina source on mullitization.

3.4 Effect of Deflocculant Quantity on Rheology

Rectangular specimens are fabricated by slip casting, using the plaster mold prepared in section 3.1, and firing in an electric furnace to synthesis mullite. Rheological properties are measure to establish best conditions for slip preparation. A

factor affecting the slip properties to study in this project is the added amount of deflocculant.

DarvanC is the most common deflocculant and is chosen for this study. It is a polyacrylic acid to disperse ceramic suspensions and does not attack the plaster mold. Moreover, the viscosity of the slips with DarvanC is much less sensitive to overdeflocculation and DarvanC works well when prolonged ball milling.

The slips used for this study have 60 wt% solid contents. Ratios of RHA to WS_H that has been heated in the solids are 40:60, 30:70 and 20:80. Each ratio is prepared in 30 g batch. Added amount of DarvanC varies from 0.1-0.5%. The mixing and milling time is 24 hrs.

Measurement of the viscosity is performed with shear rates stepped up from 10-200 rpm. Once, the relationship between these properties is established, the appropriate amount DarvanC can be estimated.

3.5 Effect of Size of Solids Content on Properties of the Final Product.

3.5.1 Slip Preparation and Casting

The slip of each RHA/WS_H ratio is prepared from a batch of 200 g solids. The ratio of solids to water is 5:3. The deflocculant is added between 0.3-0.40% (see section 4.3.1). Milling time is set to 10 and 48 hours such that two different size distributions of the solids, coded by L for 10 hrs and S for 48 hrs, are obtained. The conditions of slip preparation are summarized in Table 3.3.

Table 3.3 Conditions of slip preparation

Designate	wt% RHA in the solids	Milling time (hours)
4S	40	48
4L	40	10
3S	30	48
3L	30	10
2S	20	48
2L	20	10

Particle size and size distribution are determined by laser light scattering technique using Malvern Mastersizer S Ver. 2.19.

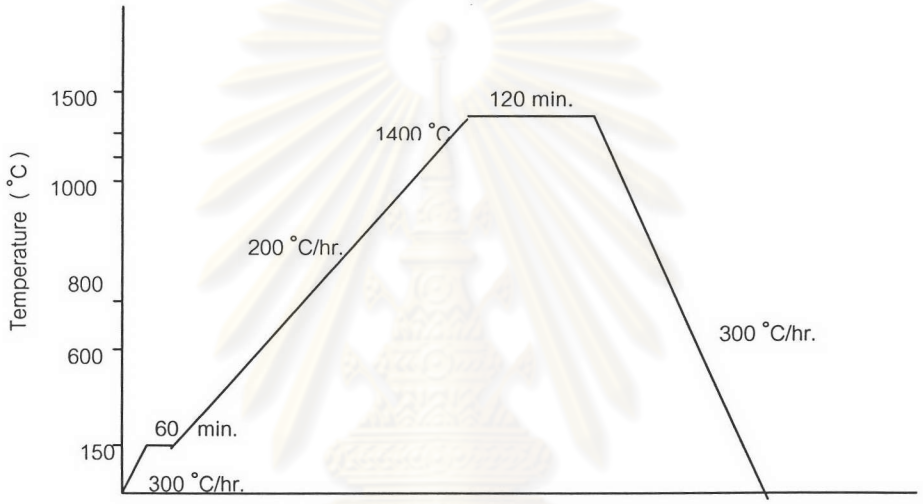
Density of slip is done by filling a measuring glass cylinder, which has been placed on a balance, with the slip upto 10 ml label, and take a reading of the increasing weight, w. The density can be calculated from

$$\text{Density of slip (g/ml)} = \text{w (g)} / \text{10 ml}$$

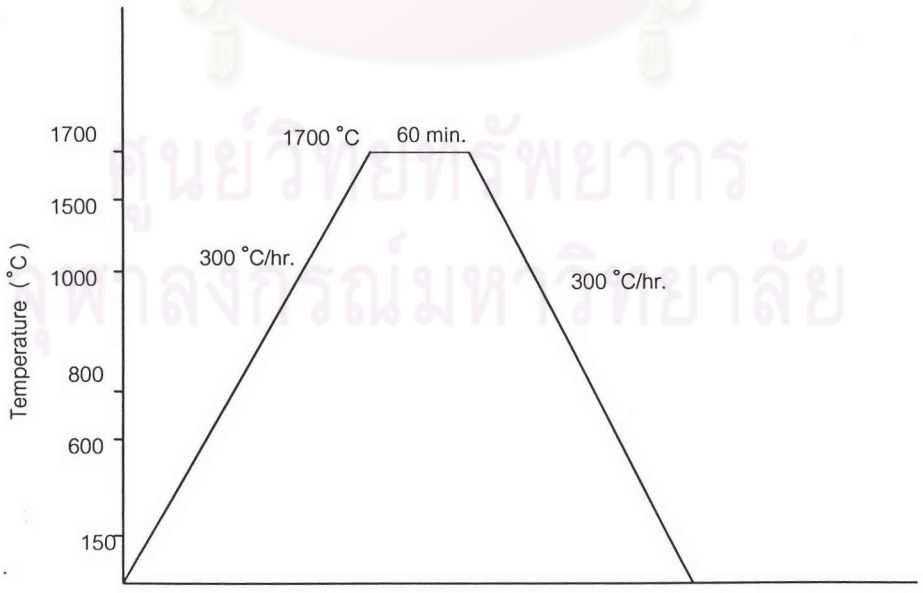
Each slip is casted in the plaster molds prepared from section 3.1 to form rectangular bars. After the removal from mold, the bars are dried at 100 °C in an oven, the surface of each side is ground flat and then size measures prior to firing.

3.5.2 Firing Conditions

Firing is performed in two steps: firstly, biscuit firing below 1400 °C and secondly, firing to complete sintering at 1700 °C. Typical heat treatment profiles for these two steps are illustrated in Figure 3.4.



(a) Profile II for biscuit firing



(b) Profile III for body sintering

Figure 3.4 Temperature profiles for biscuit firing (a) and for body sintering (b).

3.5.3 Characterizations of the Fired Specimens

Compositions and phases of fired specimens are analyzed. Physical properties: density, porosity and percentage of water absorption; mechanical properties: Young's modulus, flexural strength at room temperature, Vicker hardness and fracture toughness; thermal properties: thermal expansion and thermal shock resistance and microstructure are measured to compare with the commercial mullite.

3.5.3.1 Composition and Phase Analysis

Composition and phase analysis were characterized by means of X-ray Fluorescence Spectrometry (XRF) using a Philips spectrometer Model PW 2404 and X-ray diffractometry (XRD) using a CuKα radiation JEOL JDX-3530, respectively. A fired specimens of each designation is ground into powder to make a fused bead for the XRF analysis. While for the XRD examination, the specimen is surface ground flat.

3.5.3.2 Microstructure

The specimens are ground and polished down to 1 μm surface finish, cleaned by deionized water in ultrasonic bath, etched in hydrofluoric acid (HF) for 15-60 minutes and then gold coated to observe the etched surface in JEOL Scanning Electron Microsope model JSM 5410.

3.5.3.3 Physical Properties

Density is measured by Archemedes method following ASTM standard designated C373. The specimens under investigation are weighted to get dry weight, W_{dry}, boiled for 5 hours so that the open pores are replaced by water, allowed to cool down and soaked for 24 hours. After that, they are weighted in a basket which has been suspended in water to measure suspended weight, W_{sus}, and then taken out of

water. All excess water from the surface of specimen is wiped out, then the saturated weight, W_{sat}, is measured. The difference between W_{sus} and W_{sat} gives the bulk volume of specimen. The bulk density is calculated from

$$\text{Bulk density} = \frac{W_{dry}}{W_{sat} - W_{sus}} \quad (3.2)$$

The difference between W_{sat} and W_{dry} gives the open pores volume of specimen and the apparent density can be obtained from equation (3.3). Percentage of water absorption is calculated from equation (3.4).

$$\text{Apparent density} = \frac{W_{dry}}{(W_{sat} - W_{sus}) - (W_{sat} - W_{dry})} = \frac{W_{dry}}{(W_{dry} - W_{sus})} \quad (3.3)$$

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

The porosity is observed alternatively by means of image analysis. The specimens are polished down to 1 μm surface finish and gold coated to enhance the contrast before optical microscopy inspection.

3.5.3.4 Mechanical Properties

The samples after image analysis are used to measure Young's modulus with resonant frequency technique by a Grindosonic tester. According to ASTM designated C1198,

$$E = 0.9465 (m f_f^2 / b) (L^3 / t^3) T_1 \quad (3.5)$$

where:

E = Young's modulus, Pa

m = mass of the specimen, g

b = width of the specimen, mm

L = length of the specimen, mm

t = thickness of the specimen, mm

f_f = fundamental resonant frequency of specimen in flexure, Hz, and

T_1 = correction factor for fundamental flexural mode,

where

$$T_1 = 1 + 6.585 (1 + 0.0752 \mu + 0.8109 \mu^2)(t/L)^2 - 0.868(t/L)^4 - \left[\frac{8.340 (1 + 0.2023 \mu + 2.173 \mu^2)(t/L)^4}{1 + 6.338 (1 + 0.1408 \mu + 1.536 \mu^2)(t/L)^2} \right]$$

where

μ = Poisson's ratio.

For bending strength, four-point bending is performed using a Universal Testing Machine Model 4502 with a crosshead speed of 0.50 mm/min. Bending strength can be calculated using ASTM C1161:

$$\sigma = 3 P l / 4 b t^2 \quad (3.6)$$

where:

σ = flexural strength, MPa

P = load, N

l = length of span, mm

b = width of the specimen, mm

t = thickness of the specimen, mm

The specimens are prepared in the same way as done for the image analysis. A diamond indenter is applied to the surface of specimen with 1 kg and 5 kg loads. Half length of the crack, c, is measured. Hardness (H_v) and fracture toughness (K_c) are calculated JIS R 1610:

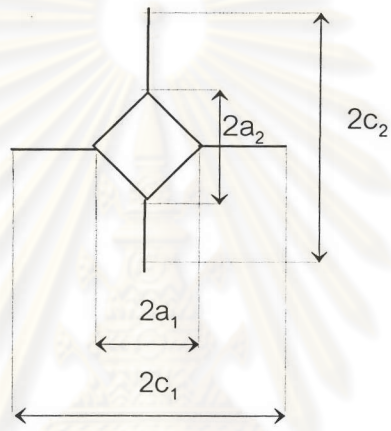


Figure 3.5 Cracks develops after the indentation.

$$H_V = 1.8544P / (2a)^2 \quad (3.7)$$

$$K_c = 0.026\, E^{1/2} P^{1/2} a / c^{3/2} \quad (3.8)$$

where

H_V = Vickers Hardness, Pa,

K_c = Fracture Toughness, Pa $m^{1/2}$,

P = Load, N,

E = Young's Modulus, Pa,

a, c = mean length of diagonal, m,

3.5.3.5 Thermal Properties

The fired specimens in rectangular bars of 3x4x25 mm^3 are prepared to measure the coefficient of thermal expansion in a Unitherm 1161 dilatometer. The temperature range and heating rate are 25-1000 °C and 3 °C/min, respectively.

For thermal shock resistance measurement, the specimens of 3x4x40 mm^3 with 20 μm surface finish are soaked at 230, 280, 330 and 430 °C for thermal differences, ΔT, of 200, 250, 300 and 400 °C, respectively. Then they are quenched in cold water and brought to measure the flexural strength by four-point bending method.