

CHAPTER III

EXPERIMENTAL PROCEDURES

In this research, $\text{Al}_2\text{O}_3\text{-TiC}$ powders were synthesized by combustion synthesis using microwave energy. Then the combusted powders were sintered via microwave or conventional heating for comparison.

3.1 Raw Materials

The effect of various types of precursors on combustion behavior and the microstructure characteristic of $\text{Al}_2\text{O}_3\text{-TiC}$ powder were examined in this study. According to equation 2.3, the precursors of reaction used are TiO_2 , C and Al. Various types of TiO_2 and C, including commercial powders (Al_2O_3 and TiC) used for comparison are shown in Table 3.1.

Table 3.1 Source and characteristics of raw materials.

Raw materials		Company	Purity (%)	Particle size (μm)	Density (g/cm^3)
SHS Precursor	Rutile	Alfa-Aesar	95.5	1-2	4.23
	Anatase	Sigma-Aldrich	99.8	0.1	3.90
	Aluminum	Alfa-Aesar	99.5	7 -15	-
	Carbon black	Cabot	-	0.075	-
	Graphite	Hoganas	97.0	<17	-
	Activated carbon	Carbokarn	-	<45	0.50
Commercial	Al_2O_3	Indal	99.5	1.8	3.90
	TiC	Alfa-Aesar	99.5	2	4.93
Additive	MgO	Sigma-Aldrich	99.0	<45	3.58
	Y_2O_3	Sigma-Aldrich	99.99	-	5.01
Binder	Polyvinyl Alcohols (PVA)	Sigma-Aldrich	98-99	-	1.269 Mw 85,000-146,000
Embed Powder	Carbon	Cabot	-	0.75 μm	-

3.2 Experimental Instruments

The experimental instruments used for analyze, examine and preparation sample were listed in Table 3.2.

Table 3.2 Experimental Instruments.

Instrument	Company	Model
High temperature furnace (2200°C)	SHIMADZU	PVS Ggr20/20
Electrical heating furnace	LENTRON	-
Microwave furnace	Linn High Therm	MHTD-1800-2.4kW
Cold-isostatic press (CIP)	KOBELCO	Dr.CIP
Uniaxial hydraulic press (pellet forming)	ENERPAC	G2535L
Uniaxial hydraulic press (square forming)	ENERPAC S.E.	SEFT-20-1
X-ray Diffractometer (XRD)	JEOL	JDX-3530
Balance and Density kit	AND	GR-200
Oven	MEMMERT	100-800
Vernia Caliper	MITUTOYO	CD-8" CS
Scanning Electron Microscope (SEM)	JEOL	JSM5401
Energy Dispersive Spectroscopy (EDS)	OXFORD	Inca 300
Density Automatic-Pycnometer	Ultrapycnometer1000	UPY-12
Particle size distribution analysis (PSD)	Malvern	Mastersizer-S
Specific Surface Area (BET)	COULTER	SA 3100
High Speed Cutting Machine	STRUER	Accutom-5
Diamond Cut-off Wheel	STRUER	352CA
Grinder and Polisher Machine	BUEHLER	Phoenix Beta
Sonic Resonant (Young's modulus)	GrindoSonic	MK5
Microhardness Tester (Vickers hardness)	Zwick I	B3212001
Universal Testing Machine (4-point bending)	INSTRON	4502

3.3 Preparation of Al₂O₃-TiC Composites

The experimental are divided into 3 main parts. First, the precursors (TiO₂, Al and C) are mixed in a stoichiometric ratio of 3:4:3 as given in equation 2.3 and then the SHS process are conducted. Second, the combusted powders are conventional sintered in high temperature furnace. Finally, the combusted powders are sintered in microwave furnace for comparison. These processes are summarized in the following flowcharts shown in Fig. 3.1.

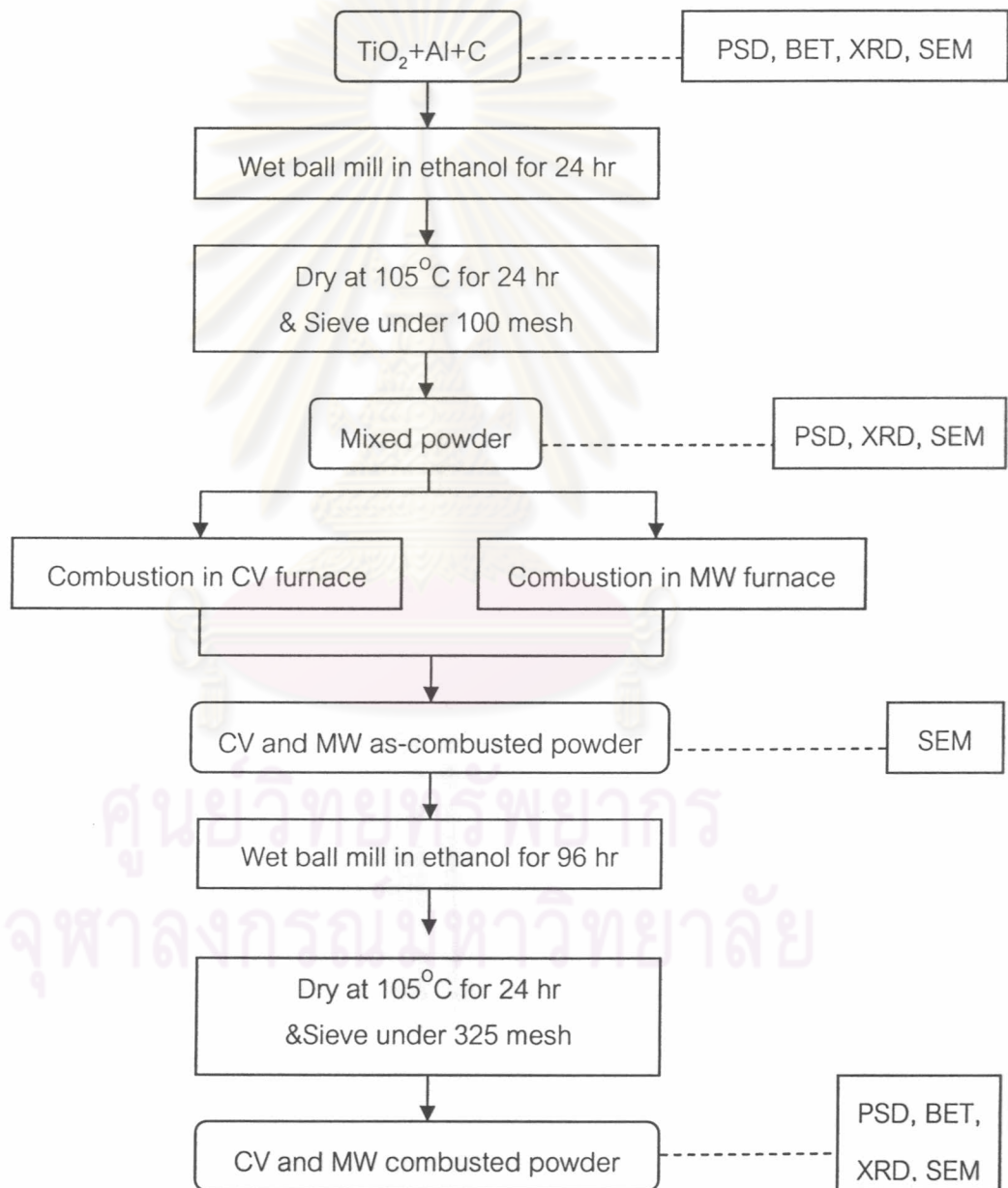


Fig.3.1 (a) Experimental procedure for combustion synthesis process (Part I).

(CV= conventional, MW= Microwave)

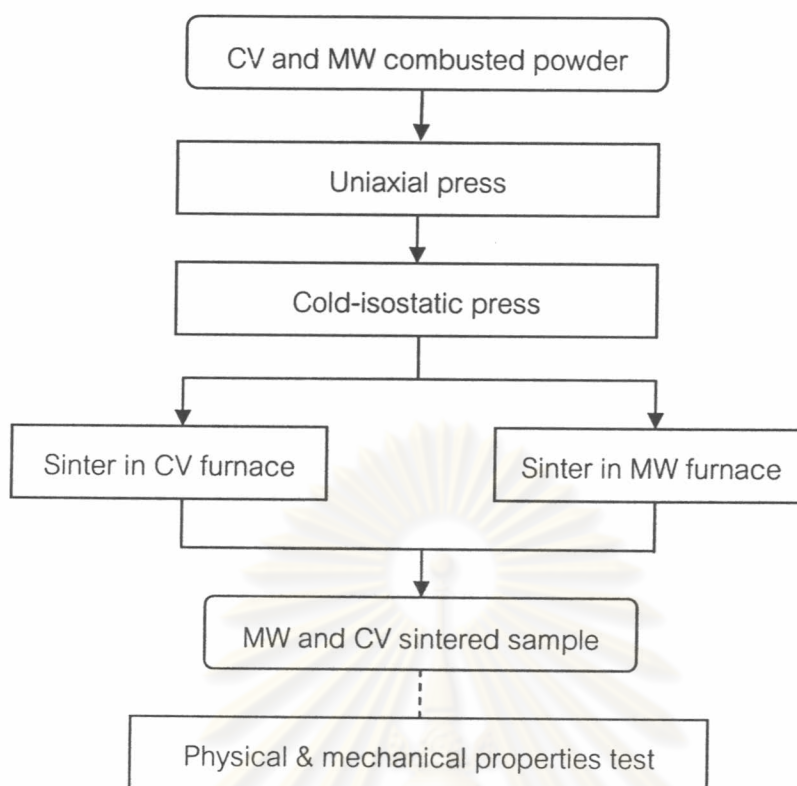


Fig 3.1 (b) Experimental procedure for conventional sintering (part 2) and microwave sintering (part 3). (CV= conventional, MW= Microwave)

3.3.1 Experimental Part 1: Combustion Synthesis Process

The six compositions, which are shown in Table 3.3, are homogeneously mixed by ball milling with alumina ball in ethanol for 24 hours. The reactant mixtures were then dry at 105°C for 24 hours and sieve through a 100 mesh to reduce the number of agglomerates.

Table 3.3 Six compositions with various TiO₂ and C used in TiO₂-Al-C combustion system.

composition	reactants		
	Al	TiO ₂	C
TC1	Aluminum	rutile	carbon black
TC2		rutile	graphite
TC3		rutile	activated carbon
TC4		anatase	carbon black
TC5		anatase	graphite
TC6		anatase	activated carbon

3.3.1.1 Conventional Combustion System

The combustions were performed by heat transfer from electrical heating element in tube furnace. The diameter and length of furnace were 7.5 cm and 120 cm respectively. The 10 g-powder was placed in a porcelain crucible and put in a middle of tube under an argon atmosphere with the flow rate of 2 lit/min. The heating rate was applied at $5^{\circ}\text{C}/\text{min}$, the temperature was measured by thermocouple type K ($-200^{\circ}\text{C} - 1250^{\circ}\text{C}$). The conventional combustion furnace and temperature measurement set up was shown in Fig. 3.2. After the combustion process, synthesized powder was milled by alumina balls in ethanol for 96 hours to reduce particle size and agglomerates and mixed with 0.5 wt% of PVA as a binder. The powder product was then dried and sieved through 325 mesh prepared for further characterization and sintering.



Fig. 3.2 Conventional combustion furnace and temperature measurement set up.

3.3.1.2 Microwave Combustion System

The ignition was performed in a 2.45GHz microwave furnace with a dimension chamber of $13.5 \times 13.5 \times 1.3.5 \text{ cm}^3$. The maximum power output is 2.4 kW. The microwave combustion system setup was shown in Fig. 3.3. The 10 g-powder was put in an alumina crucible, which was placed at the center of microwave cavity. The ignition was carried out under an argon atmosphere with a flow rate of 1.67 lit/min. The combustion temperatures were measured by an infrared pyrometer (Kleiber, Pyroskope 217-LWL). Its working temperature range was 300 to 2200°C .

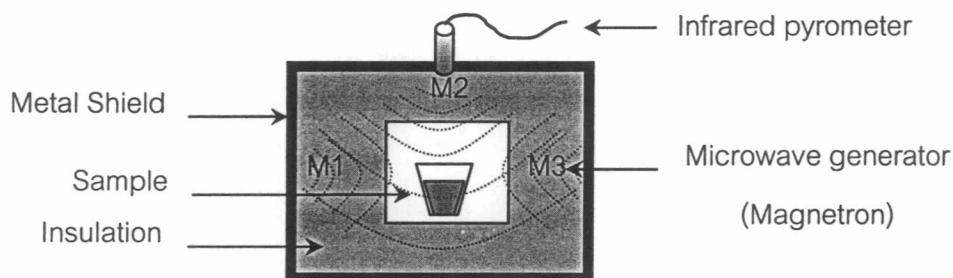


Fig. 3.3 Schematic illustration of microwave combustion system.

3.3.2 Experimental Part 2: Conventional Sintering

3.3.2.1 Conventional Sintering without Additive

The feasibility of sintering the microwave and conventional synthesized powder was preliminary studied by sintering a pellet without additive. 1 g-synthesized powder were pressed into pellet of 13 mm in diameter by uniaxial press at the pressure about 7 MPa. Then a green pellets were cold-isostatic pressed at 300 MPa for 3 min. Then all pellets were placed in a graphite crucible and embedded by carbon black powder and sintered in a high temperature furnace (Shimadzu, PVS Ggr20/20). The heating profile of conventional sintering is displayed in Fig.3.4.

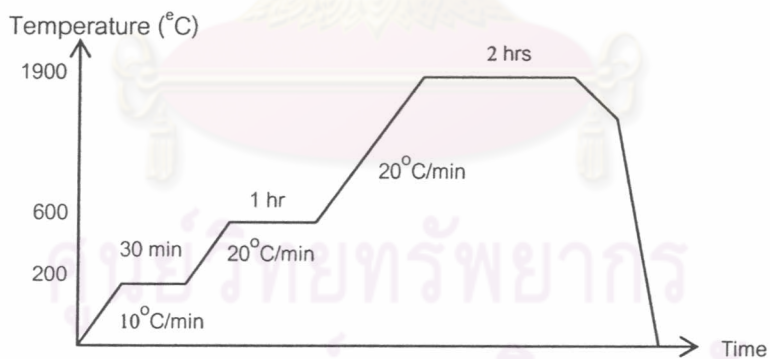


Fig.3.4 Temperature profile of conventional sintering without additive.

3.3.2.2 Conventional Sintering with Additive

The 30 g-synthesized powders amounts 30 g were pressed to form a square specimen with dimension $40 \times 40 \text{ mm}^2$ by uniaxial pressing at the pressure of about 98 MPa. Then green specimens were cold-isostatic pressed at 300 MPa for 3 min. The heating profile is similar to the sintering without additive in Fig. 3.2 with lower

sintering temperatures set at 1700°C and 1800°C. In this case, the additives were used in a preparation of synthesized powders was aimed to lower the sintering temperature and used as sintering aids. 0.5wt%MgO of alumina weight and 0.3wt%Y₂O₃ of composite weight were added during mill process. MgO is well known as the additive which reduce grain growth of alumina during sintering and Y₂O₃ is used as a gas generation suppress agent. This is due to a larger specimen may lead to more gas generation during sintering process as previously mentioned in section 2.4.1.

3.3.3 Experimental Part 3: Microwave Sintering

The M-TC1 synthesized powder was chosen to investigate the microwave sintering behavior. The synthesized powders were uniaxial pressed to form a pellet of 31 mm in diameter under pressure of 35 MPa. This experiment was carried out in order to find properly sintering condition for microwave combustion product. Maximum sintering temperature was assigned at 1700 °C, thus SiC susceptor were desired in order for sintered sample to reach the determined temperature. The samples surround by a set of SiC susceptor located at the center of microwave cavity. The sintering was done under microwave power of 2.4 kW under argon atmosphere. For comparison, conventional sintering of the same green specimens was performed under the same sintering temperature microwave processing.

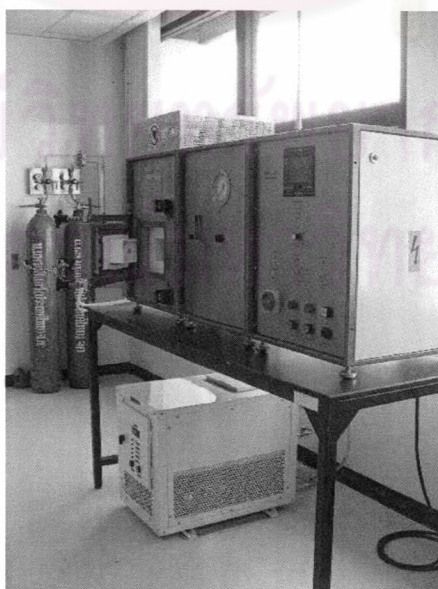


Fig.3.5 Microwave furnace for synthesis and sintering Al₂O₃-TiC composite.

3.4 Powder Characterization

The density, surface area and particle size distribution of raw materials were investigated; these data would help to understand the combustion behavior. The combusted powders were also characterized as same as raw material. The powder characterization methods are described as follow.

3.4.1 Powder density by Ultracycnometer

The Ultracycnometer 1000 is used to measure the volume and true density of powder. This accomplished by employing Archimedes' principle of fluid displacement and Boyle's law to determine the volume. The volume of powder is equal to the volume of gas it displaces. The displaced fluid is a He gas which can penetrate the finest pores, thereby assuring maximum accuracy. The powder quantity 1 g was put in micro volume cell, and then the Ultracycnometer is automatic sequentially run at ten times. Density is determined by calculation the mass to volume ratio.

3.4.2 Particle Size Distribution Analysis by Mastersizer-S

Mastersizer is basically provided a collimated He-Ne laser that pass through the sample to be measured. The small amount of powder was dispersed in the dispersant and the ultrasonic for 5 min. After that sample was poured into small volume unit with stirrer to pass sample into laser unit (Fig.3.6). The scattered laser light from the sample is detected by the receiver of the optical measurement unit. This data from the receiver is transmitted to the computer system where the operating software calculates the size distribution.

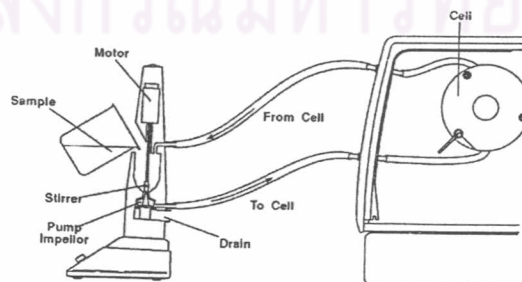


Fig.3.6 Schematic illustration of small volume unit and laser unit of Mastersizer-S for particle size distribution analysis.

3.4.3 Specific Surface Area by Brunauer, Emmett and Teller (BET) Method,

This measurement used the basic concept by gas sorption method; in this study nitrogen gas was used for adsorbates. The method is defined simple as the physical characterization of material structure using a process where gas molecules of know size are condensed on unknown sample surface. The quantity of gas condensed and the resultant sample pressure are recorded and used for subsequent calculation. Isotherm data is then subject to a Langmuir calculation model to obtain surface area. The details regarding sample preparation and analysis are described as follows. At first, the sample powder was dried at 105°C for 24 hours and cooled down in desiccator. Then approximately 0.15 g dry, pre-weighed sample was put in a specific tube. After that outgas was vacuumed from the sample for 15 min at 120°C. Finally, the sample tube was attached to the analysis port and kept tube in liquid nitrogen during analysis.

3.5 Physical Properties measurement

3.5.1 Phase Identification

The X-ray diffraction (XRD) method is a widely used technique for studying structural information in condensed matters. The crystal phase of reactants, the conversion of combusted powder products and the phase of sintered samples were confirmed by X-ray diffractometer (JEOL: JDX3530). The matching data obtained with the JCPDS data files. The measurement condition of XRD is shown in Table 3.3.

Table 3.3 Condition of X-ray diffraction analysis

Item	Condition
2θ	20 – 80 degree
step angle	0.04 degree
count time	1 sec
X-ray source	CuK α
voltage	30 kV
current	40 mA

3.5.2 Microstructure Characterization

The morphology of powders and microstructure of sintered sample were examined by scanning electron microscope, SEM (JEOL, JSM5401). The image was created from secondary electron which generated from sample by electron bombard from tungsten filament. The morphology of reactant powder is the important factor affect to sintering behavior; subsequently the combusted powders were investigated microstructure that would be affecting by different precursors. Eventually sintered samples were grinded and polished carefully to a mirror-like surface (the preparation of sample surface are describe in mechanical properties section) to observed microstructure. Gold as an electrode was sputtered on sample surface before investigation. Energy dispersive analysis (EDS: Oxford, Inca300) was sometime used to investigated the element of interesting matter.

3.5.2 Density Measurement

The densities of sintered specimens were measured according to ASTM designation number C 373-88 [42]. The test specimens were dried at 105°C over night then cooled down in desiccator and the dried mass, D , were determined. The specimens were placed in distilled water and boiled for 5 hours taking care that the specimens are covered with water at all time, then allow the specimens to soak for an additional 24 hours. After impregnation of the test specimens, the mass, S , of each specimen while suspended in water were determined. Each specimen was blotted lightly with a moistened, lint-free linen or cotton cloth to remove all excess water from the surface, and the saturated mass, M , was determined. The exterior volume, V (cm³), can be calculated as follows:

$$V = M - S \quad (3.1)$$

The volumes of open pores V_{OP} (cm³), and impervious portions (closed pores and solid) V_{IP} (cm³), are given by:

$$V_{OP} = M - D \quad (3.2)$$

$$V_{IP} = D - S \quad (3.3)$$

The apparent porosity, P (%), expresses, as a percent, the relationship of the volume of the open pores of the specimen to its exterior volume. The apparent porosity can be calculated as follows:

$$P = \left(\frac{M - D}{V} \right) \times 100 \quad (3.4)$$

The water absorption (A , %) expresses, as a percent, the relationship of the mass of water absorbed to the mass of the dry specimen. It can be determined as follows:

$$A = \left(\frac{M - D}{D} \right) \times 100 \quad (3.5)$$

The apparent density, T (g/cm^3), of that portion of the test specimen that is impervious to water, is given by:

$$T = \left(\frac{D}{D - s} \right) \quad (3.6)$$

The bulk density, B (g/cm^3), of a specimen is the quotient of its dry mass divided by the exterior volume, including pores, which can be calculated the bulk density as follows:

$$B = \left(\frac{D}{V} \right) \quad (3.7)$$

3.6 Mechanical Properties Measurement

The preparation of test specimens was carefully done. The square specimens were cut into the nearest required dimension, the width, depth and length of each specimen was 4 cm x 3 cm x 30 cm. Then the specimen surface was ground with diamond grinding plate of 75, 40 and 20 micron respectively, ranging from coarse to fine rates of material removal. The surface polishing was done with finer particulate diamond suspension of 6, 3 and 1 micron on a velvet cloth to yield a scratch-free, mirror-like surface. In particular, the direction of machining shall be parallel to the

specimen long axis. The four long edges of each specimen shall be uniformly chamfered at 45° to prevent machining damage.

3.5.1 Young's Modulus

Young's modulus can be determined by sonic resonance method that measures the resonance frequencies of test specimens of suitable geometry, the rectangular specimen dimensions are approximately 30 mm in length, 4 mm in width and 3 mm in thickness. Mechanical excitation of bar specimen was provided through the use of small tapper. The transducer senses the resulting mechanical vibrations of the specimen and transforms them into an electrical signal, and then frequency of the signal is detected by Gridosonic tester. Dynamic Young's modulus for the fundamental in flexure mode of rectangular bar can be calculated as follows [43]:

$$E = 0.9465 (mf_f^2 / b)(L^3 / t^3)T_1 \quad (3.8)$$

where

E = Young's modulus (Pa)

m = mass of bar (g)

b = width of bar (mm)

L = length of the bar (mm)

t = thickness of the bar (mm)

f_f = fundamental resonant frequency of bar (Hz)

T_1 = correction factor for bar in flexural mode

and

$$T_1 = 1 + 6.585 (1 + 0.0752 \mu + 0.8109 \mu^2)(t/L)^2 - 0.868(t/L)^4 - \left[\frac{8.340 (1 + 0.2023 \mu + 2.173 \mu^2)(t/L)^4}{1 + 6.338 (1 + 0.1408 \mu + 1.536 \mu^2)(t/L)^2} \right] \quad (3.9)$$

where

μ = Poison's ratio

= 0.22 for Al₂O₃-TiC composite

3.5.2 Flexural Strength

Four-point-bending or flexural strength is a testing method where a specimen is symmetrically loaded at two locations that are situated one quarter of the overall span, away from the outer two support bearings. This method followed ASTM designation number C 1161-02c [44]. Specimens would be tested in a fully articulating fixture as illustrated in Fig. 3.7 with cross-heading speed at 0.5 mm/min. The standard formula for the strength of beam in four-point bending is as followed:

$$S = \frac{3PL}{4bd^2} \quad (3.10)$$

where

P = load at break point (N)

L = outer (support) span (mm)

b = specimen width (mm)

d = specimen thickness (mm)

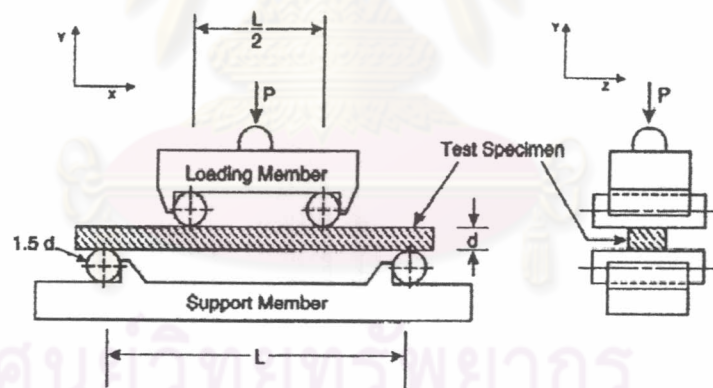


Fig. 3.7 Schematics of two semi-articulating four-point fixtures suitable for flat and parallel specimens [44].

3.5.3 Vickers Hardness

This test method describes an indentation hardness test as ASTM designation number C 1327-99 [45]. Vickers indenter was evaluated indentation at the load of 20 N. The Vickers indenter creates a square impression from which two surface diagonal lengths were measured with optical microscopes. The Vickers indenter and

surface project diagonal are illustrated in Fig.3.8. Vickers hardness is calculated from the ratio of applied load to the area of contact of the four faces of the indenter. The Vickers hardness number is computed as follows:

$$H_V = 0.1891 \frac{P}{d^2} \quad (3.11)$$

where

P = load (N)

d = average length of two diagonal of the indentation (mm)

$$= \frac{d_1 + d_2}{2}$$



Fig. 3.8 The Vickers indenter and surface diagonal project [45].

3.5.4 Fracture Toughness

After indentation, the lengths of indentation-induced cracks were immediately measure by optical microscope. For each indentation, the crack resistance was calculated with the equation proposed by Anstis et al [46].

$$K_{IC} = 0.016 \left(\frac{E}{H} \right) \frac{P}{c^{3/2}} \quad (3.11)$$

where

K_{IC} = fracture toughness (Pa)

E = elastic modulus (Pa)

H = hardness (Pa)

P = load (N)

c = average crack half-length (m)