CHAPTER 3

EXPERIMENTAL PROCEDURE

This chapter describes all the experimental procedures employed in this work to fabricate and characterize the desired high strength dental ceramic materials with their physical and mechanical properties tailored by method of ceramic nanocomposite approaches.

3.1 Sample Preparation

Preparation of dental porcelain powders and fabrication of ceramic nanocomposites have been employed as follow:

3.1.1 Powder Preparation

All commercially available starting compounds used in this study are listed in Table 3.1, along with the suppliers, formula weights and purities.

3.1.1.1 Preparation of Dental Porcelain Powders

Three groups of dental porcelain powders (detailed in Table 3.2) were prepared by employing a typical porcelain powder processing, as shown in Fig. 3.1. Thailand's raw materials (feldspar, quartz and kaolinite) were mixed by ball-milling technique for 3 h and fired at temperature ranging from 1250-1400 °C to produce red hot glass. After firing, these hot glasses were quenched into water; the frit was then milled and sieved into fine dental porcelain powders.

Raw materials	Source	Formular	Purity
		weight	(%)
Quartz	Sibelco Thailand	60.08	> 99.0
(Silica flour - C 300) [#]			
Feldspar	Sibelco Thailand	388.14	> 98.0
(Spar glaze) [#]			
Kaolinite	Sibelco Thailand	258.15	> 95.0
(Kaolin-N) [#]			
α -Al ₂ O ₃ (1-10 µm)***	Fluka Chemical, Germany	101.96	> 99.0
α-Al ₂ O ₃ (0.1-1 μm)*	Buehler, USA	101.96	> 99.0
α -Al ₂ O ₃ (0.1-0.5 µm)*	Buehler, USA	101.96	> 99.9
γ-Al ₂ O ₃ (10-100 nm)	Nanostructured & Amorphous	101.96	> 99.9
No. 1040LQ*'**	Materials, Inc., USA		
Whisker TiO ₂	Nanostructured & Amorphous	79.86	> 99.9
(No. 5480MR) ^{†,††}	Materials, Inc., USA		
${ m TiO_2}^{**,\dagger,\dagger\dagger}$	Riedel-deHaën, Germany	79.86	> 99.0
MgO**	Fluka Chemical, Switzerland	40.30	> 99.0
ZnO**	Fluka Chemical, Switzerland	81.38	> 99.0
$\operatorname{Fe_2O_3^{\dagger\dagger}}$	Riedel-deHaën, Germany	159.69	> 99.9

 Table 3.1 Specifications of the raw materials used in this study.

for dental porcelain fabrication

* for D/Al_2O_3 fabrication; ** for $D/(Al_2O_3-M_xO_y)$ fabrication

 \dagger for D/TiO₂ fabrication; \dagger † for D/(TiO₂-Fe₂O₃) fabrication



Table 3.2 Three groups of dental porcelain powders prepared in this work.

Fig. 3.1 Typical processing route for dental porcelain powders [121].

3.1.1.2 Preparation of Metal Oxides Modified Porcelain Powders

A total of 27 different chemical compositions of metal oxides modified porcelain powders were designed as the following detail. Four groups of metal-oxides modified porcelain powder i.e. Al_2O_3 -, $(Al_2O_3-M_xO_y)$ -, TiO_2 - and $(TiO_2-M_xO_y)$ modified porcelain powders were prepared from dental porcelain powders (obtained from section 3.1.1.1) and metal oxide additives (Table 3.1) by using a simple solidstate reaction process as shown in Fig. 3.2 In each group, various compositions were designed based upon several parameters such as type, size and shape (Fig. 3.3) of the Al_2O_3 (or TiO_2) and raw materials mixing ratios, as details given in Tables 3.3 and 3.4. Selected crystalline additives were mixed with dental porcelain powders by using a rapid vibro-milling for 30 min and dried at 120 °C for 6 h.





Fig. 3.2 The processing flow chart for the modified porcelain powders.

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			Chemica	l composit	tion (wt%)			
	Dental		Al	₂ O ₃		TiO ₂ *	MgO	ZnO
Group	porcelain	Alpha, Platelet,	Alpha, Irregular,	Alpha, Irregular,	Gamma, Fibrous,			
		1-10 μm	ο. <u>Modifier</u>			000		
8		Al ₂	O ₃ Modified	i porceiain	system		3	
4	60	40						
	50	50						
5	70			30			-Sach	
	60			40				
	50			50				
6	70	10	10	10			8/	
	60	13.3	13.3	13.3				
7	70			22 60	30	Ą		
	60				40			
		Al ₂ O ₃ -	M _x O _y Modi	fied porcel	ain system			
8	60	38.6		VI V		1.4		
9	60				38.6	1.4		
10	60	129	Sn	2019	38.6	Rei	1.4	1.41
11	60			0.10	37.2			2.8
	g 60 ^{°°}				34.6			5.4
	60				32.4			7.6

Table 3.3 Designed chemical composition of Al-oxides modified porcelains powders.

* Irregular-shaped TiO₂

		Chemical c	omposition (wt%)		
– Group	Dental	TiO ₂		Fe ₂ O ₃	
	porcelain -	Irregular	Whisker		
		0.2-0.5 μm	50-200 nm		
		TiO ₂ Modified porc	celain system	31	
12	90	10		3	
	80	20			
	70	30			
13	90 ह		10	295	
	80		20		
	70		30		
	TiO	2-Fe ₂ O ₃ Modified p	porcelain system	2	
14	70	27.8	A	2.2	
	70	25.6		4.4	
	70	23.4		6.6	
15	70		27.8	2.2	
	70		25.6	4.4	
	5170		23.4	6.6	
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Table 3.4 Designed chemical composition of Ti-oxides modified porcelains powders.

3.1.2 Ceramic Fabrication

All ceramic specimens in this work were carefully fabricated by using a simple process based upon the dental manufacturing guideline as shown in Fig. 3.4. Each composition of the modified porcelain powders (obtained from section 3.1.1) were mixed with PVA binder and compacted (shaping) by using a slip casting technique (Fig 3.5) as recommended by the dental manufacturer with a cavity of normal size of 30 x 6 x 2 mm^3 , reproducing the desired dimensions and shapes [122]. After molding, the specimens were then placed inside the furnace (Multimat Touch & Press, Dentsply DeTray Detech GmbH, Germany) (Fig. 3.6) and vacuum fired with the same drying and preheating time, heat rate, vacuum level at 0.05 atm pressure and cooling time (Fig. 3.7), but difference in sintering temperature (excepted dental porcelain with constant firing temperature of 950 °C [123]), dwell time and total firing time (Tables 3.5 - 3.7). After firing, all specimens were serially ground and wetpolished with 125, 40 and 10 µm grit size diamond discs (Struers A/S, Denmark) mounted on a metallographic lapping machine (Abramin, Struers A/S, Copenhagen, Denmark), to produce a rectangular test specimens with final dimensions of approximately 20 mm length, 1.2 mm thickness and 4 mm width. The opposing faces of the specimens are flat and parallel within 0.05 mm. Finally, the specimens were cleaned using an ultrasonic bath with acetone at room temperature for 15 min.



Fig. 3.4 Fabrication process for dental porcelain ceramics.

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Fig. 3.5 Industrial shaping process of dental porcelain by slip casting technique: (1) pouring slip into the metal mold, (2) excess moisture removing, (3) - (4) surface flattening, (5) unpacking and (6) green specimen.



Fig. 3.6 Vacuum furnace (for reducing sample porosity after sintering process).



Fig. 3.7 Schematic diagram of the firing schedule used; x: Heating rate, y: Firing temperature and z: Dwell time.

Group		Sintering conditions		- Total fiming
	Sample code	Heating rates (°C/min) (x)	Dwell Time (min) (z)	time (min)
1	D1	50	1	23
	D2	50	2	24
	D3	50	3	25
	D4	70	2	22
25	D5	50	1	23
	D6	50	2	24
	D7	50	3	25
	D8	70	2	22
3	D9	50	1	23
	D10	50	2	24
	D11	50	3	25
	D12	70	2	22

Table 3.5 Sintering conditions for the production of dental porcelain ceramics at 950°C.

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Group		Sintering conditions		Total firing
	Sample code	Temp. (°C)	Dwell time (min)	time (min)
		(y)	(z)	
	Al ₂	O ₃ Modified porce	lain system	
4	D13	1200	62	87
	D14	1200	100	125
5	D15	1200	55	80
	D16	1200	95	120
	D17	1200	100	125
6	D18	1200	55	80
	D19	1200	85	110
7	D20	1200	55	80
	D21	1200	90	115
	Al ₂ O ₃	<i>M_xO_y Modified po</i>	rcelain system	
8	D22	1190	60	85
9	D23	1200	62	87
10	D24	1190	62	87
11	D25	1200	67	92
	D26	1195	65 UN	1Versit
	D27	1190		87

Table 3.6 Sintering conditions for the production of Al-oxides modified porcelainsystems with constant heating rate of 55 $^{\circ}$ C/min.

Group		Sintering conditions		Total firing	
	Sample code	Temp. (°C)	Dwell time (min)	_ 10tai in ing	
		(y)	(z)	ume (mm)	
	TiO	2 Modified porcel	ain system		
12	D28	1020	1.5	24	
	D29	1040	5	28	
	D30	1060	20	43	
13	D31	1020	1.5	24	
	D32	1040	5	28	
	D33	1060	20	43	
	TiO ₂ -F	e ₂ O ₃ Modified por	rcelain system	5	
14	D34	1090	30	54	
	D35	1090	30	54	
	D36	1090	30	54	
15	D37	1090	30	54	
	D38	1090	30	54	
	D39	1090	30 30	54	
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Table 3.7 Sintering conditions for the production of Ti-oxides modified porcelain systems with constant heating rate of 55 °C/min.

3.2 Sample Characterization

The following section is intended to address the main characterization techniques used to investigate the phase formation, morphology, microstructure, physical and mechanical properties of the materials in this study.

3.2.1 Phase Analysis

X-ray diffraction (XRD) (Diffractometer PW3710, Philips, Netherlands) (Fig. 3.8) analyses were conducted to determine the crystalline phase formation within the porcelain composite materials. All samples were ground into powders, placed in the holder of a diffractometer and scanned with Cu K α X-ray, 0.154056 nm λ at 40 kV and 45 mA.

3.2.2 Microstructural Analysis

Polished samples (with diamond paste from 9 to 1 μ m) were etched with 2 vol% of HF acid for 2 min and platinum-coated (20 nm) for SEM observation with field emission SEM (JSM 6335 F, Jeol, Tokyo, Japan) equipped with an energy dispersive X-ray (EDX) analyzer (Fig. 3.9). Apart from raw material's morphologies, observation of cracks emanating from indentations on the coated surface of selected specimens was also made to investigate the character of the cracks and crack-microstructure interaction. The chemical composition of the significant microstructure tural features was also analyzed using an EDX technique.



Fig. 3.8 X-ray diffractometer.

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Fig. 3.9 Scanning electron microscope, equipped with EDX analyzer.

3.2.3 Densification Analysis

The fired shrinkages of all sintered samples were measured with a digital caliper (KEIBA: electronic digital caliper 0-100 mm resolution) from the percentage diameter change (Δl) with respect to the original diameter (l_o) before sintering.

Shrinkage (%) =
$$\frac{\Delta l}{l_o} \times 100$$
 (3.1)

The bulk density and total porosity were determined for all materials and were measured as recommended by the ASTM C 20-00 [124]. The bulk density (ρ_b) was calculated according to the equation as follows:

$$\rho_b = \frac{W_D}{V_b} \tag{3.2}$$

where W_D is the dry weight of specimen and V_b is the bulk volume, measured using a mercury volumenometer machine (Mercury volumenometer, TU Bergakademie Freiberg, Germany) (Fig. 3.10). True density of the specimens was measured using a helium pyknometer (Accupyc 1330, Micromeritics Instrument Corp, Norcross, USA). The percent total porosity (% P_{total}) was determined by the equation as follows:

$$\% P_{total} = \frac{\rho_t - \rho_b}{\rho_t} \cdot 100$$
(3.3)

where ρ_t is the true density of the specimen and ρ_b is the bulk density of the specimen.



Fig. 3.10 Mercury volumenometer.

3.2.4 Mechanical Properties Measurements

3.2.4.1 Uniaxial Flexural Strength

The uniaxial flexural strength (M) was determined with the three-point bending test (Fig. 3.11) and calculated by the equation as follows [122]:

$$M = \frac{3Wl}{2bd^2}$$
(3.4)

where W is the breaking load (N), l is the test span (mm), b is the width of the specimen (mm) and d is the thickness of the specimen (mm). The specimens were tested with a universal testing machine (Tira test 2420, Tira Maschinenbau GmbH, Rauenstein, Germany) (Fig. 3.12). Before testing the edges of the surface of the specimens undergoing tensile stresses were chamfered with a 9 µm grit size diamond disc.



Fig. 3.11 Diagram of uniaxial flexural strength test shows rectangular-shaped specimen loaded from above by steel bar and supported from below by adjustable half-round steel plates.



Fig. 3.12 Universal testing machine.

3.2.4.2 Hardness and Elastic Modulus

Hardness (H) and Young's modulus (E) were determined and calculated by the Vickers microhardness testing machine (Fischerscope H 100, Helmut Fischer GmbH + Co, Sindelfingen, Germany) (Fig. 3.13) with continuous depth recording method and indention load from 0.4-1 N in 20 steps of loading. The testing of both techniques were measured as recommended by the ASTM C 1259-01 [125] and C 1327-99 [126]. H can be calculated by the equation as follows:

$$H = (0.1020)(1.8544) \cdot \frac{p}{(d)^2}$$
(3.5)

where P is the load (N) and d is the average range of the two diagonals of the indentation (mm) (Fig. 3.14).



Fig. 3.13 Vickers microhardness testing machine.

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Fig. 3.14 Illustration of Vickers indentation and cracks formed around indentation. Dimensions of indentation and cracks to calculate indentation fracture toughness.

3.2.4.3 Indentation Fracture Toughness

Ten specimens of each composition were polished with diamond paste (DPsuspension P, Struers A/S, Denmark) from 9 to 1 µm until a mirror-like surface was achieved and subsequently cleaned in an ultrasonic bath with acetone and dried at 120°C. The specimens were coated with a thin layer of platinum for making the light contrast of microhardness tests. This procedure is similar to hardness testing, but higher loads are used to create cracking around the indentation. The indentation technique described by Anstis et al. [127,128]. Loads of 20-60 N were applied to the specimens with a Vickers microhardness testing machine (Materialprüfung, Zwick, Germany) (Fig. 3.15). Optimal testing loads for each material were determined by comparing the crack length from center of indent with the length of the half-diagonal. A load must be used that produces a ratio greater than 2. It was determined that 30 and 50 N of load for 10 s should be used for the dental porcelain and the nine composite materials, respectively. Ten indentations were recorded for the length of the



Fig. 3.15 Vickers microhardness testing machine.

cracks at the four corners of each material under the microscope and the fracture toughness (K_{IC}) of the each material was calculated with the indentation strength method and also Young's modulus. The equation proposed by Fischer and Mark [9] as follows:

$$K_{IC} = \xi \left(\frac{E}{H}\right)^{1/2} \cdot \frac{P}{c^{3/2}}$$
(3.6)
where ξ is a constant prefactor (0.018), *E* is the Young's modulus, *H* is the hardness,
P is the indentation load and *c* is the crack length, calculated from the measured

arithmetic means of c_1 and c_2 (Fig. 3.14).

3.3 Statistical Analysis

A multiple regression analysis was used to determine the significance of the influence of the surface and heat treatment on the flexural strength. Some physical property and strength data were analyzed by statistical technique of one-way ANOVA (with Scheffé's pairwise multiple comparisons were used to assess whether there was any statistical difference among groups and to identify which pairs of groups were different) and Weibull analysis [129]. Statistical significant differences of the porosity, flexural strength and fracture toughness data between materials were analyzed with one-way ANOVA and Scheffé post hoc tests at a significance level (p) of 0.05 by SPSS ver. 14 program.

The Weibull moduli (*m*) were calculated for flexural strength data to characterize variability strength of all materials. Weibull parameters were estimated using the two-parameter Weibull distribution, and curve fitting was performed with a modified maximum likelihood estimator with mean reduced biasing adjustment. Ninety-five percent confidence bounds were placed on the estimates for the Weibull modulus and characteristic strength. A likelihood contour method was used for determining whether two Weibull distributions were statistically significantly different. This method is described in the New Weibull Handbook [130,131]; however, simply stated, a horizontal slice is made in the three-dimensional contour plot of the Weibull distributions being compared at equal likelihoods. The plot has the 95% confidence bounds for the estimate of the characteristic strength $\hat{\sigma}_{\theta}$ on the X-axis. It confidence bounds intersect, Weibull parameters are not statistically significantly different.

Weibull moduli are calculated by plotting In In 1/(1-F) versus ln (s). F is the median rank and can be calculated by the equation as follows [85]:

$$F = \frac{i - 0.5}{n} \tag{3.7}$$

where *i* is the rank of a samples in terms of strength (i = 1 for the lowest strength sample), *n* is the total number of samples and *s* is the strength of sample *i*. A linear regression was done by the median rank regression method. The slope of the line is the Weibull modulus. Strength levels at 1, 5 and 10% probability of failure (P_f) were calculated using the Weibull plots by the equation as follows [132]:

$$P_f = 1 - \exp[-(\frac{\sigma}{\sigma_0})^m]$$
(3.8)

where σ is the strength at a given P_f and σ_0 is the Weibull characteristic strength, can be calculated by the equation as follows [132]:

$$\sigma_{0} = (\frac{1}{n} \sum_{i=1}^{n} s^{m})^{\frac{1}{m}}$$
(3.9)
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