Chapter 3

Experimental procedure

The experimental flow chart, composition and raw materials of mullite, the characterization of sintered mullite and physical properties are described in this chapter
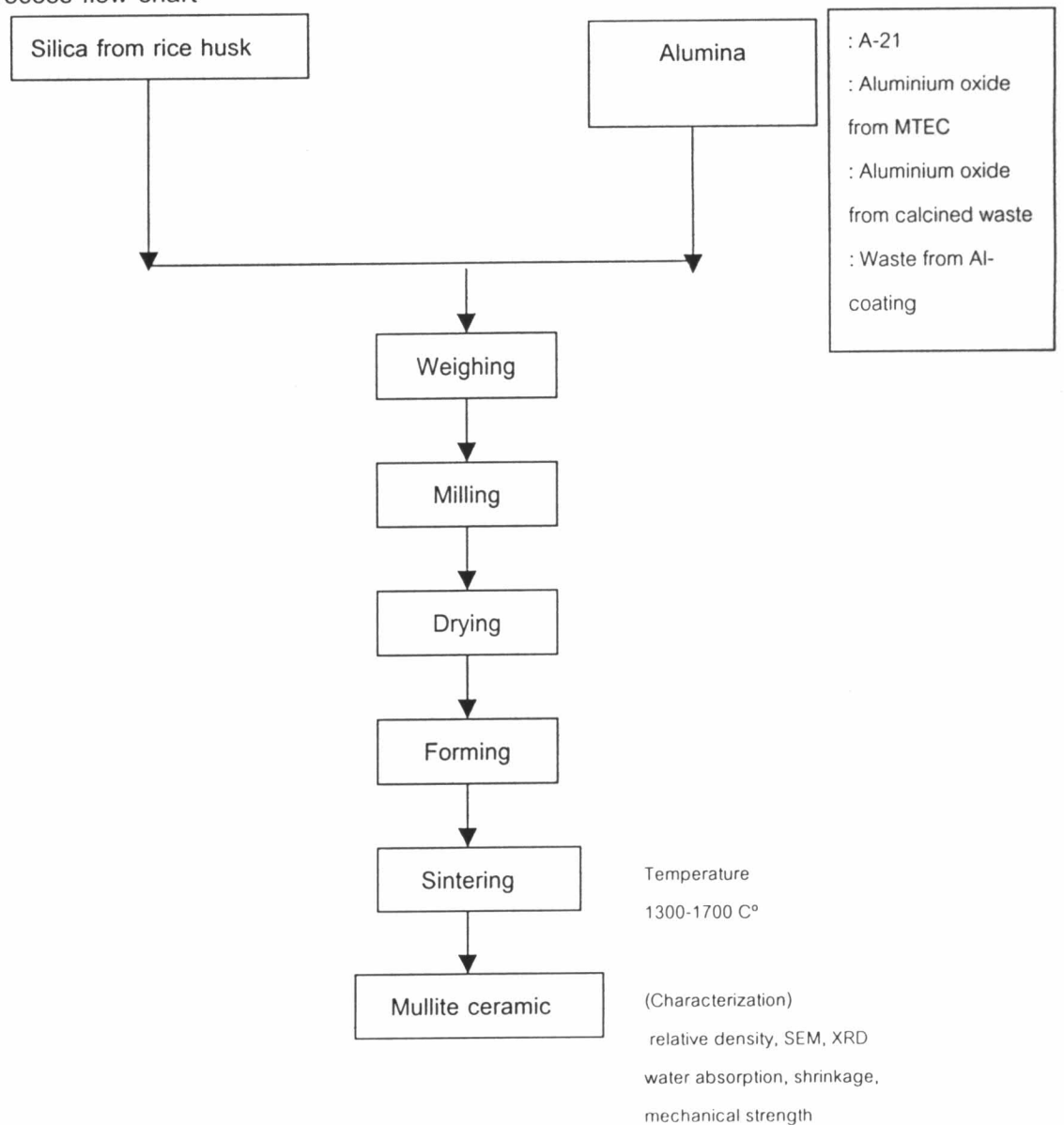
3.1 Process flow chart

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┌──────────────────────┐                      ┌──────────────┐   ┌──────────────────────────┐
│ Silica from rice husk │                      │   Alumina    │   │ : A-21                   │
└──────────────────────┘                      └──────────────┘   │ : Aluminium oxide        │
          │                                          │           │   from MTEC              │
          │                                          │           │ : Aluminium oxide        │
          │                                          │           │   from calcined waste    │
          │                                          │           │ : Waste from Al-         │
          └──────────────────────────────────────────┤           │   coating                │
                                  │                               └──────────────────────────┘
                                  ▼
                          ┌──────────────┐
                          │   Weighing   │
                          └──────────────┘
                                  │
                                  ▼
                          ┌──────────────┐
                          │   Milling    │
                          └──────────────┘
                                  │
                                  ▼
                          ┌──────────────┐
                          │   Drying     │
                          └──────────────┘
                                  │
                                  ▼
                          ┌──────────────┐
                          │   Forming    │
                          └──────────────┘
                                  │
                                  ▼
                          ┌──────────────┐     Temperature
                          │  Sintering   │     1300-1700 C°
                          └──────────────┘
                                  │
                                  ▼
                          ┌──────────────────┐   (Characterization)
                          │  Mullite ceramic  │   relative density, SEM, XRD
                          └──────────────────┘   water absorption, shrinkage,
                                                  mechanical strength
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Fig.3.1 Flow chart for the synthesis of mullite

3.2 Raw material and composition of sintered mullite

3.2.1 Raw material

Since mullite ($3Al_2O_3 \cdot 2SiO_2$) is composed of Al_2O_3 and SiO_2, starting raw materials are the mixture of chemicals containing Al_2O_3 and SiO_2.

SiO_2 was received from the treatment process of rice husk by three different treatment processes [26-30].

    1. SiO_2-H was silica powder from rice husk treated by HCl acid solution.

    2. SiO_2-N was silica powder from rice husk treated by a proprietary method

    3. SiO_2-U was silica powder from rice husk without treatment

4 different kinds of Al_2O_3 were used for this experiment.

    1. α-Al_2O_3 A-21 from Sumitomo

    2. Aluminium oxide from MTEC

    3. Aluminium oxide from calcined waste (from Al-coating)

    4. Waste from Al-coating

Al_2O_3 A-21 was ground in attrition mill for 11 h and aluminium oxide from MTEC was ground in attrition mill for 4 h just to break agglomeration. Al_2O_3 from calcined waste was pre-treated by the following process; waste from Al-coating containing Al_2O_3 was boiled in water for 3 h and dried in electric oven at 110 °C for 5 h and then calcined at 650 °C for 1 h. Waste from Al-coating was used as-received.

3.2.2 Raw material characterization

Determination of particle size distribution

Particle size analyzer, HORIBA Laser scattering particle size analyzer (LA-300), was used to reveal particle size distribution.

Specific surface area

Specific surface area was measured by BET (Brunauer, Emmett and Teller) method using surface area and pore size analyzer (COULTER SA 3100). The measurement of surface area was measured by gas sorption method. Nitrogen was used as adsorbates. The quantity of gas condensed and the resultant sample pressure are recorded and used for subsequent calculation. Isotherm data is then subjected to a variety of calculation models to obtain surface area. BET calculation was selected for this research.

Characteristics of starting raw materials

Raw materials were analyzed by X-ray fluorescence in order to check purity of raw materials.

Phase analysis

Raw materials were analyzed by X-ray diffractometer(Bruker D8 Advance) to identify phase of starting materials. The condition were 2 theta from 15° to 80°, scanning speed 0.1° /1 second , anode Cu, voltage 40 kV and 30 mA.

3.2.3 Composition and preparation of synthetic mullite

Stoichiometric mullite ($3Al_2O_3 \cdot 2SiO_2$) has the weight ratio of Al_2O_3 and SiO_2 of 72/28. In order to study the effect of ratio between Al_2O_3 and SiO_2 on mullitization temperature, the percentage of Al_2O_3 and SiO_2 were changed as follows:

Formula 1 : Al_2O_3 72 wt%: SiO_2 28 wt% (Stoichiometric)

Formula 2 : Al_2O_3 69 wt%: SiO_2 31 wt% (excess SiO_2)

Formula 3 : Al_2O_3 75 wt%: SiO_2 25 wt% (excess Al_2O_3)

In this experiment, Al_2O_3 A-21 and Silica-H were used for all formulas but for the other raw materials, only stoichiometric formula was used. All compositions are shown in Table 3.2

Table 3.2 Composition between Al_2O_3 and SiO_2 for the synthesis of mullite

Code	Composition Al_2O_3 : SiO_2	raw mat. for Al_2O_3	raw mat. for SiO_2
1	72 : 28	A-21	SiO_2-H
2	69 : 31	A-21	SiO_2-H
3	75 : 25	A-21	SiO_2-H
1-S	72 : 28	A-21	SiO_2-N
1-A	72 : 28	Aluminium oxide from MTEC	SiO_2-H
1-S-A	72 : 28	Aluminium oxide from MTEC	SiO_2-N
1-S-G	72 : 28	Aluminium oxide from calcined waste	SiO_2-N
2-S-G	72 : 28	Waste from Al-coating	SiO_2-N
1-U	72: 28	A-21	SiO_2-U
1-U-G	72: 28	Aluminium oxide from calcined waste	SiO_2-U

Raw materials were weighed on an electrical balance and wet mixed in a polypropylene mill (250 ml) for 2 h, using Al_2O_3 ball as grinding media which filled to a half volume of the mill. The slurry was sieved through a #150 screen after grinding, dried on a hot plate with stirring to prevent segregation between raw materials which have a dramatical difference in specific gravity. After stirring on hot plate until almost dry then the slurry was removed to an oven for complete drying at $110^{\circ}C$ for 2 h. The powder was pressed into pellets of 2 cm in diameter by a biaxial hydraulic press at various pressures; 0 MPa, 15 MPa and 40 MPa to check the relation between forming pressure and mullitization. Specimens were fired at $1300^{\circ}C$, $1400^{\circ}C$, $1450^{\circ}C$, and $1500^{\circ}C$ with soaking times of 2, 3 and 5 hours, respectively, and with a heating rate of $5^{\circ}C/min$. This experiment was aimed to find the time-temperature relation for complete mullitization.

Other specimens were fired at 1600$^{\text{O}}$C and 1700$^{\text{O}}$C with a soaking period of 3 h for densification of mullite specimens. All the sintered specimens were cooled to 35$^{\text{O}}$C with a cooling rate of 5$^{\text{O}}$C/min in the furnace.

3.3 Characterization of sintered specimens

3.3.1 Shrinkage

The size of specimens was measured by vernier caliper. Shrinkage of sintered specimens after pressing and after firing was calculated by the equation (3.1)

$$\% \text{ Shrinkage} = \frac{(\text{length of green specimen - length of fried specimens})}{\text{length of green specimen}} \times 100 \qquad (3.1)$$

3.3.2 Bulk density and Relative density

The bulk density of specimens was measured according to Archimedes' method. The air in opened pores of specimen was removed by applying vacuum for 30 min and then distilled water was poured over the specimens and the specimens were under vacuum for another 30 min. During this period, the vacuum equipment was shaken to get rid of the bubbles on the surface of specimens. After finishing each specimen was weighed in water. The suspended weight was taken as W_2. The same specimen, after removing the water adhering on the surface with a piece of damp cloth was weighed again and the weight was taken as W_3 (saturated weight). Then the specimen was dried in an oven at 110$^{\text{O}}$C for 2 h and weighed again. This weight was W_1 (or dry weight)

The bulk density was calculated according to equation (3.2),

$$\text{Bulk density} = \left[\frac{W_1}{W_3 - W_2} \right] \rho \text{ water} \qquad (3.2)$$

Where ρ is density of water at the measurement temperature

Relative density was calculated from bulk density and theoretical density using equation (3.3)

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

Theoretical densities of sintered mullite were calculated from the specific gravity of each component using equation (3.4)

$$\text{Theoretical density} \quad = \quad \frac{1}{f_1 / \rho_1 + f_2 / \rho_2 + ...} \qquad (3.4)$$

Where f is fraction of each component

ρ is specific gravity of component

1, 2 ... is number of component

Stoichiometric mullitie is composed of 72 wt% Al_2O_3 and 28 wt% SiO_2

In this experiment, the theoretical density of mullite = 3.17 g/cm^3, Al_2O_3 = 3.98 g/cm^3 (ρ_1) and SiO_2 = 2.02 g/cm^3 (ρ_2) were taken as references. The density of SiO_2 was checked using pycnometer.

Using equation (3.4) the theoretical density of each formula was calculated and shown in Table 3.3, and from these values, relative densities were calculated based on equation 3.3.

Table 3.3 Theoretical density of each formula from calculation

Code of formula	theoretical density
1	3.13
2	3.06
3	3.20
1-S	3.13
1-A	3.13
1-S-A	3.13
1-S-G/2-S-G	3.13

3.3.3 Water absorption

Water absorption of specimens was measured according to Archimedes' method and calculated using equation (3.5)

$$\% \text{ Water absorption} = \left[\frac{W_3 - W_1}{W_1} \right] \times 100 \qquad (3.5)$$

3.3.4 Phase analysis by X-Ray diffraction (XRD)

The phases of sintered mullite were analyzed by x-ray diffractometer (BRUKER D8 ADVANCE) using 2 theta in the range of 15° to 80°, scanning speed of 0.1° /1 second, and power voltage of 40 kV and 30 mA with Cu anode. The sintered mullite was crushed in a mortar, and sieved through 100 mesh screen prior to XRD determination in order to get a good compact when prepare the specimen.

3.3.5 Microstructure examination by scanning electron microscope (SEM)

Microstructure of sintered mullite ceramic was inspected by scanning electron microscope (JEOL JSM-6301 F). The surfaces of sintered specimens were ground with SiC paper [#]140, [#]240 and [#]400, respectively, and polished with diamond particles of 6, 3 and 1 μm in size. The specimens were cleaned by ethanol in an ultrasonic bath after polishing. Then, the specimens were etched by 15 % HF acid for 10-30 min.

3.3.6 Thermal expansion coefficient

Thermal expansion coefficient of sintered mullite ceramic was inspected by dilalometer (NETZSCH DIL 402 C) up to 1100°C and at a heating rate of 10°C/min. The size of specimens was 5x5x8 mm and sintered at 1700 ºC for 3h.

3.3.7 Bending strength

Powders of composition code 1, 1-S, 1-A, 1-S-A were each pressed into a rectangular mould by a hydraulic press at 40 MPa pressure. All specimens were sintered at 1700ºC for 3 h. The surfaces of sintered specimens were ground with SiC paper [#]140, [#]240 and [#]400 , respectively, in order to get smooth surface and less error in measurement.

3-point bending test was performed using load cell (Instron 4502) and crosshead speed of 0.30 mm/min.